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Synthesis and Evaluation of Acrylate Polymers in Lubricating Oil

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ABSTRACT: Additives based on polymers of alkyl acrylate used in lubricant composition improve the viscometric and rheological properties of the lubricant and provide fuel economy. However, the recent demand for eco-friendly technology prompted us to develop biodegradable additives for the lubricant formulation. Thus, in anticipation of getting an ideal blend of performance as well as eco-friendly chemistry, the present investigation comprising the incorporation of an α-pinene (α-p) moiety into the acrylate (dodecyl acrylate, DDA, and isodecyl acrylate, IDA) skeleton through copolymerization was undertaken. The analysis of different properties of the polymers indicates that copolymers of α-pinene with DDA have more thermal stability and better pour point and viscosity index (VI) values than the copolymers of α-pinene with IDA. However, the study of the biodegradability test indicates that the copolymers of α-pinene with IDA are better than the other and they show significant biodegradability against the fungal pathogen, *Alterneria alernata*. In both of the cases, homopolymers are found to be less efficient in performance than the copolymers.

INTRODUCTION

Base fluid mineral oil generally cannot satisfy the requirements of high performance lubricants without using modern additive technology. Thus, to meet the specifications provided by the original equipment manufacturers, modern lubricants are being formulated from a range of base fluids and chemical additives. Again, increasing environmental awareness has increased the breadth of the investigation about new environmental lubricants and additive chemistry. Keeping this view in mind, researchers have already started working in this direction to meet the above needs.[1,2] In our last communication we used additives based on the acrylate + sunflower oil system and obtained very good results toward its biodegradability as well as its additive performance as a pour point depressant (PPD) in lube oil.[3] In continuation of our efforts for the development of eco-friendly polymeric additives for lube oil, this time we have chosen α-pinene as a potential candidate to incorporate biodegradability in its acrylate copolymer. Thus, the present investigation comprises the synthesis, characterization, and evaluation of these copolymers as a potential biodegradable additives for lubricating oil. The study includes the synthesis of copolymers using different mass fractions of α-pinene with dodecyl acrylate (DDA) and isodecyl acrylate (IDA), their characterization, a performance evaluation, and an evaluation of the biodegradable nature of the polymers. The homopolymers of DDA and IDA have also been prepared under identical conditions for a comparison of their performance with respect to the prepared copolymers. Physical characterization of the polymers has been carried out employing thermogravimetric analysis (TGA), IR, and NMR techniques. The performance of the polymer additives has been tested with respect to their PPD[4] and viscosity index improver (VII) properties.[5,6]

Since viscosity is a very important property of a lubricant[7−9] and viscometric studies in dilute solution may give valuable information about the structure and morphology of the polymer chain in desired solvent, the present investigation also included the viscometric study of the copolymers as well as the homopolymers.

The molecular weight of the macromolecules in solution can also be determined by using viscometric analysis. According to the Mark−Houwink−Sukurda equation (eq 1), the value of intrinsic viscosity, $[\eta]$, changes with the molecular weight of the polymer in a solvent as:

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

where M is the viscosity average molecular weight and K and a are the Mark−Houwink constants. The values of K and a are specific for every polymer−solvent combination. So, to get an accurate measure of molecular weight, these constant values are to be known for appropriate polymer−solvent combinations.

A graphic extrapolation method based on Huggins, Kraemer, Martin, and Schulz-Blaschke equations[10−14] and the single point determination method[11−13] based on Solomon−Ciuta and Deb−Chatterjee relations are most useful for the study of the viscometric properties of a dilute polymer solution at a particular temperature. The latter method has the advantage of being considerably faster and is better than the graphic extrapolation method when a large number of samples must be analyzed in a short period of time, a practical use in industrial laboratories.

These equations have been derived under the supposition of the validity of the relationship $k_h + k_k = 0.5$[11] (Table 5). Since the behavior of polymers especially the copolymers in solution is a complex phenomenon, a comparison involving the values of their intrinsic viscosity obtained by graphic extrapolation and by single-point determination should be interesting. In this work, the intrinsic viscosity of toluene solution for samples of poly(alkyl acrylate) and copolymers of that consisting of different mass fractions of α-pinene were obtained by graphic extrapolation and the single-point determination method. The viscosity average molecular weight, determined by using different equations, was calculated and compared for different polymers.

EXPERIMENTAL SECTION

Materials. Toluene (GC 99.5 %), hydroquinone (GC 99 %), and H_2SO_4 were purchased from Merck Specialties Pvt., Ltd.

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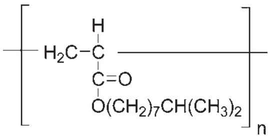

Figure 1. Poly(isodecyl acrylate).

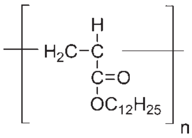

Figure 2. Poly(dodecyl acrylate).

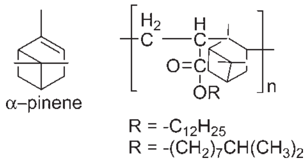

Figure 3. α-Pinene and its copolymer with IDA and DDA.

Acrylic acid (GC 99 %, stabilized with 0.02 % hydroquinone mono methylether) and isodecanol (GC 98 %) were obtained from Sisco Research Laboratories Pvt., Ltd. 1-Dodecanol (GC 98 %) and hexane (GC 99.5 %) were purchased from SD Fine Chemicals, Ltd. α-Pinene (GC 98 %) was obtained from Acros Organics. Methanol (GC 98 %) was purchased from Thomas Baker (Chemicals) Pvt., Ltd. Benzoyl peroxide (GC 98 %), obtained from LOBA Chemicals, was recrystallized from $CHCl_3$-MeOH before use. The rest of the materials were used as they were obtained without further purification. Base oils were collected from IOCL, Dhakuria, West Bengal, India. The fungal specimens were collected from the Department of Microbiology, North Bengal University, West Bengal, India.

Esterification. Isodecyl acrylate was prepared by reacting 1.1 mol of acrylic acid with 1 mol of isodecyl alcohol. The reaction was carried out in a resin kettle in the presence of concentrated sulfuric acid as a catalyst, 0.25 % hydroquinone with respect to the reactants as polymerization inhibitor, and toluene as a solvent. The esterification reaction was carried out under a slow stream of deoxygenated nitrogen. The reactants, which were mixed with toluene, were heated gradually from room temperature to 403 K using a well-controlled thermostat. The extent of reaction was followed by monitoring the amount of liberated water to give the ester, IDA. Under the same procedure, DDA was also prepared from acrylic acid and dodecyl alcohol.

Purification of Prepared Esters. The prepared esters were purified according to the following procedure: a suitable amount of charcoal was added to the ester. It was allowed to reflux for 3 h and then filtered off. The filtrate was washed with 0.5 N sodium hydroxide in a separating funnel and then shaken well. The entire process was repeated several times to ensure complete removal of unreacted acid. The purified ester was then washed several times with distilled water to remove any traces of sodium hydroxide; the ester was then left overnight on calcium chloride and was then removed by distillation under reduced pressure and was used in the polymerization process.

Preparation of Copolymer and Homopolymer. The polymerization was carried out in a four-necked round-bottom flask equipped with a stirrer, condenser, thermometer, an inlet for the introduction of nitrogen, and a dropping funnel through which to add α-pinene dropwise. In the flask, the desired mass (Table 3) of IDA and initiator benzoyl peroxide (BZP) was placed followed by dropwise addition of desired mass of α-pinene (Table 3) for 2 h in the presence of toluene as a solvent. The reaction temperature was maintained at 353 K for 6 h. At the end of the reaction time, the reaction mixture was poured into methanol with stirring to terminate the polymerization and precipitate the polymer. The polymer (Figure 3) was further purified by repeated precipitation of its hexane solution by methanol followed by drying under vacuum at 313 K.

The homopolymer of IDA (HIDA, Figure 1), homopolymer of DDA (HDDA, Figure 2), and also the copolymer of DDA with α-pinene (Figure 3) were similarly prepared and purified under the same conditions for use in reference experiments.[15]

MEASUREMENTS

Spectroscopic Measurements. IR spectra were recorded on a Shimadzu FT-IR 8300 spectrometer using 0.1 mm KBr cells at room temperature within the wavenumber 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 solvent and tetramethylsilane (TMS) as reference material.

Viscometric Measurements. Viscometric properties were determined at 313 K in toluene solution, using an Ubbelohde OB viscometer. The experimental determination was carried out by counting time flow at least eight different concentrations of the sample solution. 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 calculation. The viscosity results were checked against viscosity of known solutions, and the uncertainty was found to be nearly 0.17 %. Precautions regarding the prevention of evaporation of the solvent were taken in all of the cases. For the viscosity–average molecular weight determination, the constants $K = 0.00387\ \mathrm{dL \cdot g^{-1}}$ and $a = 0.725$[15,16] were employed in the Mark–Houwink–Sukurda relation.

Thermogravimetric Analysis (TGA). The thermograms in air were obtained on a Mettler TA-3000 system, at a heating rate of $10\ \mathrm{K \cdot min^{-1}}$.

Biodegradability Test. Biodegradability of the polymers was tested (i) by the disk diffusion method against fungal pathogens and (ii) by the soil burial degradation test of polymer films as per ISO 846:1997 and by measuring the shift of IR frequency of the ester carbonyl after the biodegradability test.

Disc Diffusion Method. The biodegradability of the prepared polymer samples (both the copolymer and the homopolymer) were tested against five different fungal pathogens, namely, *Calletotricheme camellia* (CC), *Fussarium equisitae* (FE), *Alterneria alternata* (AA), *Colletrichum gleosproides* (CG), and *Curvularia eragrostidies* (CE). All glass apparatuses 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 yellow to blackish. All experiments were performed in Petri dishes and were incubated at 310 K for 30 days after the addition of definite weight (1.5 g) of polymer samples. The whole process was carried out in an inoculation chamber.

Table 1. Composition of the Monomers in the Copolymers in Terms of Mass Fraction Determined by NMR and FT-IR Spectrophotometric Method[a]

polymer sample	mass fraction in the feed		mass fraction of in α-pinene copolymer by NMR method	mass fraction of α-pinene in copolymer by FT-IR
	DDA	α-pinene		
P-1	1			
P-2	0.970	0.025	0.01	0.015
P-3	0.95	0.05	0.03	0.022
P-4	0.925	0.075	0.035	0.037
P-5	0.90	0.10	0.04	0.05

[a] P-1: HDDA, P-2: 2.5 % α-p+DDA, P-3: 5 % α-p+DDA, P-4: 7.5 % α-p+DDA, P-5: 10 % α-p+DDA.

Table 2. Composition of the Monomers in the Copolymers in Terms of Mass Fraction Determined by NMR and FT-IR Spectrophotometric Method[a]

polymer sample	mass fraction in the feed		mass fraction of in α-pinene copolymer by NMR method	mass fraction of α-pinene in copolymer by FT-IR
	IDA	α-pinene		
P-6	1			
P-7	0.970	0.025	0.01	0.015
P-8	0.95	0.05	0.04	0.021
P-9	0.925	0.075	0.038	0.037
P-10	0.90	0.10	0.041	0.049

[a] P-6: HIDA, P-7: 2.5 % α-p+IDA, P-8: 5 % α-p+IDA, P-9: 7.5 % α-p+IDA, P-10: 10 % α-p+IDA.

Table 3. Intrinsic Viscosity [η] Values for Prepared Polymer Samples Calculated by Using Different Equations[a]

sample	$[\eta]_h$[b]	$[\eta]_k$[b]	$[\eta]_m$[b]	$[\eta]_{sb}$[b]	$[\eta]_{sb}$[c]	$[\eta]_{sc}$[c]	$[\eta]_{dc}$[c]
P-1	4.059	4.361	4.336	4.512	4.637	4.599	4.773
P-2	5.742	6.103	6.221	6.570	6.294	6.267	6.591
P-3	4.923	5.292	5.317	5.601	5.535	5.502	5.751
P-4	4.459	4.716	4.730	4.922	4.976	4.939	5.141
P-5	4.338	4.562	4.572	4.762	4.711	4.673	4.856

[a] h, k, m, sb, sc, and dc refer to the Huggins, Kraemer, Martin, Schulz-Blaschke, Solomon−Ciuta, and Deb−Chatterjee equations, respectively. P-1: HDDA, P-2: 2.5 % α-p+DDA, P-3: 5 % α-p+DDA, P-4: 7.5 % α-p+DDA, P-5: 10 % α-p+DDA. [b] Extrapolation of graph. [c] Single-point determination (k_{sb} = 0.28).

Table 4. Intrinsic Viscosity [η] Values for Prepared Polymer Samples Calculated by Using Different Equations[a]

sample	$[\eta]_h$[b]	$[\eta]_k$[b]	$[\eta]_m$[b]	$[\eta]_{sb}$[b]	$[\eta]_{sb}$[c]	$[\eta]_{sc}$[c]	$[\eta]_{dc}$[c]
P-6	3.774	3.845	3.881	3.945	4.020	3.983	4.119
P-7	6.057	6.116	6.353	6.565	6.297	6.274	6.606
P-8	5.680	5.596	5.842	5.977	5.629	5.594	5.847
P-9	5.492	5.393	5.629	5.747	5.407	5.373	5.611
P-10	5.117	5.017	5.223	5.314	4.997	4.961	5.165

[a] h, k, m, sb, sc, and dc refer to Huggins, Kraemer, Martin, Schulz-Blaschke, Solomon−Ciuta, and Deb−Chatterjee equations, respectively. P-6: HIDA, P-7: 2.5 % α-p+IDA, P-8: 5 % α-p+IDA, P-9: 7.5 % α-p+IDA, P-10: 10 % α-p+IDA. [b] Extrapolation of graph. [c] Single-point determination (k_{sb} = 0.28).

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.[3,17]

Soil Burial Degradation Test. The soil burial degradation test of polymer films was conducted as per ISO 846:1997.[18] The films of polymer samples were buried in soil. The soil used in this study had been taken from North Bengal University (West Bengal, India) campus. The soil was taken in a tray, in which the relative humidity was adjusted to 50 % to 60 % and temperature was thermostatted at 303 K with the help of a humidity chamber. 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. The dried samples were weighed.

Evaluation of Prepared Polymer as Pour Point Depressants (PPDs) in Base Oils. The prepared additives were evaluated as PPDs using base oils (BO1 and BO2) through the pour point test according to the ASTM D97-09 method using the Cloud and Pour Point Tester model WIL-471 (India). The properties of base oils are given in the Table 5. The effect of additive concentration on pour point was investigated by using different doping concentrations. The experimental data were noted by taking an average of three experimental results under identical conditions.

Determination of Viscosity Index (VI). The various blends were prepared by using two different types of lubricating oil. Viscosities and the viscosity index (VI) of these oils were calculated according to ASTM D2270-10. The kinematic viscosity of the oil containing the tested copolymer was determined at (313 and 373) K. Different concentrations between $1 \cdot 10^3$ ppm to $6 \cdot 10^3$ ppm were used to study the effect of concentration on VI of the additive-doped lube oil. All of the experimental data as mentioned above were noted by taking an average of three experimental results under identical conditions.

Table 5. Viscometric Constants Obtained for Poly(dodecyl acrylate) and Its Copolymeric Samples[a]

sample	k_h	k_k	k_m	k_{sb}	$k_h + k_k$
P-1	0.760	0.044	0.478	0.347	0.804
P-2	0.640	0.082	0.379	0.260	0.722
P-3	0.727	0.059	0.437	0.302	0.786
P-4	0.652	0.071	0.422	0.307	0.723
P-5	0.655	0.062	0.435	0.316	0.717

[a] k_h, k_k, k_m, and k_{sb} are Huggins, Kraemer, Martin, and Schulz-Blaschke coefficients, respectively.

Table 6. Viscometric Constants Obtained for Poly(isodecyl acrylate) and Its Copolymeric Samples[a]

sample	k_h	k_k	k_m	k_{sb}	$k_h + k_k$
P-6	0.475	0.107	0.359	0.294	0.582
P-7	0.418	0.124	0.284	0.214	0.542
P-8	0.331	0.142	0.250	0.198	0.473
P-9	0.322	0.143	0.247	0.198	0.465
P-10	0.316	0.145	0.249	0.203	0.461

[a] k_h, k_k, k_m, and k_{sb} are Huggins, Kraemer, Martin, and Schulz-Blaschke coefficients, respectively.

Table 7. Determination of the Molecular Weight, *M*, by the Mark−Houwink Equation $[\eta] = KM^a$, Where $K = 0.00387$ and $a = 0.725$[a]

sample	M_h[b]	M_k[b]	M_m[b]	M_{sb}[b]	M_{sb}[c]	M_{sc}[c]	M_{dc}[c]
P-1	14672	16199	16071	16977	17630	17431	18347
P-2	23674	25752	26441	28508	26870	26711	28634
P-3	19147	21154	21292	22876	22505	22320	23726
P-4	16703	18045	18119	19141	19432	19233	20326
P-5	16081	17238	17290	18288	18019	17819	18788

[a] h, k, m, sb, sc, and dc refer to the Huggins, Kraemer, Martin, Schulz-Blaschke, Solomon−Ciuta, and Deb−Chatterjee equations, respectively. P-1: HDDA, P-2: 2.5 % α-p+DDA, P-3: 5 % α-p+DDA, P-4: 7.5 % α-p+DDA, P-5: 10 % α-p+DDA. [b] Extrapolation of the graph. [c] Single-point determination ($k_{sb} = 0.28$).

Table 8. Determination of Molecular Weight, *M*, by the Mark−Houwink Equation $[\eta] = KM^a$, Where $K = 0.00387$ and $a = 0.725$[a]

sample	M_h[b]	M_k[b]	M_m[b]	M_{sb}[b]	M_{sb}[c]	M_{sc}[c]	M_{dc}[c]
P-6	13270	13616	13792	14107	14478	14295	14972
P-7	25484	25827	27218	28478	26887	26752	28724
P-8	23323	22848	24245	25021	23034	22837	24274
P-9	22265	21713	23034	23703	21791	21602	22933
P-10	20195	19653	20774	21275	19545	19351	20457

[a] h, k, m, sb, sc, and dc refer to Huggins, Kraemer, Martin, Schulz-Blaschke, Solomon−Ciuta, and Deb−Chatterjee equations, respectively. P-6: HIDA, P-7: 2.5 % α-p+IDA, P-8: 5 % α-p+IDA, P-9: 7.5 % α-p+IDA, P-10: 10 % α-p+IDA. [b] Extrapolation of the graph. [c] Single-point determination ($k_{sb} = 0.28$).

■ RESULTS AND DISCUSSION

Spectroscopic Analysis. Fouier transform infrared (FT-IR) spectra of homopolymers of IDA exhibited absorption at 1732 cm^{-1} for the ester carbonyl stretching vibration along with other peaks at (1456.2, 1379, 1260, and 1166.9) cm^{-1}, owing to the CO stretching vibration and absorption bands at (750 and 710) cm^{-1} were due to the bending of C−H bond. In its ^{1}H NMR spectra, homo IDA showed a broad singlet centered at 4.02 ppm due to the proton of $-OCH_2$ group; a broad singlet at 0.86 ppm was due to methyl groups of isodecyl chain. The proton decoupled ^{13}C NMR of the above sample was in complete agreement with the homopolymer, and the probable structure is shown in Figure 1. The formation of the copolymer of IDA and α-pinene was indicated by the absence of sp^2 hydrogen and sp^2 carbon in its ^{1}H and ^{13}C NMR, respectively.[19]

FT-IR spectra of the homopolymer of DDA exhibited absorption at 1732 cm^{-1} due to ester carbonyl stretching vibration along with other peaks at (1456, 1260, 1164.9, 1112, 1028, and 711) cm^{-1} due to the bending of C−H bond. ^{1}H NMR spectra of the homopolymer indicated the existence of a $-OCH_2$ group at 4.02 ppm (broad singlet) along with the methyl protons ranging between (0.86 to 0.90) ppm together with methylene protons ranging between (1.3 and 1.6) ppm. The proton-decoupled ^{13}C NMR of the above sample was in complete agreement with the homopolymer, and the probable structure is shown in Figure 2.

The absence of peak between (4 and 6) ppm in the ^{1}H NMR and that between (130 and 150) ppm in the ^{13}C NMR spectrum indicated the formation of copolymer of DDA−α-pinene. The extent of incorporation of the α-pinene monomer (Tables 1 and 2) in the polymer chain was determined through IR and NMR spectral analysis as was reported earlier.[19] The structures of α-pinene and its copolymer with IDA and DDA are shown in Figure 3.

Viscometric Analysis. Tables 3 and 4 presents intrinsic viscosity, that is, $[\eta]$ values related to all equations for the samples analyzed. Taking into account the data for homo and all copolymer samples, it can be noticed that, except for one or two cases, the values are consistent. A comparison among the copolymers indicated that there is a gradual decrease of $[\eta]$ values with the increase of α-pinene content in the monomer composition in both cases. Intrinsic viscosity values are lower in homopolymer (P1 and P6) compared to the copolymeric sample. Although different intrinsic viscosity values may be found by the graphic extrapolation method (Huggins, Kraemer, Martin, and Schulz-Blaschke equation), but in this work the data obtained from these four equations showed a tendency to be close for both homo and copolymers. Irrespective of the nature of the polymer, the $[\eta]$ value obtained by the single-point determination method shows higher values than the values obtained by using the graphical extrapolation method.

Tables 5 and 6 present the viscometric constant values obtained for all equations using the graphic extrapolation method. Although k_k values are not negative and $k_{sb} \neq 0.28$ (for most of the cases), the values of $k_h + k_k$ are nearly equal to 0.5, and values of k_h are less than 0.5 for the polymers of IDA, which indicates better solvation[11] of these polymers compared to those of DDA.

Viscometric molecular weight (Mv) obtained by using the Mark−Houwink equation is presented in Tables 7 and 8. As is expected, the homopolymer showed a lower viscometric molecular weight (Mv) compared to the copolymers. There is also a gradual decrease of Mv with the increase in α-pinene concentration in the case of the copolymers, and the values are in line with the intrinsic viscosity values of the polymers.

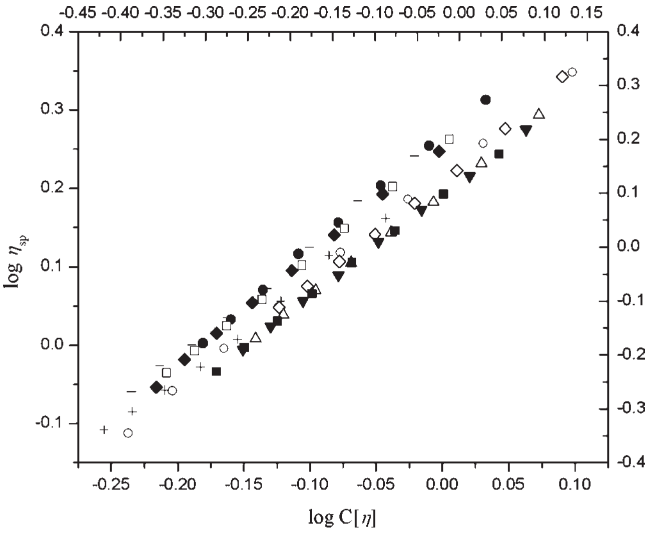

Figure 4. Plot of log η_{sp} vs log $C[\eta]$, where η_{sp} is the specific viscosity of the polymer solution in toluene, C is the concentration of the solution in $g\cdot cm^{-3}$, and $[\eta]$ is the intrinsic viscosity of the polymer solution in toluene obtained by using the Huggins equation. ○, P-1; —, P-2; ●, P-3; □, P-4; ♦, P-5; +, P-6; ♢, P-7; △, P-8; ▼, P-9; ■, P-10.

Table 9. Thermogravimetric Analysis (TGA) Data for All Polymers[a]

	TGA data	
sample	decom. temp./K	PWL
P-1	503/603	32/91
P-2	503/683	8/84
P-3	503/703	10/91
P-4	513/653	30/89
P-5	513/633	37/91

[a] Decom. temp. is decomposition temperature, and PWL is percent weight loss.

Table 10. TGA Data for All Polymers[a]

	TGA data	
sample	decom. temp./K	PWL
P-6	453/573	15/86
P-7	493/613	30/90
P-8	493/603	32/91
P-9	483/593	33/90
P-10	483/630	35/96

[a] Decom. temp. is decomposition temperature, and PWL is percent weight loss.

A linear relation for the plot of log η_{sp} versus log $C[\eta]$, obtained for all samples (Figure 4), indicated that measurements were performed in a Newtonian flow.[10,13]

Thermogravimetric Analysis. Tables 9 and 10 present a comparison between the TGA data for homo and copolymers. The TGA data show that the copolymers are better in thermal stability than the homopolymers. Also, with the decreasing α-pinene concentration in the feed, the thermal stability increases. A comparison among the copolymers indicates that the copolymers of DDA are more stable than the copolymers made from IDA.

Table 11. Physical Properties of Base Oils

	base oils	
base oil properties	BO1	BO2
viscosity at 40 °C in cSt	7.136	23.392
viscosity at 100 °C in cSt	1.857	3.915
cloud point, °C	−10	−8
pour point, °C	−3	−6
density ($g\cdot cm^{-3}$) at 40 °C	0.83698	0.86803

Table 12. Pour Point (PP) of the Additive (P-1 to P-5) Doped Base Oil (BO1)

	PP (°C) in the presence of				
conc. of the additive in ppm ($\cdot 10^3$)	P-1	P-2	P-3	P-4	P-5
0	−3	−3	−3	−3	−3
2	−9	−21	−21	−18	−18
4	−6	−18	−18	−15	−15
6	−6	−15	−15	−15	−12

Table 13. PP of the Additive (P-6 to P-10) Doped Base Oil (BO1)

	PP (°C) in the presence of				
conc. of the additive in ppm ($\cdot 10^3$)	P-6	P-7	P-8	P-9	P-10
0	−3	−3	−3	−3	−3
2	−6	−18	−15	−15	−12
4	−6	−12	−12	−12	−12
6	−3	−9	−9	−12	−9

Table 14. PP of the Additive (P-1 to P-5) Doped Base Oil (BO2)

	PP (°C) in the presence of				
conc. of the additive in ppm ($\cdot 10^3$)	P-1	P-2	P-3	P-4	P-5
0	−6	−6	−6	−6	−6
2	−12	−18	−15	−15	−12
4	−9	−12	−12	−12	−12
6	−6	−9	−12	−9	−9

Table 15. PP of the Additive (P-6 to P-10) Doped Base Oil (BO2)

	PP (°C) in the presence of				
conc. of the additive in ppm ($\cdot 10^3$)	P-6	P-7	P-8	P-9	P-10
0	−6	−6	−6	−6	−6
2	−9	−15	−15	−15	−12
4	−6	−12	−15	−12	−9
6	−6	−12	−12	−9	−9

Table 16. VI Values of the Additive (P-1 to P-5) Doped Base Oil (BO1)

conc. of the additive in ppm ($\cdot 10^3$)	VI in the presence of				
	P-1	P-2	P-3	P-4	P-5
6	109	132	126	132	137
5	106	125	121	125	130
4	103	122	120	119	122
3	100	120	119	116	113
2	98	110	112	109	107
1	95	105	101	99	95
0	85	85	85	85	85

Table 17. VI Values of the Additive (P-6 to P-10) Doped Base Oil (BO1)

conc. of the additive in ppm ($\cdot 10^3$)	VI in the presence of				
	P-6	P-7	P-8	P-9	P-10
6	105	122	113	109	102
5	102	117	112	106	99
4	100	114	110	100	97
3	95	109	107	98	94
2	94	103	101	96	92
1	92	98	95	95	91
0	85	85	85	85	85

Table 18. VI Values of the Additive (P-1 to P-5) Doped Base Oil (BO2)

conc. of the additive in ppm ($\cdot 10^3$)	VI in the presence of				
	P-1	P-2	P-3	P-4	P-5
6	104	112	94	102	95
5	102	104	92	98	95
4	100	99	91	88	90
3	97	94	86	86	85
2	93	87	83	81	79
1	90	85	79	77	76
0	80	80	80	80	80

Table 19. VI Values of the Additive (P-6 to P-10) Doped Base Oil (BO2)

conc. of the additive in ppm ($\cdot 10^3$)	VI in the presence of				
	P-6	P-7	P-8	P-9	P-10
6	105	109	102	99	96
5	102	106	99	94	91
4	100	101	94	89	88
3	95	95	90	86	85
2	94	90	87	82	80
1	92	85	83	80	78
0	80	80	80	80	80

Table 20. Result of Biodegradability Test by (i) the Disc Diffusion Method and (ii) Soil Burial Degradation[a]

pathogen used	Disc Diffusion Method weight loss (g) in the presence of				
	P-1	P-2	P-3P	P-4	P-5
CC	0	0	0	0	0
FE	0	0	0	0	0
AA	0	0.17	0.22	0.20	0.26
CG	0	0	0	0	0
CE	0	0	0	0	0

Soil Burial Degradation Test weight loss (g) in the presence of				
P-1	P-2	P-3	P-4	P-5
0	0.08	0.07	0.08	0.09

[a] CC, FE, AA, CG, and CE are the pathogens named *Calletotricheme camellia* (CC), *Fussarium equisitae* (FE), *Alterneria alternata* (AA), *Colletrichum gleosproides* (CG), and *Curvularia eragrostidies* (CE) for polymeric additives (P-1 to P-5).

Performance of the Homo and Copolymers as PPD. Properties of base oils are reported in Table 11. Pour points of the different levels of additive-doped lube oils (BO1 and BO2) were tested and tabulated in Table 12 to 15. The values indicate that the prepared copolymers of DDA with α-pinene samples are more efficient as PPD than the copolymers of IDA with α-pinene, and the efficiency increases with the decrease in concentration of the additive in base oil. This may be explained on the basis that, when the molecular weight of the additive and its concentration increases, solvation power decreases and so does PPD.[20]

Performance of the Homo and Copolymers as VII. It is clear from the VI data, as evaluated in the present investigation (Tables 16 to 19), that irrespective of the polymer (homo and copolymer) and nature of the base oil VI values increase with the increase in additive concentration in the base oils studied. A critical observation of the VI values indicated that better performance is obtained for the copolymers of DDA with α-pinene than copolymers of IDA with α-pinene. It is also noticed that all copolymers show better VII properties than homopolymers (P1 and P6).

As the temperature is raised, the lube oil viscosity decreases; meanwhile the polymer molecule expands due to the increase in the solvation power and the increased size of the micelle. This increase in micelle size counterbalances the reduction of the viscosity of the lube oil and, hence, decreases the changes of viscosity with the temperature of the mixture. The increase in concentration of the polymer leads to an increase in the total volume of polymer micelles in the oil solution, thus exerting greater thickening effect and so as to VI.[5]

Analysis of Biodegradability Test Results. Tables 20 and 21 present biodegradability test results obtained by using the disk diffusion method and the soil burial test method. The copolymer of α-pinene with IDA showed significant biodegradability against the fungal pathogen, *A. alernata*. The result of soil burial test also indicated the similar extent of biodegradability. It was further confirmed by the shift of IR frequency of the ester carbonyl after

Table 21. Result of Biodegradability Test by (i) the Disc Diffusion Method and (ii) Soil Burial Degradation[a]

pathogen used	Disc Diffusion Method weight loss (g) in the presence of				
	P-6	P-7	P-8	P-9	P-10
CC	0	0	0	0	0
FE	0	0	0	0	0
AA	0	0.24	0.28	0.29	0.32
CG	0	0	0	0	0
CE	0	0	0	0	0

Soil Burial Degradation Test weight loss (g) in the presence of				
P-6	P-7	P-8	P-9	P-10
0	0.08	0.08	0.09	0.10

[a] CC, FE, AA, CG, and CE are the pathogens named *Calletotricheme camellia* (CC), *Fussarium equisitae* (FE), *Alterneria alternata* (AA), *Colletrichum gleosproides* (CG), and *Curvularia eragrostidies* (CE) for polymeric additives (P-6 to P-10).

the test is over. The copolymer of α-pinene with dodecylacrylate also shows biodegradability but to a smaller extent.

CONCLUSIONS

A consideration of the chemical structures of DDA and IDA may be taken into consideration to explain the differences of performance between DDA- and IDA-made homopolymers and their respective copolymers. The thermal stability of the copolymers is always greater than the corresponding homopolymers, and the copolymers of α-pinene with DDA are thermally more stable than that of IDA. Both the intrinsic viscosity and the viscometric molecular weight of the copolymers decreases with an increase in α-pinene concentration in the feed of the copolymers. The pour point of the samples is found to be better for the copolymers of α-pinene with DDA than the copolymers of α-pinene with IDA, and the values decrease with the increasing concentration of the polymer-doped base oil. VI values are in accordance with the molecular weight of the polymer samples. The greater the molecular weight is, the greater the VI is. With increasing concentration of the additive-doped oil solution, the VI is found to increase. The copolymer of α-pinene with IDA showed significant biodegradability against the fungal pathogen, *A. alernata*. The copolymer of α-pinene with dodecylacrylate also shows biodegradability but to a smaller extent.

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