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Synthesis and Characterization of Biodegradable Polymer - Used as a Pour Point Depressant for Lubricating Oil

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Additives based on polymers of alkyl methacrylate used in lubricant composition improve the viscometric and rheological properties of the lubricant and provide fuel economy. They are also looked upon to provide additional performance characteristics such as improved low temperature fluidity, dispersancy and thickening. However, the recent demand for eco-friendly technology guided us to incorporate the sunflower chemistry into the acrylate skeleton through the process of copolymerization in anticipation of getting an ideal blend of performance as well as eco-friendly chemistry. The present investigation comprises the homo and copolymerization of sunflower oil with different mass fraction of methyl methacrylate (MMA), decyl acrylate (DA) and styrene, characterizations and their evaluations as a pour point depressant in base oils.

Keywords base oil, biodegradable additives, copolymer, pour point, viscometric studies

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INTRODUCTION

The use of oil-soluble additives in lubricating oil to improve their performance is well-known. They improve performances by either enhancing the desirable properties already present or by introducing new properties into the oil without disturbing its original performance.

The decreasing of the natural resources of mineral oil and increasing environmental awareness have increased investigation into new environmental lubricant and additive chemistry. Keeping this view in mind, people have already started working in this direction to meet the above needs [1]. The use of biodegradable vegetable oils was known for a long time. Today, due to growing environmental concern, these oils are again finding application in lubricants for transportation as well as for industrial applications. They can offer significant environmental advantages with respect to fuel consumption, biodegradability and displaying satisfactory performance in field application. They are also reported to show excellent tribological properties when used as base stocks or as additives [2]. But the major limitations are their high cost and thermal and oxidative instability. Keeping this in mind and in continuation of our studies towards the development of chemical additives for lubricating and crude oils, in the present investigation an attempt has been made to synthesize a pour point additive based on sunflower oil.

Pour point is the temperature at which lubricating oil is just able to flow and below which there is complete absence of flow in it. Polymeric additives known as flow improvers or pour point depressants are generally used to lower the pour point, viscosity and yield stress of lubricating oil [3–7].

Since performance of such additives in field conditions is very much dependent on the structure and morphology of the polymer in the desired solvent [8], viscometric studies in dilute solutions may give valuable information as far as the quality of the solvent or base stock employed and chain conformation in dilute solution are concerned. Since reports regarding such information are scanty [9,10] and almost nil for polymers used as lube oil additives the present research also include a viscometric study of the copolymers as well as the homopolymer.

According to the Mark Houwink–Sukurda relation (Eq. (1)), the value of intrinsic viscosity changes with the molecular weight of the polymer in a solvent as:

$$[\eta] = K M^a \quad (1)$$

where $[\eta]$, the intrinsic viscosity, can be calculated by using (Eq. (2) to Eq. (7)), parameter 'K' and 'a' depends on the type of polymer, solvent, and temperature.

Because of the simplicity of the procedure, viscometry is usually employed to complement the results obtained from another technique, generally in

determination of the molecular mass of samples with the available literature value of the constants used in the particular equation. A number of mathematical relations are available in the literature for the study of viscometric properties of a dilute polymer solution at a particular temperature by graphic extrapolation [11–17]. The most commonly used equations are:

$$\text{Huggins} \quad \eta_{\text{sp}}/C = [\eta]_{\text{h}} + K_{\text{h}} [\eta]_{\text{h}}^2 C \quad (2)$$

$$\text{Kraemer} \quad \ln \eta_{\text{r}}/C = [\eta]_{\text{k}} - k_{\text{k}} [\eta]_{\text{k}}^2 C \quad (3)$$

$$\text{Martin} \quad \ln(\eta_{\text{sp}}/C) = \ln [\eta]_{\text{m}} + k_{\text{m}} [\eta]_{\text{m}} C \quad (4)$$

$$\text{Schulz-Blaschke} \quad \eta_{\text{sp}}/C = [\eta]_{\text{sb}} + k_{\text{sb}} [\eta]_{\text{sb}} \eta_{\text{sp}} \quad (5)$$

where $\eta_{\text{r}} = t/t_0$, relative viscosity or viscosity ratio; η_{sp} = specific viscosity

$[\eta]_{\text{h}}$ = intrinsic viscosity, respective to Huggins equation;

$[\eta]_{\text{k}}$ = intrinsic viscosity, respective to Kraemer equation;

$[\eta]_{\text{m}}$ = intrinsic viscosity, respective to Martin equation;

$[\eta]_{\text{sb}}$ = intrinsic viscosity or limiting number, respective to Schulz-Blaschke equation; k_{h} , k_{k} , k_{m} and k_{sb} Huggins, Kraemer, Martin and Schulz-Blaschke coefficients, respectively.

Some relations have been proposed for determining the intrinsic viscosity in dilute polymer solution from a single point determination. These methods have the advantage of being considerably faster and can be adequate when a large number of samples must be analyzed in a short period of time, practical in industrial laboratories. Most useful [13–17] are the Solomon-Ciute (SC, Eq. (6) and Deb–Chanterjee (DC, Eq. (7) relations.

$$[\eta] = [2(\eta_{\text{sp}} - \ln \eta_{\text{r}})]^{1/2}/C \quad (6)$$

$$[\eta] = (3 \ln \eta_{\text{r}} + 3/2 \eta_{\text{sp}}^2 - 3\eta_{\text{sp}})^{1/3}/C \quad (7)$$

The use of these equations has been derived under the supposition of the validity of the relationship $k_{\text{h}} + k_{\text{k}} = 0.5$ [15].

EXPERIMENTAL

Measurements

Spectroscopic: IR spectra were recorded on a Shimadzu FT-IR 8300 spectrometer using 0.1 mm KBr cells and the spectra were recorded at room temperature within the wave number range 400 to 4000 cm^{-1} . NMR spectra were recorded in Bruker Avance 300 MHz FT-NMR spectrometer using a 5 mm BBO probe. CDCl_3 was used as a solvent and TMS as reference material.

Viscometric Measurements

Viscometric properties were determined at 40°C in a toluene solution, using an Ubbelohde OB viscometer. Experimental determination was carried out by counting the time flow of at least eight different concentrations of the sample solutions. The time flow of the solution was manually determined by using a chronometer. In the single point measurement the lowest value of solution concentration was chosen for the calculation. For the viscosity – average molecular weight determination, the constants $K=0.00387$ dl/g and $a=0.725$ were employed in Mark Houwink – Sukurda relation [15–17].

Thermogravimetric Analysis (TGA)

The thermograms in air were obtained on a Mettler TA – 3000 system, at a heating rate of 10°C/min.

Biodegradability Test

In this work we studied the biodegradability of the prepared polymer samples (both the copolymer and homopolymer) against five different fungal pathogens namely *Colletotrichum camelliae*, *Fusarium equisetiae*, *Alternaria alternata*, *Colletotrichum gloeosporioides* and *Curvularia eragrostidis*. All experiments were performed in petri dishes and were incubated at 37°C for 30 days after the addition of definite weight of polymer samples. The fungal growth was confirmed by a change of yellow to blackish color. Culture media for fungal strains were prepared by mixing suitable proportions of potato extract, dextrose and agar powder. All glass apparatus and culture media were autoclaved before use. 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 [18].

Evaluation of Prepared Polymer as Pour Point Depressant in Base Oils

The prepared additives were evaluated as a pour point depressant using base oils (BO1 and BO2), each of them collected from two different sources (S1 and S2), through the pour point test according to the ASTM–D-97 method using WIL-471 cloud and pour point test apparatus model 3 (India). The effect of additive concentration was investigated by using different doping concentrations. The experimental data were noted by taking an average of three experimental results under identical conditions.

RESULTS AND DISCUSSION

^1H NMR of sunflower oil indicated the presence of unsaturation (δ 5.31, 4.27 and 4.12 ppm) along with other peaks due to methyl and methylene protons (δ 0.87 to 1.27 ppm) and (δ 1.59 to 2.75) ppm), respectively. The existence of homopolymer was indicated by the disappearance of the peaks in the unsaturation region (δ 4.0 to 6.0 ppm) along with a shift in the methyl and methylene signals. Formation of copolymer of sunflower oil and styrene was indicated by the absence of unsaturation in the NMR spectrum (no peak between 4–6 ppm) and the appearance of broad multiplet centered at δ 8.2 ppm for the aromatic ring protons of styrene. Similar results were also obtained in the NMR spectrum of other copolymers, e.g., sunflower oil – MMA and sunflower oil – DA.

IR spectra of the homo and copolymer of sunflower oil showed characteristic peaks for ester carbonyl at 1745.5 cm^{-1} and at 3408 cm^{-1} .

Using the graphic extrapolation method, respective intrinsic viscosities and constants were evaluated. In single point determinations, SB, SC and DC equations were employed to determine the intrinsic viscosity. Although dependent on a constant, the SB equation is commonly applied in single point determination because the constant k_{sb} is found to be very close to 0.28 in most of the polymer solvent system. The same is used here also.

Table 1 presents intrinsic viscosity values of all prepared samples in toluene solvent. In general it has been found that intrinsic viscosity values of homopolymer are greater than the copolymer except (P-3). Increase in monomer concentration (MMA, DA and styrene) intrinsic viscosity increases. It is interesting to note that by using several equations, values are identical for each polymer. For all polymeric samples intrinsic viscosity values obtained by using single point determination method are found to be greater than graphical extrapolation method.

Table 1: Intrinsic viscosity values of all polymeric samples. P-1 polymer of sunflower oil, P-2 copolymer of sunflower oil +5% MMA, P-3 copolymer of sunflower oil +10% MMA, P-4 copolymer of sunflower oil +5% DA, P-5 copolymer of sunflower oil +10% DA, P-6 copolymer of sunflower oil +5% styrene, P-7 copolymer of sunflower oil +10% styrene (a) graphic extrapolation method, and (b) single point determination method.

Samples	$[\eta]_{\text{h}}^{\text{a}}$	$[\eta]_{\text{k}}^{\text{a}}$	$[\eta]_{\text{m}}^{\text{a}}$	$[\eta]_{\text{sb}}^{\text{a}}$	$[\eta]_{\text{sb}}^{\text{a}}$	$[\eta]_{\text{sc}}^{\text{b}}$	$[\eta]_{\text{dc}}^{\text{b}}$
P-1	6.1	5.25	3.94	6.92	7.43	7.93	8.91
P-2	5.0	5.45	3.42	6.37	5.92	6.95	6.69
P-3	6.75	6.05	6.50	7.46	6.91	7.55	8.44
P-4	4.20	4.20	4.10	4.30	4.41	4.44	5.30
P-5	5.50	4.50	4.00	4.90	5.25	5.35	5.80
P-6	4.80	3.80	2.79	5.12	5.95	6.15	6.74
P-7	5.20	4.85	3.82	6.09	6.79	7.15	7.95

Table 2: Viscometric constant values of all samples.

Samples	k_h	k_k	k_m	k_{sb}	$k_h + k_k$
P-1	0.88	-0.242	1.523	0.35	0.638
P-2	0.70	-0.041	1.468	0.437	0.659
P-3	0.55	-5.83×10^{-3}	0.475	0.252	0.544
P-4	0.46	-0.027	0.513	0.278	0.496
P-5	0.314	-0.187	0.78	0.35	0.127
P-6	0.89	-0.59	2.27	0.284	0.30
P-7	1.06	-0.223	1.41	0.183	0.837

Although different intrinsic viscosity values may be found by graphic extrapolation of Huggins, Kraemer, Martin and SB equation (Eqs. 2 to 6), in this work the data obtained from these four equations showed a tendency to be close for homo and copolymers. For the homopolymer and copolymer, the $[\eta]$ values obtained by Huggins and Kraemer's equation were identical.

Both homopolymer and copolymers in a toluene medium indicate good solvation (Table 2) as is evident from the respective viscometric constant values, and this conclusion is further supported by the negative values of the Kraemer coefficient of the all the systems analyzed. However, it is interesting to notice that for a few polymers in toluene, k_{sb} values were close to 0.28. But there is a close tendency to attain the $k_h + k_k = 0.5$.

By comparing $[\eta]$ values (Table 3) of homo and copolymers determined through graphic extrapolation using Kraemer, Martin and SB equations and single point determination with the values determined by the Huggins equation, it is observed that the range of variation ($\Delta\%$) is similar in both the cases, e.g., -41.87 to 17.13% and -4.54 to 52.80%, respectively.

Table 4 presents a comparison between the value of molecular weight obtained by viscometric methods for the homopolymer and copolymers analyzed. The general trend in all the cases is a gradual increase in molecular weight with an increase of monomer concentration.

Table 3: Percentual differences of intrinsic viscosity ($\Delta\% = (100((\eta)/(\eta)_h) - 100$) (a) graphic extrapolation method, and (b) single point determination method.

Samples	K_k	K_m	K_{sb}	K_{sb}	K_{sc}	K_{dc}
P-1	-13.98	-35.36	13.48	21.74	30	46.08
P-2	-15.46	-31.6	3.40	18.6	22.08	33.74
P-3	-10.30	-3.70	10.54	2.43	30.70	25.06
P-4	-0.047	-2.33	2.44	5.0	5.74	26.19
P-5	18.18	-27.27	-10.90	-4.54	-2.70	5.49
P-6	-20.83	-41.87	6.75	23.96	28.125	40.41
P-7	-6.78	-26.54	17.13	30.57	37.5	52.80

Table 4: Viscometric molecular weight determined by using the Mark—Houwink equation $(\eta) = KM^a$ where, $K = 0.00387$ and $a = 0.725$.

Samples	M_h^a	M_k^a	M_m^a	M_{sb}^a	M_{sb}^b	M_{sc}^b	M_{dc}^b
P-1	25735	20906	14097	30638	33756	36956	43406
P-2	19561	15516	11585	20486	24681	25758	29211
P-3	29592	25471	28091	33979	30588	34567	40287
P-4	15365	33877	32728	35142	36462	36845	47974
P-5	33901	37578	31520	42672	47300	48665	54912
P-6	18473	13384	8783	20214	24842	26001	29503
P-7	20629	18739	13481	25658	25658	32007	37023

Table 5: TGA data of all prepared samples.

Samples	Decomposition temperature	PWL
P-1	320/350	48/80
P-2	320/350	45/75
P-3	340/385	38/82
P-4	350/390	47/78
P-5	370/410	38/82
P-6	360/400	40/75
P-7	370/410	50/80

Table 6: Results of biodegradability test.

Fungal pathogens	Polymer samples	Incubation period (Days)	Initial wt (gm)	Final wt (gm)	Wt loss (gm)
<i>Colletotrichum camelliae</i>	P-1	30	1.5	1.5	Nil
	P-2	30	1.5	1.5	Nil
	P-4	30	1.5	1.5	Nil
	P-6	30	1.5	1.5	Nil
<i>Fusarium equisetiae</i>	P-1	30	1.5	1.5	Nil
	P-2	30	1.5	1.5	Nil
	P-4	30	1.5	1.5	Nil
	P-6	30	1.5	1.5	Nil
<i>Alternaria alternata</i>	P-1	30	1.5	0.9	0.6
	P-2	30	1.5	1.1	0.4
	P-4	30	1.5	1.4	0.1
	P-6	30	1.5	1.48	0.02
<i>Colletotrichum gloeosporioides</i>	P-1	30	1.5	1.5	Nil
	P-2	30	1.5	1.5	Nil
	P-4	30	1.5	1.5	Nil
	P-6	30	1.5	1.5	Nil
<i>Curvularia eragrostidis</i>	P-1	30	1.5	1.5	Nil
	P-2	30	1.5	1.5	Nil
	P-4	30	1.5	1.5	Nil
	P-6	30	1.5	1.5	Nil

Table 5 presents TGA values of all the polymers. All the copolymers are thermally more stable. Increases in % concentration of monomers increase the thermal stability.

Table 6 presents biodegradability test results obtained by using the disk diffusion method. Homopolymer and copolymer of sunflower oil with decyl acrylate showed that sunflower oil was found to have significant biodegradability against the fungal pathogen, *Alternaria alternata*. It was further confirmed by the shift of IR frequency of the ester carbonyl to 1712 after the biodegradability test. Copolymer of sunflower oil with MMA also shows biodegradability but in a smaller extent. Biodegradability was not found in the copolymer of sunflower oil with styrene. The presence of styrene (aromatic moieties) may be key to the observed less biodegradability.

Table 7 presents PPD properties of the polymers evaluated in two different base stocks, each of them collected from two different sources (S1 and S2), and indicates that P-2 and P-5 showed best performance in both the base oils. The

Table 7: PPD properties of base oils collected from different sources.

Sample	Base oils	Pour point of base oil	Pour point of additive-doped base oil			
			2.5%	5%	10%	
P-1	BO1	S1	-3	-6	-6	-6
		S2	-3	-3	-3	-3
	BO2	S1	-6	-9	-9	-9
		S2	-6	-9	-9	-9
P-2	BO1	S1	-3	-12	-12	-12
		S2	-3	-12	-15	-15
	BO2	S1	-6	-15	-15	-15
		S2	-6	-15	-15	-15
P-3	BO1	S1	-3	-12	-12	-12
		S2	-3	-15	-15	-12
	BO2	S1	-6	-15	-12	-12
		S2	-6	-15	-12	-12
P-4	BO1	S1	-3	-15	-12	-12
		S2	-3	-15	-12	-12
	BO2	S1	-6	-15	-12	-12
		S2	-6	-15	-12	-12
P-5	BO1	S1	-3	-15	-18	-15
		S2	-3	-15	-18	-21
	BO2	S1	-6	-18	-21	-21
		S2	-6	-18	-21	-24
P-6	BO1	S1	-3	-9	-9	-9
		S2	-3	-9	-9	-9
	BO2	S1	-6	-9	-12	-12
		S2	-6	-9	-12	-12
P-7	BO1	S1	-3	-9	-9	-9
		S2	-3	-9	-9	-9
	BO2	S1	-6	-9	-9	-9
		S2	-6	-9	-9	-9

values are always better than the respective homopolymer and both of them are made from sunflower oil.

CONCLUSIONS

The incorporation of monomers (MMA, DA and styrene) in the sunflower oil backbone raises the thermal stability of the copolymer and extent of monomer incorporation directly proportional to the thermal stability of the copolymer.

Intrinsic viscosity values of the copolymer are less than the corresponding homopolymer (except P-3) and the values obtained by single point determination method are higher than the values obtained by graphical extrapolation method.

Viscometric molecular weight of the copolymer is less than the homopolymer of decyl acrylate.

Pour point depressant (PPD) performance of the copolymer is always better than the homopolymer in all the base oils studied.

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