Soybean Oil as a Biocompatible Multifunctional Additive for Lubricating Oil

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S *Supporting Information*

ABSTRACT: The application of greener additives based on vegetable oils in the formulation of biolubricants has attracted considerable interest due to their biocompatibility and enhanced multifunctional performances compared to conventional additives. In this investigation, homopolymers of soybean oil and copolymers with methyl acrylate, 1-decene and styrene were synthesized by a thermal method using azobisisobutyronitrile as a radical initiator. Characterization of the prepared polymers was performed by spectral (NMR, IR), viscometric analysis and gel permeation chromatography. Performance evaluations of the polymers as pour point depressant, viscosity modifier/viscosity index improver (VII) and antiwear in different base oils (mineral) were conducted by standard ASTM methods. Biodegradability of the prepared additives was tested

against fungal pathogens and micro-organisms by the disc diffusion method and soil burial test method, respectively. Thermal stability of each of them was evaluated and included. The multifunctional performances were compared and reported.

KEYWORDS: *Thermogravimetric analysis, pour point depressant, viscosity index improver, antiwear, ASTM method, biodegradability*
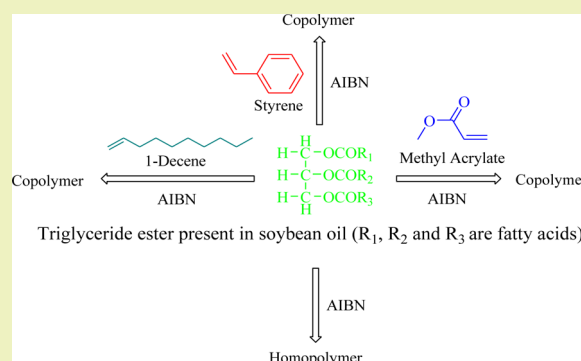
INTRODUCTION

Lubricants, composed of a majority of base oil and an additive package (1% to 30%), generally are used to reduce friction of two moving surfaces contacting with each other in engines. The base fluids may be of synthetic or vegetable based oils or mineral oil that contains a mixture of hydrocarbons (paraffinic or naphthenic) with 20−30 carbon atoms. The role of additives in a lubricant is very significant. They are added to the base oil to optimize the performance of the lubricant in certain applications. Pour-point depressants,[1] viscosity index improvers,[2,3] dispersants/detergents,[4] antiwear[5] and extreme-pressure,[6] antioxidant and corrosion inhibitors,[7] etc. are the examples of additives generally used.

Most of the additives used generally are synthetic ester based[8,9] and harmful to the environment and costly too. The use of vegetable oils, i.e., triglycerides of long chain carboxylic acids combined with glycerol (Figure 1), as base fluids is highly expected from the viewpoint of increasing global environmental pollution. They have been recognized as being biodegradable,[10] nontoxic, having high viscosity index (VI)[11] and shown excellent tribological properties.[12,13] But due to the poor oxidative and hydrolytic stability, high temperature sensitivity in tribological behavior, poor cold flow properties, higher cost and gumming effect[14,15] they are very limitedly used as base fluids in the formulation of industrial lubricants. As such, petroleum based lubricants are still dominating the lubricant market. Currently, chemically or genetically modified vegetable oils[16,17] are used to formulate biodegradable lubricants. But their
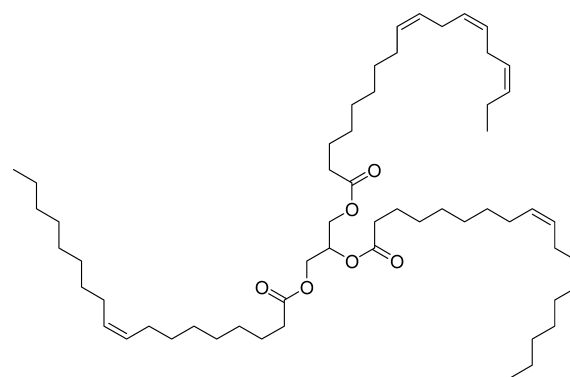
Figure 1. General structure of triglyceride of long chain fatty acids, the major constituents of soybean oil.

application as a base fluid is still not widespread due economical reasons and their insufficiency to meet bulk demands. These vegetable oils can also be used as additives[18−20] in the formulation of biolubricants, and their application as environmentally benign multifunctional additives not only increases the lifetime of engines but also increases its field service performances. In our earlier publications, the use of vegetable oils as VII and pour point depressant (PPD) has been mentioned.[21−23] Electronized vegetable oils were used as an

additive in mineral base oil to enhance the extreme pressure property in formulation of metalworking lubricants.[24] U.S. Patent No. 4970010 has disclosed the use of vegetable oil derivatives as lubricating oil additive. The use of sulfurized vegetable oil has been described as an extreme pressure additive in U.S. Patent 5282989. Li et al.[25] have shown the application of natural garlic oil as a high-performance and environmentally friendly extreme pressure additive in lubricating oils. Biresaw et al.[26] have mentioned the application of biobased polyesters as extreme pressure additive in mineral oil. Kumar et al.[12] have discussed the tribological and emission studies on two stroke petrol engine lubricated with sunflower methyl ester.

Therefore, the objective of the present work is to synthesize lube oil additives based on vegetable oil and evaluate their additive performances blending with different mineral oils. In the present investigation, a homopolymer of soybean oil (SBO) and its copolymers with methyl acrylate, 1-decene and styrene in two different concentrations were prepared, characterized and their performances as multifunctional lube oil additive tested and compared. In addition, biodegradability of each of them was tested also.

■ EXPERIMENTAL SECTION

Materials. Refined SBO (85% unsaturation) was from SK Oil Industries (India), and its fatty acid composition[27] is given in Table 1.

Table 1. Fatty Acid Profile of SBO

fatty acid	% composition (max)
saturated	
C 12:0 (lauric acid)	
C 14:0 (myristic acid)	0.1
C 16:0 (palmitic acid)	11
C 18:0 (stearic acid)	2.8
unsaturated	
16:1 (palmitioleic acid)	0.21
18:1 (oleic acid)	24
18:2 (linoleic acid)	55.8
18:3 (linolenic acid)	5.1
20:1 (gadoleic acid)	0.1

Toluene (GC 99.5%) was from Merck (Mumbai, India). Azobisisobutyronitrile (AIBN, GC 98%, Spectrochem Pvt. Ltd. Mumbai, India) was recrystallized from CHCl$_3$−MeOH before use. Styrene (GC 99%, Acros Organics, USA), methyl acrylate (GC 99%, Thomas Baker (Chemicals) Pvt. Ltd, Mumbai, India), 1-decene (GC 95%, Acros Organics, USA) and methanol (GC 99.8%, Thomas Baker (Chemicals) Pvt. Ltd, Mumbai, India) were used as received. Mineral base oils, SN1 and SN2, were collected from IOCL, Dhakuria, West Bengal, India. The physical properties of the base stocks are shown in Table 2. The fungal specimens were collected from Department of Microbiology, North Bengal University, West Bengal, India.

Synthesis of the Polymer. Preparation of homopolymer of SBO and its copolymer with methyl acrylate, 1-decene and styrene in two

Table 2. Physical Properties of Base Oils

properties	method	SN1	SN2
density (g cm^{-3}) at 40 °C	ASTM D 4052	0.84	0.941
viscosity at 40 °C in cSt	ASTM D 445	6.708	24.229
viscosity at 100 °C in cSt	ASTM D 445	1.774	4.016
viscosity index	ASTM D 2270	80.05	89.02
cloud point, °C	ASTM D 2500	−6	−8
pour point, °C	ASTM D 97	−3	−6

different concentrations [5% and 10%, (w/w)] was carried out in a four necked round-bottom flask fitted with a mechanical stirrer, condenser, thermometer and an inlet for the introduction of nitrogen at 90 °C for 6 h by radical pathway. In this reaction, toluene was used as a solvent and AIBN as an initiator. At the end of the reaction time, the reaction mixture was poured into methanol while the reaction mixture stirred to terminate the polymerization and precipitate the polymer. The polymers were further purified by repeated precipitation of their hexane solution by methanol followed by drying under vacuum at 40 °C.

Determination of Average Molecular Weight. The average molecular weight of the prepared polymeric additives was determined by a viscometric technique[28] using Mark−Houwink−Sukurda (MHS) relation cited in eq 1 and GPC. The viscometric study was carried out at 40 °C taking eight different concentrations (g cm^{-3}) of the polymeric additives in toluene by an Ubbelohde OB viscometer having viscometer constant values $K' = 0.002\,68$ cm^2 s^{-1} and $L = -19.83$ cm^2. The volume of the bulb and length of the capillary tube were 3 cm^3 and 11.3 cm, respectively. A chronometer was used for recording the flow-times of the solutions. The intrinsic viscosity values, used in the MHS equation for evaluating the average molecular weights, were determined by a graphical extrapolation method using the Huggins equation mentioned earlier.[28]

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

Here $[\eta]$ stands for the intrinsic viscosity (dL g^{-1}) and M_v stands for the viscosity average molecular weight. K and a are viscometric constants for a given solute−solvent system and temperature. In the MHS equation, the constant K stands for the value of 0.003 87 dL g^{-1} and an a value of 0.725 was employed. During this experiment, adequate precautions against evaporation of the solvent were taken. The number-average molecular weight (M_n), weight-average molecular weight (M_w) and polydispersity indices (PDI, M_w/M_n) were determined by a Waters GPC system having the molecular weight range $10^2 - 5 \times 10^5$ g mol^{-1} equipped with a 2414 refractive index detector, Waters 515 HPLC pump and 717 plus autosampler. THF (0.4%, wt/vol) was used as an eluent at a flow rate of 1.0 mL/min at 40 °C. The instrument was calibrated with polystyrene before the experiment.

Spectroscopic Analysis. Shimudzu FT-IR 8300 and Bruker AVANCE 300 MHz FT-NMR instruments were used to characterize the polymers. Infrared (IR) spectra were taken within the range of 400 to 4000 cm^{-1} using 0.1 mm KBr cells at room temperature. For ^{1}H NMR, a 5 mm BBO probe, CDCl$_3$ solvent and TMS as the reference material were used (for detailed analyses, see the Supporting Information).

Thermal Stability Analysis. The thermo-oxidative stability of all the polymers was determined by thermogravimetric analysis (Shimudzu TGA-50) in air using an alumina crucible at a heating rate of 10 °C/min. The percent weight loss (PWL) of the polymers with rise in temperature was calculated.

■ PERFORMANCE EVALUATION

Evaluation of Viscosity Index. Viscosity index (VI),[29] an arbitrary number, indicates the resistance of the change of viscosity of the base oils along with change in temperature. A higher value of VI indicates a relatively small change in viscosity with the temperature variation. The efficiency of an additive as VII is determined by the increment of VI of the base oils by the addition of that additive. It was calculated according to the ASTM D2270-10 method by measuring kinematic viscosity values of the base oils (SN1and SN2) at 40 and 100 °C after blending additives at different concentration (mass fraction) levels.

Evaluation of Pour Point (PP). The PP of the base oils (SN1 and SN2) at different blending concentrations of the additive was evaluated based on the ASTM-D97 method using

cloud and pour point test equipment (Wadegati labequip Pvt. Ltd, India) in the temperature range 0 to −71 °C.

Evaluation of Tribological Properties. The tribological properties of the base oils blended with the additives at different concentration levels were evaluated by a four-ball wear test apparatus (FBWT) following the ASTM D 4172-94 method.[20] In this experiment, the wear scar diameter (WSD), a parameter for the determination of antiwear (AW) performance of the oils, was measured applying a weld load of 392 N (40 kg) at 75 °C for 60 min. The diameter and rotating speed of the ball were 12.7 mm and 1200 rpm, respectively. The coefficient of friction (COF) was also calculated by multiplication of the mean friction torque and spring constant. The frictional torque on the lower balls may be expressed as

$$\mu = \frac{T\sqrt{6}}{3W \times r} \tag{2}$$

where, μ = coefficient of friction, T = frictional torque (kg/mm), W = applied load (kg), r = distance from the center of the contact surfaces on the lower balls to the axis of rotation, which is 3.67 mm.

Biodegradability Test. The main advantage of using vegetable based additives over synthetic acrylate based ones is their excellent biodegradability. The biodegradability test of the additives was performed by disc diffusion (DD) and soil burial test (SBT) methods (ISO 846:1997).[22,23] The test solutions were prepared by adding the polymers in different mass fractions (0.00 to 0.04) in the base fluids. Ultimate biodegradation was achieved when the substance was totally converted into carbon dioxide, water, mineral salts and biotic mass. The extent of degradation calculated in terms of percentage of weight loss (PWL) of the samples is as follows

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

where M_0 is the initial mass and M_1 is the remaining mass after the test and subsequent drying until constant weight. The degradation of the polymers was confirmed by the percent weight loss and a shift in IR frequency of the ester carbonyl group after the test.

Disc Diffusion (DD) Method. Biodegradation of the prepared polymer samples was tested in a bacteriological incubator apparatus against different fungal pathogens. 1.5 g of each of the test solutions of the polymeric additives in base oils was placed in Petri dishes and incubated for 30 days at 37 °C with different fungal pathogens. The fungal pathogens used for this test are *Calletotricheme amellia*, *Fussarium equisitae*, *Alterneria alternata* and *Colletrichum gleosproides*. The culture media for fungal strains was prepared by mixing suitable proportions of potato extract, dextrose and agar powder. The fungal growth was confirmed by a change in color, from yellow to blackish. After 30 days, the samples were recovered, washed several times with chloroform and dried. Finally, the percentage weight loss for each of the samples was calculated.

Soil Burial Test (SBT) method. In the SBT method , 1.5 g of each of the sample solutions was taken to produce films[30] and then buried in the soil compost (collected from near landfill)[31] at pH 7.2, moisture 25% and relative humidity 60% in a bacteriological incubator apparatus (Sigma Scientific Instruments Pvt. Ltd., Chennai, India) for 3 months and thus subjected to the action of micro-organisms in which soil is their major habitat. The test was carried out at 30 °C following the ISO 846:1997 norms.[32] The buried films were removed for

evaluation at regular intervals of 15 days for up to 3 months. Recovered films were washed with chloroform, purified and finally dried in a vacuum oven at 50 °C to constant weight. The dried samples were weighed. The degradation was calculated in terms of percentage weight loss of the polymeric additives.

■ RESULTS AND DISCUSSION

The IR absorptions at 1745.5, 1740, 1732, 1741, 1736.8, 1737.7 and 1732 cm^{-1} for a homopolymer of SBO (S-1), copolymer with methyl acrylate (10%) (S-2), methyl acrylate (5%) (S-3), 1-decene (10%) (S-4), 1-decene (5%) (S-5), styrene (10%) (S-6) and styrene (5%) (S-7), respectively, showed the presence of ester carbonyl group. Peaks at 1167.8 to 1155 cm^{-1} were due to the C−O stretching vibration of the ester carbonyl and from 1099.3 to 712.6 cm^{-1} for C−H bending vibrations. The absence of olefinic peaks for the polymers and its presence in their respective monomers support the phenomenon. Absorptions recorded from 2851.6 to 2944.1 cm^{-1} for the paraffinic C−H bonds. ^{1}H NMR of homo- and copolymers of SBO showed broad peaks in the range of 4.080 to 4.327 ppm due to ester carbonyl protons of the triglyceride. Peaks appeared in the range of 0.820 to 0.911 ppm, 1.220 to 1.608 ppm and 2.000 to 2.770 ppm for methyl and methylene protons, respectively. The proton decoupled ^{13}C NMR showed peaks at 172.91 to 173.97 for protons of −OCH$_2$ groups of the triester. The absence of unsaturation was indicated by the absence of peaks in the range 130 to 150 ppm. The percent incorporation of different monomers in SBO was determined by NMR and FT-IR,[33] and is given in Table 3.

Table 3. Composition of the Monomers in the Copolymers in Terms of Mass Fraction Determined by PMR and FT-IR Spectrophotometric Method[a]

additives	mass fraction of the monomer in SBO	mass fraction of the monomer by PMR method	mass fraction of the monomer by FT-IR method
S-1	0		
S-2	0.1	0.039	0.046
S-3	0.05	0.018	0.02
S-4	0.1	0.035	0.037
S-5	0.05	0.017	0.019
S-6	0.1	0.032	0.035
S-7	0.05	0.015	0.018

[a]S-1 is a homopolymer of SBO and S-2 to S-7 are the copolymers of SBO with different monomers.

The thermal analysis report of the polymers evaluated by a Shimadzu TGA-50 thermobalance in terms of percentage weight loss (PWL) of the polymers with increase in temperature (10 °C/min) in air is shown in Figure 2. It is clearly found that the percentage of degradation of the copolymers of SBO at a particular temperature is lower compared to its homopolymer, which signifies that the thermal stability of the copolymers is relatively higher. Further, it is clearly seen that the copolymers of SBO with 1-decene (S-4 and S-5) showed better stabilities at higher temperatures compared to other copolymers. This may be due to less degree of branching of the respective polymer.[34]

The average molecular weight values determined by the viscometric method and GPC of the polymeric additives, as reported in Table 4, show that the molecular weight of the homopolymer of SBO is slightly higher followed by its
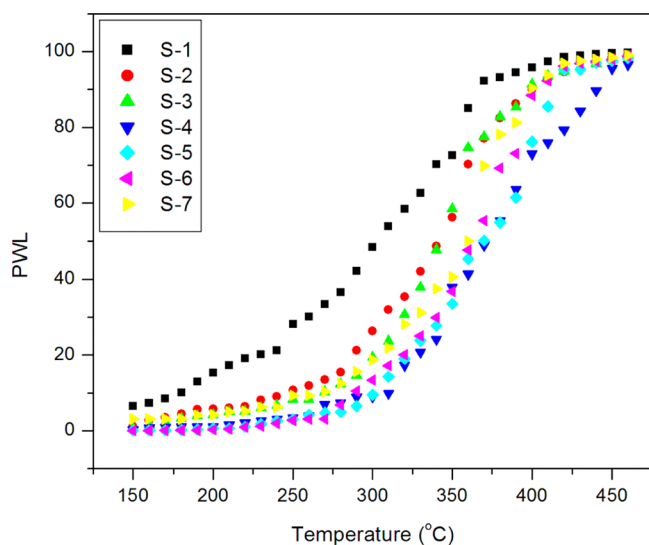
Figure 2. Thermogravimetric analysis of the homopolymer and copolymers of SBO, where PWL is the percent weight loss of the additives.

Table 4. Average Molecular Weight Values (g mol^{-1})^a

	viscosity average		GPC		
samples	$[\eta]$	M_v	$M_w \times 10^4$	$M_n \times 10^4$	PDI
S-1	7.522	34356	4.516	3.153	1.432
S-2	6.585	28598	3.331	2.817	1.182
S-3	6.628	28854	3.41	2.842	1.2
S-4	6.680	29168	3.348	3.015	1.11
S-5	7.037	31342	3.507	3.047	1.151
S-6	6.98	30991	3.431	2.82	1.217
S-7	7.283	32862	4.236	3.431	1.235

^{a}M_v, M_w and M_n refer to viscosity average, weight-average and number-average molecular weights, respectively. $[\eta]$ is the intrinsic viscosity and PDI is the polydispersity index.

copolymer with styrene compared to the other copolymers. It was also reflected in their corresponding intrinsic viscosities and PDI values. The result indicates that, in the case of S-1, S-6 and S-7, the degree of polymerization is higher and the possibility of branching is greater compared to the others that are not desirable for effective interactions of the additives with the base fluids. The lower PDI values for S-4 and S-5 reveal that the copolymer of SBO with 1-decene is relatively more linear and well ordered compared to the others and therefore interacts better with the base oil.

The data, as given in Table 5, indicate that the VI values of the base oils doped with additives are higher compared to those of the base oils (Table 2) without additives. The result also shows that VI values gradually increase with increasing the additive concentration of in the base fluids. This signifies that the additives perform excellent as VII. The homopolymer of SBO showed excellent results. The incorporation of styrene and 1-decene to SBO enhances the VI values whereas copolymers of SBO with methyl acrylate (S-2 and S-3) showed the least VI. Moreover, it was found that all the polymers have much higher VI values compared to commercially available acrylate based or olefin polymers.[3,35] The polymer molecules in base fluid remain as a curled shape. With increasing temperature, they uncoiled and hence their hydrodynamic volume becomes bigger, which increases the viscosity of the lubricant. This increment of

Table 5. Viscosity Index (VI) Values of the Additive Doped Base Oils

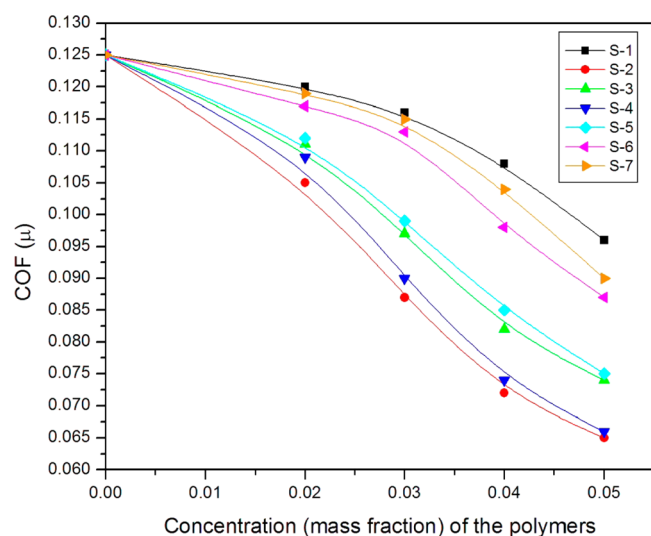|		mass fractions of the additives			
sample	base oil	0.02	0.03	0.04	0.05
S-1	SN1	132	170	211	227
	SN2	140	200	227	256
S-2	SN1	113	127	135	138
	SN2	113	133	153	177
S-3	SN1	116	134	145	160
	SN2	122	144	173	189
S-4	SN1	156	199	232	240
	SN2	150	212	234	262
S-5	SN1	142	184	218	232
	SN2	152	210	242	270
S-6	SN1	162	201	232	242
	SN2	166	211	244	272
S-7	SN1	152	192	217	236
	SN2	162	199	231	268

viscosity counterbalances its decrease by rise in temperature.[36] In the case of copolymers of soy oil with styrene and 1-decene, the degree of solvation becomes higher. This may be due to better interaction with the paraffin based mineral oil with the respective copolymers having the nonpolar ends. On the other hand, due to comparatively more polar character, the solvated volume of the acrylate copolymers of soy oil are smaller and therefore their VI is the lowest among them.

The antiwear and frictional properties of the lubricant composition prepared by blending the polymers in SN1 oil were determined by a FBWT apparatus at a 392 N applied load, shown in Figures 3 and 4. The decreased WSD values (Figure
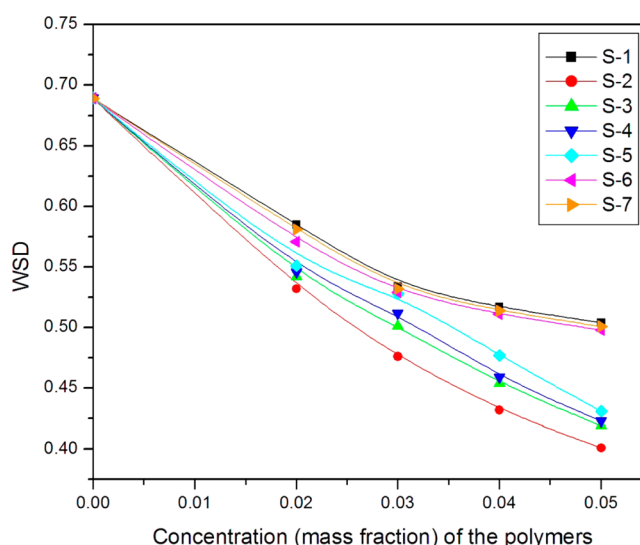
Figure 3. Wear scar diameter (WSD) of the base oil (SN1) blended with the additives in different mass fractions.

3) indicate that the base oil blended with the additives suffers reduced wear compared to the base oil without additive. It was found that all the copolymers showed better results compared to the homopolymer of SBO. The lower WSD values with increasing concentrations of the doped additives also support this fact. The base oil doped with S4 and S-5 additives have lowest WSD values compared to others. The SN1 base oil doped with soy-methyl acrylate copolymer (S-2) at 0.05 mass

Figure 4. Cofficient of friction (COF) values of the SN1 base fluid blended with additives in different mass fractions.

Table 6. Pour Points of the Polymeric Additives in Different Base Oils

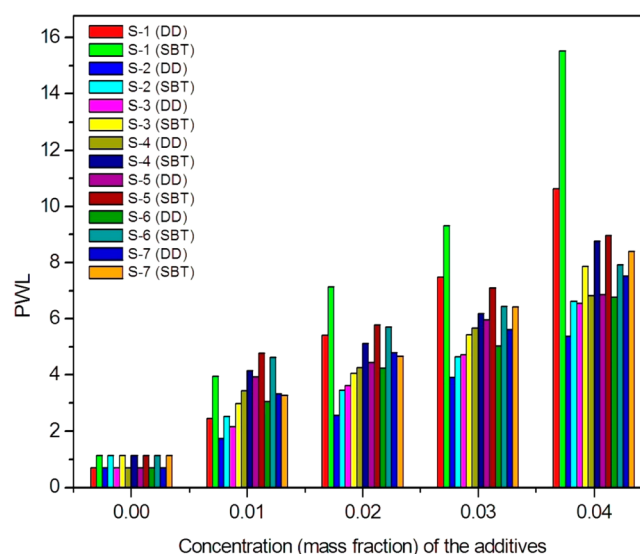| polymers	base oils	PP values (°C) of the base oils doped with additives in different mass fractions			
		0.02	0.03	0.04	0.05
S-1	SN1	−3	−7	−8	−12
	SN2	−6	−8	−9	−15
S-2	SN1	−6	−9	−12	−18
	SN2	−8	−12	−15	−20
S-3	SN1	−6	−8	−9	−15
	SN2	−8	−10	−12	−15
S-4	SN1	−3	−7	−9	−9
	SN2	−6	−8	−9	−10
S-5	SN1	−3	−7	−9	−9
	SN2	−6	−6	−8	−10
S-6	SN1	−3	−6	−9	−12
	SN2	−6	−8	−10	−15
S-7	SN1	−5	−7	−8	−12
	SN2	−6	−8	−9	−15

fraction showed maximum reduction (41.8%) in WSD whereas, in the case of S-1, the reduction is minimal (26.8%). The decrease in the COF value (determined by eq 2) with increase in concentration (Figure 4) also supports this fact. The maximum reduction in the COF was observed in the case of the soy-acrylate copolymers followed by the soy-1-decene copolymers. The base fluid forms a protective layer on the contacting metal surfaces of the engines and, during the tribochemical process, this film protects the surfaces from wear. The antiwear additive molecules strengthen the film by chemical and physical bonding through functional groups of the additives and metal atoms present in the rubbing zone. The long hydrocarbon chain of the fatty acid provides an excellent molecular barrier while the polar ester groups coordinate with iron to form a protective film on the metal surface.[37] Soy-methyl acrylate copolymers, which are chemically bonded with iron in the rubbing zone by their polar ester side chains, stabilize the layer better. On the other hand, the film particularly formed due to long hydrocarbon side chains of soy-1-decene copolymers, which protect the metal surface and hence stabilize the layer also.

Table 6 shows that the PPD properties of the additives in different base stocks (SN1, SN2) gradually improve with an increase in their concentrations (except S-4 and S-5). The copolymer of soybean oil with methyl acrylate exhibits better PPD performance compared to the others. The improvement in the PPD properties by the addition of additives is due to disruption of the wax crystals that are formed due to the deposition of the paraffinic compounds present in mineral oil at lower temperatures. Experimental results show that polarity of side chains of the additive may be a crucial factor in pour point depressing ability.[38] The soy-acrylate copolymers, due to their more polar nature, fight better against the formation of wax crystals and therefore show higher pour point values that are comparable with those of commercially available polymethacrylates.[39]

The results of the biodegradability test obtained by the DD and SBT methods are shown in Figures 5 and 6. The test results indicate that the degradation of the blend increases with increasing the concentration of the additives. In the DD method, the degradation of the homopolymer of SBO is the


Figure 5. Biodegradability test (DD and SBT method) results of SN1 base oil doped with additives in different mass fractions. PWL is percentage of weight loss.

highest, which is expected. It was noticed that the other copolymers also decomposed significantly, among which the degradation of the copolymer of SBO with 1-decene is observable. In the soil burial test, the degradation of recovered samples was measured for 15 day intervals up to 90 days. It was found that the degradation increased with increased concentrations of the polymers as well as time periods in the SBT (Figure 6), and the homopolymer of soy oil (S-1) showed the highest degradation followed by its copolymers with 1-decene (S-4 and S-5).

■ CONCLUSION

The above findings revealed that all the polymers showed excellent multifunctional performances as additives in lubricants. The viscosity index, antiwear and pour point properties of the base fluids were enhanced significantly by the addition of these additives. Polymerization increases the thermo-oxidative stability of soybean oil. Copolymers of SBO with 1-decene and styrene perform as better viscosity index improvers. Copoly-
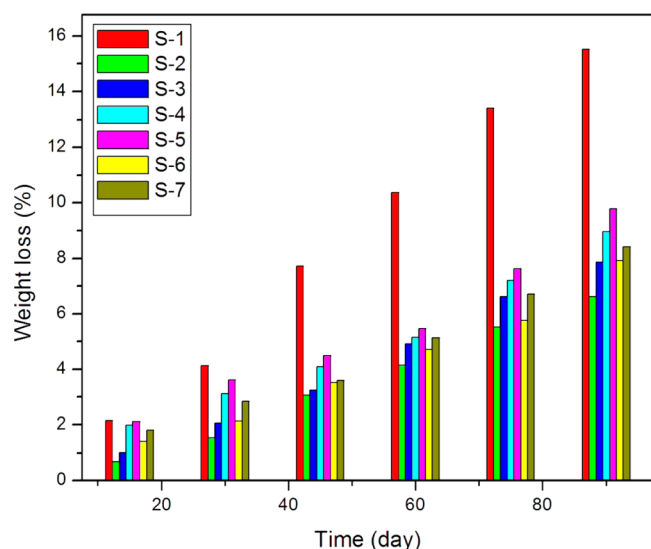
Figure 6. Degradation of the SN1 base oil blended with additives at 0.04 mass fraction measured after each 15 day span up to 90 days in soil burial test.

mers of SBO with methyl acrylate and 1-decene perform as better antiwear additives. The soy-methyl acrylate copolymer has better pour point depressant properties. Moreover, due to being biodegradable, the additives are eco-friendly also. Therefore, the above work will definitely enrich the field of lubricant technology to produce a cost-effective as well as eco-friendly lubricant composition.

◼ ASSOCIATED CONTENT

Ⓢ Supporting Information

Viscometric measurement and spectral characterization (FT-IR, ^{1}H and ^{13}C NMR) data 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.

◼ ACKNOWLEDGMENTS

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