

DODECYL METHACRYLATE – VINYL ACETATE COPOLYMER: A MULTIFUNCTIONAL PERFORMANCE ADDITIVE FOR LUBRICATING OIL

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ABSTRACT

Homopolymer of the prepared dodecylmethacrylate (DDMA) monomer was synthesized and a series of copolymers of it were prepared by varying the ratio between the ester and vinyl acetate (VA) by free radical polymerization using BZP as initiator. The synthesized polymers were characterized by spectral studies (FT-IR and NMR) and by gel permeation chromatography (GPC). Thermogravimetric analysis (TGA) was used to investigate the thermal behaviour of the polymers at high temperature. Performances of the polymers as additives, and their responses as PPD and viscosity modifiers in the base oil were evaluated by standard ASTM methods in terms of pour point and viscosity index. Wax crystallization behaviour of the additives was examined by photo micrographic image. The copolymers showed better thermal stability, better flow improving efficiency and induced better viscosity modification than the homopolymer. It is also observed that the viscosity modification and the pour point performance of the additives depend on the concentration of the additives in the base fluid.

KEYWORDS: Base Oil, Additive, Pour Point Depressant, Viscosity Modifier, GPC, TGA

Article History

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INTRODUCTION

The lubricating oil, also called the base oil, is the main ingredient of lubricants but is usually associated with many performance limitations. Hence, they are blended with some specialty chemicals called additives ¹. Among the various important additives, PPDs and VMs are of prime importance for the effective formulation of the lubricant for their field application.

Poly alkyl acrylates, poly alkyl methacrylates, styrene butadiene copolymers are some of the widely used additives applied in specific composition and architecture for improving the tribological properties of lubricating oils ². However, most of the reported additives developed so far function either simply as VM or as PPD. Moreover, despite their promising properties, only few of them have been evaluated as multifunctional additives. Therefore, in continuation of our endeavour to further explore this area of chemistry and to construct the effective multifunctional performance additives at reduced cost, this investigation is an attempt to determine whether a combination of C₁₂ acrylate and VA group can suitably control both the viscometric and low temperature properties of the base fluid. This present work thus reveals the synthesis, characterization and performance evaluation of additives based on the copolymers of long chain dodecyl

methacrylate and VA. A comparative assessment of their performances as additive in contrast to the homopolymer of dodecylmethacrylate was also studied.

EXPERIMENTAL

Materials Used

Methacrylic acid was obtained from SRL Pvt., Ltd., (India). Dodecylalcohol (DDA) and hexane were from S D Fine-Chem Ltd., (India). Vinyl acetate (VA) was purchased from Acros Organics and methanol was from Thomas Baker Chemicals Pvt., Ltd., (India). Toluene and H₂SO₄ were obtained from Merck Specialties Pvt., Ltd., (India). Benzoyl peroxide (BZP) obtained from Spectrochem Pvt., Ltd. (India) was recrystallized from CHCl₃-CH₃OH before use. Other chemicals were used as received. Mineral base fluid (SN1) was obtained from Indian Oil Corporation Ltd. (IOCL), India. The properties of the base fluid are provided as footnote of table 1.

Instrumentations

FT-IR and NMR Spectroscopy

Shimadzu FT-IR 8300 (Japan) spectrometer was used within the wavenumber range of 400 to 4000 cm⁻¹ at room temperature for recording the IR spectra, using 0.1 mm KBr cells. The NMR spectra were recorded in Bruker Avance 300 MHz (Germany) FT-NMR instrument using CDCl₃ as a solvent, TMS as reference and 5 mm BBO probe.

Gel Permeation Chromatography (GPC)

The average molecular weight (number-average and weight-average) of the additives were measured in Waters (USA) GPC equipment using HPLC grade THF as eluent at room temperature. The system was fitted with a 2414 refractive index detector (polystyrene calibration) and Waters 515 HPLC pump. The PDI (M_w/M_n) was also calculated by GPC.

Thermogravimetric Analysis (TGA)

The thermo-oxidative stabilities (TGA) or the decomposition pattern of the prepared additives in air were determined by a Shimadzu TGA-50 (Japan) thermo gravimetric analyser, at a heating rate of 10 °C min⁻¹. The percent weight loss (PWL) of mass (of the additives) with rise in temperature was used to measure the thermal stability of the additives. The PWL was measured by the equation,

$$\text{PWL} = [(M_0 - M_1)/M_0] \times 100 \quad \text{eq. (1)}$$

Where M_0 is the original mass taken and M_1 is the remaining mass after the test. The initial decomposition temperature and the temperature of completion of decomposition of the additives were obtained from the TGA curve.

Photo Micrograph and Wax Modification

The effectiveness of an additive in controlling the crystallization of wax can be studied by photo micrographic image of the base fluid. A Banbros polarizing microscope (BPL-400B, India), with magnification 200X, was used to study the wax modification of the base fluid. The microscope was also attached with a cooling thermostat to control the temperature at 0°C.

Performance Evaluation as Pour Point Depressants in Base Oil

The effect of additive concentration on pour point of the lube oil was tested by using different doping concentrations ranging (1% to 5% (w/w) for each of the prepared polymer according to the ASTM D 97-09 method. The pour points of the prepared solutions were measured using cloud and pour point tester model WIL-471 (India).

Evaluation of Viscosity Index

An Ubbelohde viscometer was used here to determine the VI of the additive doped base fluid. The viscometer was thoroughly dried and calibrated with triply distilled, degassed water and purified methanol at the experimental temperatures (40°C and 100°C) to determine the value of the viscometric constants³. The variation of kinematic viscosity (ν) of oil with the change of temperature, was evaluated according to the equation,

$$\nu = (Kt - L/t) \rho \quad \text{eq. (2)}$$

Where ρ is the density of experimental solution, t is the time of flow of the solution and K and L are the viscometric constants⁴. The densities of the experimental solutions were determined with a vibrating-tube density meter (Anton paar, DMA 4500 M, Austria) and the time of flow was recorded with a digital stopwatch. The VI, which reflects the variation of kinematic viscosity of oil with the change of temperature, was calculated according to ASTM D2270 method at five different doping concentrations (ranging between 1 to 5%) of the additives according to the equation,

$$\text{VI} = 3.63(60 - 10^n) \quad \text{eq. (3)}$$

and n was determined by the equation,

$$n = (\ln \nu_1 - \ln k) / \ln \nu_2 \quad \text{eq. (4)}$$

Where ν_1 and ν_2 are the kinematic viscosities of the additive doped oil at lower and higher temperature respectively. For the given temperature range, the value of k was determined to be 2.714⁵.

Preparation of Ester (Monomer) and Its Purification

The ester (dodecyl methacrylate, DDMA) was prepared by reacting 1.1 mol of methacrylic acid with 1 mol of dodecyl alcohol using concentrated sulphuric acid as a catalyst, 0.25 % hydroquinone with respect to the total reactants as polymerization inhibitor, and toluene as a solvent. The method of esterification and its purification were carried out by the process as reported in the earlier publication³⁰.

Preparation of Polymers

The polymers (homo and copolymers) were prepared by free radical polymerization (scheme1) at different percentage composition of monomers (table 1) in presence of BZP as initiator (0.4% w/w, with respect to the total monomer). The process of polymerization and purification of polymer was carried out by the procedure as reported in our earlier publication⁶.

RESULTS AND DISCUSSION

Molecular Weight Analysis

From the experimental values of M_n , M_w and PDI (polydispersity index) of the prepared homo and copolymers (as tabulated below, table 1), it is clear that on increasing the percentage of vinyl acetate in the copolymer feed both the number average

molecular weight and weight average molecular weight gradually increases. The DDMA-VA co-polymers are found less dispersed than the DDMA homopolymer.

Spectroscopic Analysis

The homopolymer of dodecyl methacrylate shows IR absorption band at 1735.8 cm^{-1} corresponds to the ester carbonyl group. For the copolymers of dodecyl methacrylate and vinyl acetate (P-2 to P-5) the IR spectrum showed the following absorptions: Peaks at 1732.9 cm^{-1} and 1716.5 cm^{-1} indicate the presence of ester carbonyl groups. In its ^1H NMR spectra, the homopolymer showed the presence of the methyl and methylene protons in the range of 0.89 to 1.93 ppm for all alkyl groups and a broad peak at 3.93 ppm for the protons of $-\text{OCH}_2$ group. Absence of any peak in the range of 5-6 ppm confirms the absence of any sp^2 hydrogens in the system and hence indicated the conversion of the monomer in to the polymer. In the ^1H NMR of the DDMA-VA copolymers, a broad peak at 3.93 -4.16 ppm indicated the protons of $-\text{OCH}_2$ and $-\text{OCH}_3$ groups. The hydrogen atoms attached to sp^3 carbons appeared in the range of 0.86 ppm to 2.64 ppm. Absence of any peak in the range of 5-6 ppm confirmed the conversion of the homopolymer in topolymerisation successfully.

In ^{13}C NMR of the homopolymer, the peaks at 177.54 ppm indicated the presence of ester carbon. The peaks at 65.03 ppm and 64.88 ppm confirmed the presence of $-\text{OCH}_2$ carbon and peaks in the range of 14.16–45.12 ppm accounted for all sp^3 carbon atoms of alkyl groups. Absence of sp^2 carbon and hence total polymerization was confirmed by the absence of any peak in the range of 120-150 ppm. In ^{13}C NMR of the copolymers of vinyl acetate the peaks at δ 176.60 - 176.70 ppm were due to the presence of ester carbonyl group. The peaks at 64.66 - 65.06 ppm corresponded to the $-\text{COCH}_3$ methyl carbon and $-\text{OCH}_2$ carbons, peaks ranging from 14.08–45.09 ppm for all other sp^3 carbons. Absence of peak in the range of 120-150 ppm indicated the absence of sp^2 carbons and confirmed the polymerization.

Analysis of Pour Point Values

The experimental values of pour point are given in table 2. The values suggest that all the prepared polymers (P-1 to P-5) can be used effectively as pour point depressants (PPD) or flow improvers (FI) for base oil. The copolymers (P-2 to P-5) are better than the homopolymer (P-1) as FI. But with varying concentration, the pour point values do not linearly correlate. The vinyl acetate copolymers (P-2 to P-5) showed better results than the homopolymers of DDMA. These polymers are better as FI and may be due to the presence of acetate group in the polymer backbone which reduces the adsorption of the polymer molecule on the wax crystals⁷(Abdel-Azim et al., 2005) that happened in case of flat DDMA homopolymer architecture. The P-3 copolymer having 5% (w/w) vinyl acetate proved to be the best flow improver among all the prepared polymers. At 5% concentration this polymer showed lowest pour point of 4°C . Polymers with higher molecular weights especially P-5 showed comparatively poor results. It may be because of their low solubility in the base oil.

Analysis of the Influence of Additives on Viscosity Index Value

The data presented in table3, compared the dependence of the VI values with the nature and on the concentrations of the additive, and the results indicated that all the prepared additives effectively modified the viscosity properties of the base fluid. The additive DDMA homopolymer showed the least viscosity modification and with the increase of VA content in the additive feed, the VI values are found to rise gradually in case of the copolymer. For any viscosity modifier, the potential to improve the VI relies on the conduct of the additive molecules in the base fluid, where its molecular weight, solubility and chain topology are crucial 8parameters¹¹. Also, the viscosity of the base fluid depends on the temperature, where with an increase in temperature, the viscosity normally decreases⁹. Various researchers suggested that at low

temperatures, the additive molecules is poorly soluble in the base fluid and remain in a round coiled up conformation with a minimal effect on the base fluid viscosity¹⁰. But with the increased solubility and interaction between the additive chains and the solvent molecules at higher temperature, the additives change its shape from tightly coiled to inflated spread out ones. This successfully thickens the oil and counters the normal reduction in viscosity of the base fluid with increasing temperature¹¹. Here the DDMA-VA copolymer additive with 10% VA content in the feed, P-5 showed the highest VI increment, and this outcome is possibly due to higher degree of solvation and enhanced interaction of the additive having non polar ends with the paraffinic base fluid. On the other hand, the additive DDMA, which only consists of dodecyl methacrylate monomers, has more polar character compared with the others. Due to this polar nature, the additive has less interaction with the base fluid and, therefore, has a lesser solvated volume, consequently leaving it with the lowest VI among others⁶. Moreover, in accordance with our earlier publication, the VI values become more pronounced on increasing the overall additive doping percentage in the base fluid. This is because of the fact that the increase in concentration of the additive leads to an increase in total volume of the polymer coils. This inflated coils, together with their increased interaction with the base fluid leads to greater thickening effect and subsequently increases the viscosity index of the base stock¹².

Analysis of the Photo Micrographic Image

A comparison of the photo micrographs of pure base fluid and the base fluid blended with different polymeric additives indicated that the original base fluid (pour point = -6°C) showed long rod liked wax crystals in its photo micrographic image whereas additive doped base oils (4%, w/w solution) showed a significant reduction in the shape and size of the wax crystals in their images. Thus, the reduction in the size of wax crystals seems to be responsible for improving the pour point values. Hence, the pour point values obtained earlier are in complete correlation with the wax modification results.

CONCLUSIONS

It conclusion, the copolymer of dodecyl methacrylate with vinyl acetate are found effective as multifunctional additive (flow improver and viscosity improver) for the lube oil. Moreover, it was also found that copolymers with lower molecular weight are more effective as flow improver than copolymers with higher molecular weight. Therefore, molecular weight of polymer has a significant role in relation to the performance of the polymers as flow improvers for lube oil. In addition, the VA copolymer induced excellent VM properties as well when added to the base oil.

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FIGURE

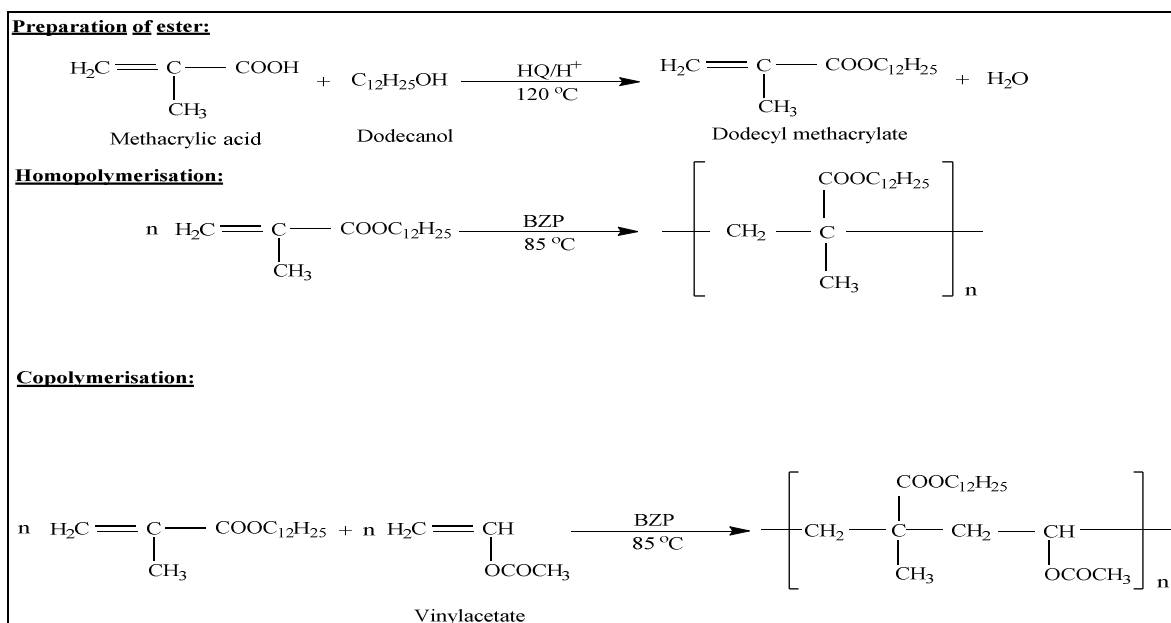


Figure 1: Scheme 1

TABLES

Table 1: Percentage composition, M_n , M_w and PDI values of polymers (P-1 to P-5)

Polymer Code	% of DDMA	% of VA	M_n	M_w	PDI
P-1	100	-	20482	49682	2.4256
P-2	97.5	2.5	22475	33018	1.5300
P-3	95	5	24613	35842	1.4920
P-4	92.5	7.5	54766	66210	1.1640
P-5	90	10	60790	81219	1.3100

DDMA = Dodecyl methacrylate, VA = Vinyl acetate, M_n = Number average molecular weight, M_w = Weight average molecular weight, PDI = Polydispersity index

Table 2: Pour Point Data with Respect to the Different Concentrations of the Additives in Base Oil*

Polymer Code	Pour Point ($^{\circ}$ C) of Additives Doped Base Oil (% in w/w)						
	0%	1%	2%	3%	4%	5%	6%
P-1	24	13.5	12.9	12.2	11.5	10	10.3
P-2	24	8	7.8	7.5	8.1	9.2	10
P-3	24	7.5	6.5	6.0	5.5	4.0	4.5
P-4	24	8.5	8	7.5	8.0	8.5	9
P-5	24	10.0	10.5	12	12.5	13	13.8

* Properties of the base oil - Density ($\text{g}\cdot\text{cm}^{-3}$) at 40°C : 0.855; Viscosity at 100°C in cSt: 3.979; Viscosity index: 86; Pour point, $^{\circ}\text{C}$: -6

Table 3: Viscosity Index Data with Respect to the Different Concentrations of the Additives in Base Oil

Polymer Code	Pour Point ($^{\circ}$ C) of Additives Doped Base Oil (% in w/w)						
	0%	1%	2%	3%	4%	5%	6%
P-1	86	89	92	102	111	116	120
P-2	86	94	101	107	119	121	126
P-3	86	98	118	123	127	131	135
P-4	86	112	126	128	131	135	139
P-5	86	118	129	130	132	137	138

