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Green Additives for Lubricating Oil

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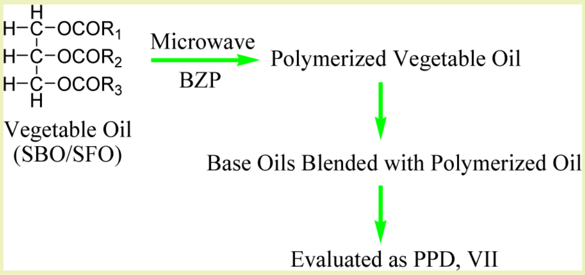
Ⓢ *Supporting Information*



ABSTRACT: The increasing focus toward diminishing the impact on the environment has driven efforts to develop new environmentally benign lubricating oil additives. Keeping this view in mind, the present investigation comprises the syntheses of homopolymers of sunflower oil (SFO) and soybean oil (SBO) for their evaluation as lube oil additives. Each of them was characterized by spectral techniques (IR, NMR), SEC-GPC, and viscometric analysis. Additive performances mainly as a pour point depressant (PPD) and viscosity index improver (VII) or modifier (VM) were evaluated by standard ASTM methods. The shear stability of the polymers was also determined as per the ASTM D6022-06 method. Biodegradability of all the polymers was tested by the disc diffusion method against fungal pathogens and by a soil burial degradation test (SBT) of the polymer films as per ISO 846:1997. The oil thickening property of the polymers has also been investigated and reported here. Thermal stability of the polymers was determined by thermogravimetric analysis. A comparison of their performances has also been reported.

KEYWORDS: *Viscometric analysis, Pour point depressant, Viscosity index improver, Shear stability, Biodegradability*

■ INTRODUCTION

Lubricants are widely used to reduce the friction between the surfaces of moving parts and thereby reduce wear and prevent possible damage to the parts. The reduction of friction and wear results from the formation of a lubricant film separating the rubbing surfaces. The thickness of the lubricant film depends upon constituent chemistry (base oil and additives), as well as upon the operating conditions, specifically the applied load and sliding velocity. At a sufficiently high load, lubricant may be expelled from the friction zone, leaving the rubbing surface unlubricated. In this case, severe friction and wear occur. Most lubricants are comprised principally of a base stock or lube oil (mainly petroleum origin), which is generally a mixture of high molecular weight hydrocarbons and an additive package. The major portion of the base stocks is a mixture of paraffinic hydrocarbons (>85%) of different chain length. Naphthenic and aromatic hydrocarbons are also present in different rations. Whatever the quality of the base stock, the paraffinic components of the base stock forms a wax crystal network at low temperature that inhibits the normal flow properties of the base oil. Other problems associated with the lube oils are the change in viscosity of the base stocks with the change in temperature, low thermo-oxidative stability, tribological behavior, etc. To overcome these drawbacks, additives with suitable formulation are blended with the base stocks. These additives, polymeric in nature, improved the field service performance of the base lubricating fluids. Additive molecules typically have long oil soluble hydrocarbon (nonpolar) tails and smaller hydrophilic (polar) head groups. Because the two parts of the molecule have different solubilities in oil, additives therefore tend to exist in the colloidal form as inverse micelles. Viscosity index improvers,[1] antioxidant,[2] detergent dispersant,[3] antiware,[4] and pour point depressants[5] are some of the important additives added to lube oil.

Although additives of many diverse types have been developed to meet the needs of modern lubricants, acrylate-based polymers for lube oil additives have been widely for a long time.[1] These conventional acrylate-based additives are extremely harmful for the biosphere. Vegetable oils have many promising natural properties including good lubricity, good resistance to shear, a high flash point, and a high viscosity index and low evaporative loss over the mineral oils.[6−8] They are primarily triglycerides, that is, tri-esters of long chain fatty acids (both saturated and unsaturated) combined with glycerol. There are examples where vegetable-based oils have been used as lubricating oils as an alternative to petroleum-based oils.[9−11] But these vegetable oils are costly, and in general, are about twice as expensive as petroleum-based oils. Beside this, they have very low oxidation stability and cold temperature properties.[12] The main reason for the thermal and oxidative instability of plant-based oils is the structural "double bond" elements in the fatty acid part and the "β-CH group" of the alcoholic components.[13] So, if the thermal stability and fluidity at low temperature of the oil of plant origin can be effectively increased by chemical modification,[14] then their use as an additive into the lube oil will not only add performance but also will maintain the overall cost of the product. There exists lot of references on the use of modified vegetable oils as lube oil additive.[15−17] U.S. Patent 4970010 in 1990 has described the use of vegetable oil derivatives as a lubricating oil additive. U.S. Patent 5282989 in 1994 disclosed the use of sulfurized

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vegetable oil as a lube oil additive (as extreme pressure). U.S. Patent 4925581 in 1990 claimed the application of meadowfoam oil and meadofoam oil derivatives as lubricant additives. Sulfurized vegetable wax esters were described in U.S. Patent 4152278 as antiwear and friction modifiers and extreme pressure additives. The synthesis and evaluation of vegetable oil-based lubricant additive, which can be used as thermal oxidative stability enhancers and viscosity improvers was discussed in U.S. Patent 5229023. U.S. Patent 4873008 described the synthesis of jojoba oil-based lube oil additives. Recently, in the International Conference on Chemical Processes and Environmental issues (ICCEEI'2012) held on July 15−16, 2012, in Singapore, the synthesis of pour point depressant from sunflower oil was discussed. Thus, there exists an ample opportunity to work on this area in order to develop environmental benign lube oil additives with better performance than the conventional synthetic chemical-based additives.

From the above literature work, the authors felt necessary to undertake a systematic study toward the synthesis, characterization, and performance evaluation (mainly of PPD and VII) of some polymeric additives based on vegetable oil (sunflower oil and soybean oil) for lubricating oil.

EXPERIMENTAL SECTION

Materials. Refined SFO and SBO were collected from SK Oil Industries (India). The fatty acid composition of soybean oil and sunflower oil is given in Table 1, and the structure of its major constituent (triglyceride of fatty acids) is shown in Figure 1. Benzoyl peroxide (GC 98%), obtained from LOBA chemicals, was recrystallized from $CHCl_3$−MeOH before use. Base oils BO1 and BO2 (paraffinic in nature) were collected from IOCL, Dhakuria, West Bengal, India, and their properties were tested before the experiment. The fungal specimens were collected from the Department of Microbiology, North Bengal University, West Bengal, India.

Table 1. Fatty Acid Profile of Soybean Oil and Sunflower Oil

	fatty acids	% composition sunflower oil	 soybean oil
saturated	C 12:0 (lauric acid)	0.29	0.16
	C 14:0 (myristic acid)	0.56	0.28
	C 16:0 (palmitic acid)	7.5 (4−9)	11
	C 18:0 (stearic acid)	4 (1−7)	4.1
	C 20:0 (arachidic acid)	0.41	0.31
unsaturated	16:1 (palmitioleic acid)	0.30	0.26
	18:1 (oleic acid)	23 (14−40)	22
	18:2 (linoleic acid)	60 (48−74)	54
	18:3 (linolenic acid)	2.9	7.5

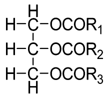

Figure 1. Triester of long chain fatty acids with glycerol. Here R_1, R_2, and R_3 are long chain hydrocarbon parts of different fatty acids.

Synthesis of the Polymer. Ten grams of each of the monomers (Figure 2), SFO and SBO, with 0.01 g BZP was taken in vials. The vials were then sealed with a Teflon septum, and argon was bubbled through each solution. The reaction mixtures were magnetically stirred at 90 °C with microwave heating for 30 min in a focused monomode microwave oven (CEM Corporation, Matthews, NC) applying 300 WT without any solvent, which were subsequently quenched by quickly cooling to room temperature.[18] The polymerization reaction took place via radical mechanism. A little portion of the polymers of SFO (S-1) and SBO (S-2) thus obtained were diluted with THF and used for GC measurements to determine the molecular weight. A pictorial diagram of a probable structure of the prepared polymers is given in Figure S7 of the Supporting Information.

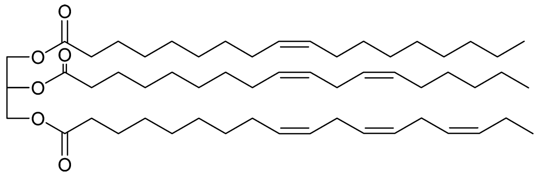

Figure 2. Structure of the monomer.

Determination of Average Molecular Weights of the Polymers. The average molecular weight of the additives was determined by GPC and the viscometric method. The number average molecular weight (M_n) and weight average molecular weight (M_w) were measured in GPC method. In this method, the samples were dissolved in tetrahydrofuran (0.4%, wt/vol) (used as mobile phase) in the water GPC system (polystyrene calibration) at 40 °C. In the viscometric method, the viscosity average molecular weight (M_v, viscosity average) was calculated by the Mark−Houwink−Sukurda relation (eq 1).

$$[\eta] = KMv^{a} \tag{1}$$

where $[\eta]$ is the intrinsic viscosity in dL g^{-1}, M_v is the viscosity average molecular weight, and K and a are viscometric constants for a given solute−solvent system and temperature. The intrinsic viscosities of the dilute polymer solution at a particular temperature can be evaluated by a number of mathematical relations by graphic extrapolation.[19−22] The most commonly used equations are as follows

$$\text{Huggins (H)} \quad \frac{\eta_{sp}}{C} = [\eta]_h + k_h[\eta]_h{}^2 C \tag{2}$$

$$\text{Kraemer (K)} \quad \ln \eta_r/C = [\eta]_k - k_k[\eta]_k{}^2 C \tag{3}$$

where $\eta_r = t/t_o$ = relative viscosity or viscosity ratio, i.e., time of flow of the solution/time of flow of the pure solvent, $\eta_{sp} = \eta_r - 1$ = specific viscosity, $[\eta]$ = intrinsic viscosity, k is reaction coefficient and C is concentration (g cm^{-3}). The subscripts h and k denote for Huggins and Kraemer equation, respectively. In the MHS equation, the constants K = 0.00387 dL g^{-1} and a = 0.725 were employed, and adequate precautions against evaporation of the solvent during viscometric measurements were taken.

The use of these equations have been derived under the supposition of the validity of the relationship $k_h + k_k = 0.5$.[23]

MEASUREMENTS

Spectroscopic Measurement. The IR absorptions of the two polymers were recorded on a Shimudzu FT-IR 8300 spectrometer using 0.1 mm KBr cells at room temperature within the wavenumber range of 400−4000 cm^{-1}. NMR spectra were recorded in Bruker Avance 300 MHz FT-NMR spectrometer using 5 mm BBO probe. $CDCl_3$ was used as solvent and TMS as reference material.

Viscometric Measurements. Viscometric measurements were carried out at 40 °C in a toluene solution using a Ubbelohde OB viscometer for eight different concentrations of the sample solution. The time of flow of the solution was manually determined by using a chronometer. For the viscosity average molecular weight calculation using the Mark−Houwink−Sukurda relation, the constants K = 0.00387 dL g^{-1} and $a = 0.725$[24] were employed.

Thermogravimetric Analysis (TGA). The thermal stability was measured with a Shimadzu TGA-50 thermobalance in terms of percent degradation of weight of the polymers with an increase in temperature (10 °C/min) in air using an alumina crucible.

Evaluation of Thickening Property. Kinematic viscosity of the base oils and that of the polymer-doped base oils in different

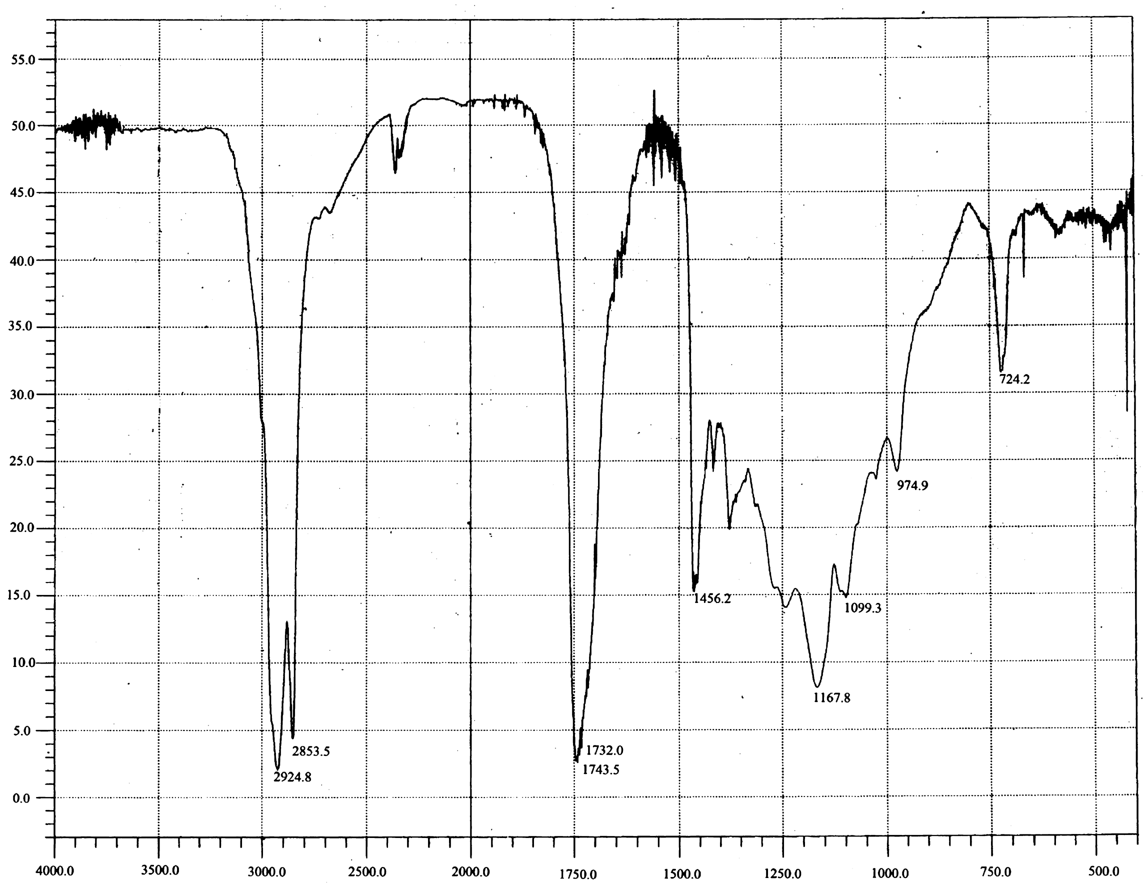

Figure 3. FT-IR of homopolymer of SFO (S-1).

concentrations were evaluated. Thickening power of the polymer was determined by evaluating the percent increase in viscosity of the base stocks by the addition of unit amount of additive.

Evaluation of Pour Point. The pour points of the base oils (BO1 and BO2) at different doping concentrations of the additive were evaluated using the WIL-471 cloud and pour point test apparatus model 3 (India) according to ASTM D97 method.

Evaluation of Viscosity Index. Viscosity indexes of the prepared polymers were evaluated in different base stocks (BO1 and BO2) according to the ASTM D2270 method. The kinematic viscosities (KV) of the base oils containing different concentrations (ppm) of the additive were determined at 40 and 100 °C. Each sample was measured three times in order to minimize the error. Finally, the viscosity index was determined according to the ASTM D2270 formula.

Evaluation of Shear Stability Index. The shear stability of the two polymer solutions in base oils were determined by ASTM methods. The KV values before and after shear were evaluated at 100 °C. Then permanent viscosity loss (PVL) and permanent shear stability index (PSSI) were determined by ASTM D6022-06 formula.

Biodegradability Test. Biodegradability is the most important aspect with regard to the environmental fate of a substance. Vegetable-based oils are easily biodegradable under anaerobic conditions, whereas mineral oils are not.[9,25] Ultimate biodegradation is when the substance is totally converted by microorganisms into carbon dioxide, water, mineral salts, and biotic mass. Several tests have been developed to measure biodegradability. Here, the microbial degradation of the polymers were tested by the (i) disc diffusion method[16] against fungal pathogens and (ii) soil burial degradation test of polymer films as per ISO 846:1997[26] and by measuring the shift of IR frequency of the ester carbonyl after the biodegradability test.

Disc Diffusion Method. In this process, biodegradation of the prepared polymer samples were tested against four different fungal pathogens, namely, *Calletotricheme camellia*, *Fussarium equisitae*, *Alterneria alternata*, *Colletrichum gleosproides*. All glass apparatus and culture media were autoclaved before use. Culture media for fungal strains were prepared by mixing suitable proportions of potato extract, dextrose, and agar powder. The fungal growth was confirmed by a change of color from yellow to blackish. The experiment was performed in Petri dishes and was incubated at 37 °C for 30 days after addition of a definite weight of polymer samples. The whole process was carried out in an inoculation chamber. After 30 days, polymer samples were recovered from the fungal media and washed with chloroform, purified, and dried in an open vessel. The dried samples were weighed.

Soil Burial Degradation Test. In soil burial degradation, the effect of microorganisms arises on the surface of the polymer film.[27] The films of polymer samples were buried in soil (pH 7.2, soil moisture 25%). The soil used in this study had been taken from the North Bengal University (West Bengal, India) campus. The soil was taken in a tray, in which the relative humidity was adjusted to 50–60%, and temperature was thermostatted at 30 °C with the help of a humidity chamber. The soil was conditioned for 1 week before it was used for the actual test. The buried films were removed at regular intervals of 15 days up to a span of 3 months. Recovered films were washed with chloroform, purified, and dried in a vacuum oven at 50 °C to constant weight. The weights of the sample, before and after drying, were recorded. The percentage of weight loss of the samples was calculated as follows

$$\text{Weight loss} = [(M_0 - M_1)/M_0] \times 100$$

where M_0 is the weight of the original films before SBT, and M_1 is the weight of residual films after SBT and subsequent drying until a constant weight was reached for the different times. As the exposure time increased, the weight of the biodegradable mulching film

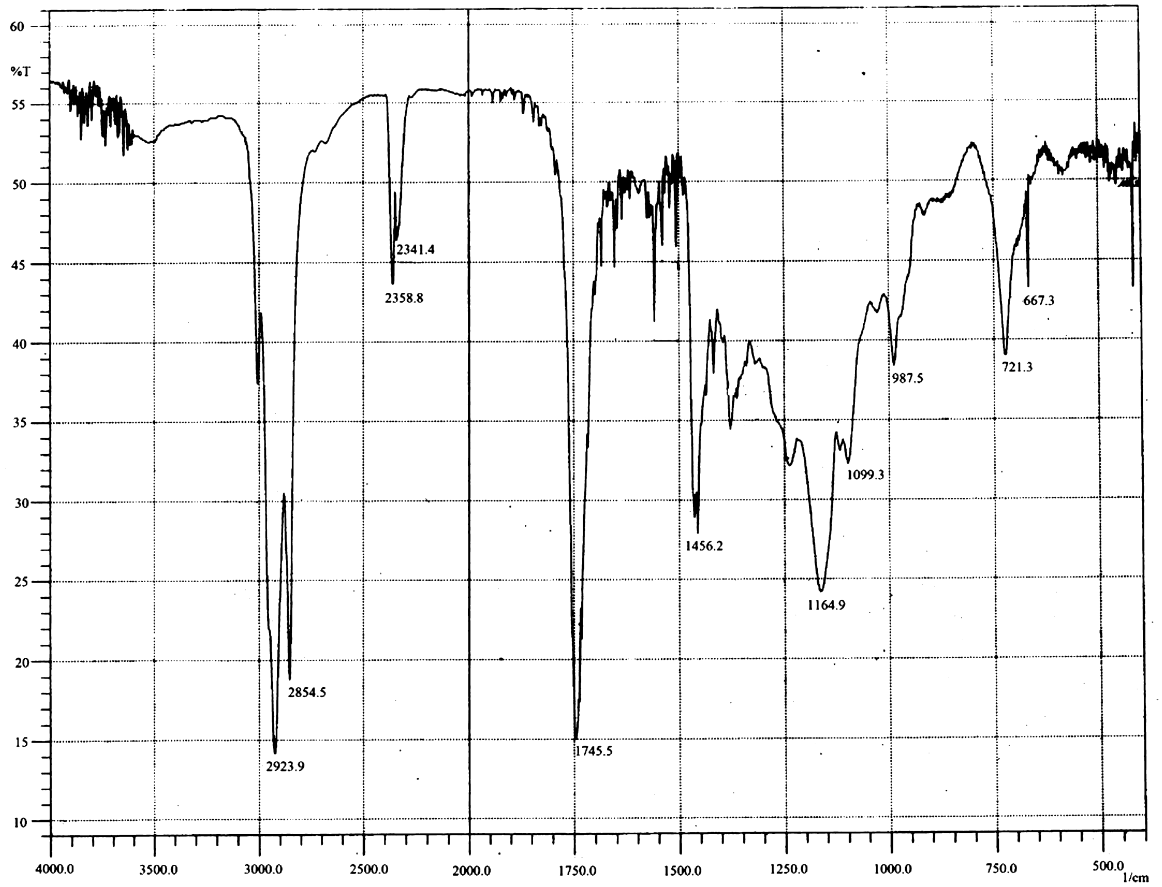

Figure 4. FT-IR of homopolymer of SBO (S-2).

decreased gradually. This is possibly due to the constant erosion from soil microorganisms.

■ RESULTS AND DISCUSSION

The IR absorptions at 1745.5 and 1732 cm^{-1} for the homo polymer of SBO and SFO (Figures 3 and 4) showed the presence of an ester carbonyl group. Broad peaks in the regions of 1164.9 and 1167.8 cm^{-1} were due to the ester C−O stretching vibration of the two additives S-2 and S-1, respectively. Peaks appearing in the regions of 1099.3 and 721.3 cm^{-1} were for C−H bending vibrations. Absorptions observed in the regions of 2854.5 and 2923.9 cm^{-1} were for the paraffinic C−H bonds of S-2 and those from 2853.5 to 2924.8 cm^{-1} were for S-1. The ^{1}H NMR of the homopolymer of SFO and SBO showed broad peaks in the range of 4.117−4.315 ppm due to ester carbonyl protons of the triglyceride. Peaks also appeared in the range of 0.857−0.911, 1.255−1.607, and 2.001−2.769 ppm for methyl and methylene protons, respectively. The proton decoupled ^{13}C NMR showed peaks in the range of 172.90−178.92 ppm for protons of the $-OCH_2$ groups of the triester. The absence of unsaturation was indicated by the absence of peaks in the range of 130−150 ppm. All the ^{1}H and ^{13}C NMR data are given in Supporting Information.

The TGA data listed in Table 2 indicates that before polymerization 95% of sunflower oil was decomposed at 320 °C, whereas 94% was decomposed at 410 °C after polymerization. In the case of soybean oil, 92% was decomposed at 355 °C before polymerization and 93% was decomposed at 440 °C after polymerization. Thus, the lower thermo-oxidative stability of both soybean and sunflower oil could be significantly increased by their polymerization, and the homopolymer of soybean oil (S-2) showed better performance than the homopolymer of sunflower oil (S-1).

Table 2. Thermal Stability (TGA Data)

sample	decom. temp.[a] (°C)	PWL[b]
sunflower oil	230/320	41/95
soybean oil	250/355	37/92
homopolymer of sunflower oil (S-1)	340/410	38/94
homopolymer of soybean oil (S-2)	350/440	25/93

[a]decom. temp.: decomposition temperature. [b]PWL: percent weight loss.

The intrinsic viscosity values calculated by two different equations (eqs 1 and 2) for both the polymers are shown in Table 3. The higher intrinsic viscosity value for S-2 indicates that the polymer of soybean oil has a fairly strong interaction with the solvent. The $k_h + k_k$ value of S-2 also supports that in base oil the solubility of S-2 is better than S-1 and thus points toward the formation of the chain-like structure of the present polymer as discussed earlier.[21] From the intrinsic viscosity values, the viscosity average molecular weights (M_v) were obtained. From Table 3, it is shown that the average molecular weight of S-2 polymer is slightly higher compared to S-1. This may be due to the presence of relatively higher percentage of linolenic acid in SBO compared to SFO (Table 1) that causes the higher degree of branching of the S-2 polymer. Spectral data supports the fact that the double bonds are involved in a polymerization process, and as a consequence, the monomers

Table 3. Intrinsic Viscosity, Vicometric Constant, and Molecular Weight Values Determined by the Mark−Houwink Equation.

						average molecular weight values (g/mol)				
	intrinsic viscosities[a]		viscometric constants[a]			viscosity average[a] (M_v)		GPC		
samples	$[\eta]_h$	$[\eta]_k$	k_h	k_k	$k_h + k_k$	M_h	M_k	$M_w \times 10^4$	$M_n \times 10^4$	PDI[b]
S-1	7.281	6.879	0.275	0.139	0.414	32849	30374	3.51	3.3	1.06
S-2	9.58	9.167	0.356	0.116	0.472	47963	45134	4.85	4.64	1.05

[a] h and k refers to Huggins and Kraemer equations, respectively. [b] PDI: polydispersity index.

Table 4. Viscosity Index (VI) and Thickening (THK) Values of Additive-Doped Base Oils

		conc. of additive-doped base oils (ppm $\times 10^3$)							
		2		3		4		5	
sample	base oil	THK (%)	VI	THK (%)	VI	THK (%)	VI	THK (%)	VI
S-1	BO1	2.841	121	3.935	131	5.432	158	6.807	161
	BO2	1.093	135	1.619	150	2.259	164	3.198	198
S-2	BO1	6.06	130	6.38	169	6.731	201	6.363	211
	BO2	5.718	141	5.326	172	3.788	220	4.103	238

are getting attached to each other. The polydispersity index data also indicated linear distribution with little branching of individual molecular masses in case of both the polymers.

Thickening power of both the homopolymers (Table 4) as evaluated in different base stocks (Table 5) indicated a gradual increase with an increase in concentration of the additive. This may be because of the fact that the polymer molecule assumes a coiled-like aggregation with an increase in its concentration in the base stock. The result also showed that the S-2 polymer exibits a better thickening effect than that of the S-1 polymer. This indicates that as far as fuel economy is concerned the polymer of soybean oil performs better than the polymer of sunflower oil.

Table 5. Physical Properties of Base Oils

properties	method	BO1	BO2
density (g cm^{-3}) at 40 °C	ASTM D4052	0.84	0.94
viscosity at 40 °C in cSt	ASTM D445	6.708	24.229
viscosity at 100 °C in cSt	ASTM D445	1.774	4.016
viscosity index	ASTM D2270	80.05	89.02
cloud point,°C	ASTM D2500	−10	−8
pour point,°C	ASTM D97	−3	−6

The prepared homopolymers were tested for their effectiveness as viscosity index improvers in comparison to the pure base oils by measuring the VI of the respective additive-doped base oils by the ASTM D2270 method.[28] The test method comprises the determination of the kinematic viscosities of the different base oils containing different concentrations of the additives at 40° and 100 °C. The data (Table 4) indicates that VI values of the base oils (Table 5) are significantly increased by the addition of both of the additives. Moreover, the values increase with increasing the concentration of the prepared additives, and the S-2 polymer shows higher VI in comparison to the S-1 polymer in BO1 and BO2 base oils. As the temperature is raised, the polymer molecule expands, and because of this, its hydrodynamic volume increases. This increase in the micelle size of the solvated polymer molecules counterbalanced the reduction of the viscosity of the lube oils with temperature.[29] This effect is more pronounced in the case of the S-2 polymer rather than S-1. The increase in concentration of the polymer leads to an increase in the total volume of the polymer micelles in the oil solutions. Consequently, the higher concentration of additive will impart a higher viscosity index.[30]

The PSSI of both the polymers was evaluated as per the ASTM D6022-06 method in two base oils (Table 6). The stability of the polymers against shear decreases with increasing PSSI values.[31] It is observed that with increasing the concentration of the additive the PVL values increases, and as a result, the PSSI values increase. This may be explained based

Table 6. Shear Stability of Polymer-Doped Base Oils (BO1 and BO2)

		KV							
		before shear		after shear		PVL		PSSI	
base oils	conc. in ppm ($\times 10^3$)	S-1	S-2	S-1	S-2	S-1	S-2	S-1	S-2
BO1	1	2.137	2.28	2.011	2.1	5.896	8.57143	34.71	35.5731
	2	2.32	2.34	2.121	2.13	8.578	9.85915	36.45	37.1025
	3	2.428	2.58	2.185	2.26	10.01	14.1593	37.16	39.7022
	4	2.517	2.85	2.208	2.37	12.28	20.2532	41.59	44.6097
	5	2.617	3.01	2.282	2.45	12.8	22.8571	39.74	45.3074
BO2	1	4.404	4.85	4.201	4.4	4.609	10.2273	52.32	53.9568
	2	4.729	5.45	4.511	4.58	8.839	18.9956	58.63	60.6695
	3	5.169	6.6	4.401	4.85	14.86	36.0825	66.61	67.7245
	4	5.77	7.02	4.551	4.97	21.13	41.2475	69.5	68.2423
	5	6.656	7.9	5.015	5.18	24.65	52.5097	62.16	70.0309

on the molecular weight of the polymers. With an increase in polymer concentration, molecular mass distribution increases, and the system undergoes degradation. The higher PSSI values of S-2 compared to S-1 reveal that the homopolymer of soybean oil is relatively less stable against shear.

The result of the biodegradability tests (Table 7) in both disc diffusion and the SBT method indicate that polymers S-1 and S-2 show significant degradation against the fungal pathogen *Alterneria alternata* and microorganisms present in the soil.

Table 7. Result of Biodegradability Test by Disc Diffusion Method and Soil Burial Degradation for Polymeric Additives (S-1 and S-2)

disc diffusion method				
pathogen used	polymer	initial wt (g)	final wt (g)	% wt loss
Calletotricheme camellia	S-1	0.5843	0.5783	1.03
	S-2	0.5785	0.5705	1.38
Fussarium equisitae	S-1	0.5874	0.5768	1.80
	S-2	0.5658	0.5532	2.23
Alterneria alternata	S-1	0.5742	0.3814	33.58
	S-2	0.5483	0.4010	26.86
Colletrichum gleosproides	S-1	0.5921	0.5765	2.63
	S-2	0.5651	0.5445	3.64
Curvularia eragrostidies	S-1	0.5610	0.5580	0.53
	S-2	0.5531	0.5501	0.54
soil burial degradation test				
microorganism present in soil	S-1	0.5881	0.4215	28.33
	S-2	0.5972	0.4528	24.18

PPD properties of both the polymers as evaluated in different base stocks showed a good depression (Table 8) in the base stocks studied. It was also found that pour points of the base oils increase gradually by increasing the concentration of the additives, and the S-1 polymer showed better depression in pour point than S-2. Thus, it may be concluded that both polymers may be used as potential PPD for the base stocks, but the homopolymer of sunflower oil is still better compared to soybean oil.

Table 8. Pour points (°C) of Polymeric Additives in Different Base Oils

		conc. in ppm (× 10^3)			
polymers	base oils	2	3	4	5
S-1	BO1	−6	−9	−15	−18
	BO2	−9	−12	−15	−18
S-2	BO1	−6	−9	−9	−12
	BO2	−6	−8	−9	−12

The comparative study between the pure base oils and additive-doped base oils in reference to VI and PPD properties indicated that a great extent of performance modifications have been achieved by the addition of prepared additives in the base oils.

CONCLUSION

From the above discussion, it is clear that both additives perform as excellent viscosity index improvers and thickeners, and their stability against shear is also significant. The VI, THK, and PSSI properties increase with an increase in concentration of the polymers. The SBO polymer showed higher thermo-oxidative stability, higher viscosity index, and higher shear stability index values compared to the SFO polymer. However, when PPD properties and biodegradability were considered, the polymer of sunflower oil showed better performance. Thus, a significant modification of base oil properties has been achieved by addition of these newly developed greener additives.

ASSOCIATED CONTENT

Supporting Information

Characterization data (^{1}H and ^{13}C NMR) and pictorial diagram of a general structure of the polymers. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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