



Investigation of polyacrylates copolymers as lube oil viscosity index improvers

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ABSTRACT

Six copolymers, based on polyacrylates, were prepared and evaluated as viscosity index improvers for lube oil. The synthesizing process begins by esterification of acrylic acid with different alkyl chain length alcohols (octyl, decyl, octadecyl, tetradecyl, and hexadecyl alcohol), ranging from C₈ to C₁₆. The completion of the esterification process was confirmed by FTIR spectrometry. Linear copolymerization was carried out to produce six copolymeric viscosity index improvers. All copolymers were tested for solubility in the selected base oil (SAE 30) Society of Automotive Engineers. Acceptable solubility in the base oil has been recorded. Molecular weight of the prepared copolymers was determined by the technique of Gel Permeation Chromatography (GPC). Samples with different concentrations from each copolymer (0.5%, 1%, 1.5%, 2%, 2.5%, 3% by weight) were prepared and evaluated as viscosity index improvers for lube oil. It has been found that all of the prepared compounds are effective as viscosity index improvers for lube oil, and their effectiveness becomes more pronounced by increasing either the molecular weight of copolymer (140,000–236,000) or the alkyl chain length (C₈–C₁₂). Effectiveness could be increased by increasing the concentration of the additives in the base oil (0.5%–3%). There are no reflection points through the tested range of concentrations.

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1. Introduction

Lubrication is simply the use of a material to improve the smoothness of movement of one surface over another, and the materials which are used in this way are called lubricant. Lubricants may be liquid, solid, or gas. Most modern lubricants are petroleum based although vegetable oils and fats are also used. The most important single property of lubricating oil is its viscosity. Lubricating oils are classified as refined and synthetic. Refined oils are produced from crude oil refinery. Crude oil refinery produces paraffinic oils, naphthenic oils and small amount of aromatic oils. Synthetic lubricants are produced via chemical synthesis. Selected chemicals could be blended with the lubricating oils to impart them certain specific properties. Resistance of a lubricant to viscosity change with temperature is determined by its viscosity index (VI) which is an arbitrary number calculated from the observed viscosities at two widely separated temperatures. The normal range of viscosity index is from zero up to 100. Oils of high VI could resist excessive thinning at high temperatures whereas those of low VI experience an extremely thinning at high temperatures. Viscosity index of the paraffinic based lubricants is often greater than that of the naphthenic based ones. Viscosity index improvers (VII) can be regarded as the key to high

performance multigrade oil. They are generally oil soluble polymers. The added polymeric molecules may interact with the base oil affecting its final viscosity. Oils containing viscosity index improvers can achieve a viscosity index up to 150.

Three major families of viscosity index improvers are known; olefin copolymers, hydrogenated diene copolymers, and acrylic acid based copolymers (Wills, 1980; Akhmedov and Mamedova, 2003). Different polymer concentrations are always tested in order to determine the performance of the additives under the engine running conditions. The optimum improver means higher viscosity index and shear stability. It is also soluble in the base oil and compatible with the other additives. Schiff et al. (1971) used hydrogenated random butadiene–styrene copolymer to produce a shear stable, lubricant with viscosity index of about 140. The butadiene content was ranged from 30% to 44% weight, and its molecular weight started from 25,000 to 125,000. Dawans et al. (1993) presented a viscosity index improver based only on the butadiene polymer. Molecular weights up to about 450,000 were employed later on by Forbes et al. (1976). They described a graft copolymer of polystyrene and poly isobutylene.

Solubility has an important effect on the viscosity index, as mentioned by Bataille et al. (1994). They prepared and tested two copolymers, α -methyl styrene and 2-ethylhexyl acrylate. The copolymers obtained were blended with a paraffinic (SAE 10) of 110 VI and a naphthenic base oil of 56 VI. The copolymers were tested according to the ASTM 445 IP-71 method. Nassar et al. (2005)

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synthesized polymeric acrylates VI improvers by copolymerization of four esters (decyl acrylate, dodecyl acrylate, tetradecyl acrylate, and hexadecyl acrylate) with different amount of styrene. Their effectiveness as VI improvers was found proportional to molecular weight of the copolymer. Solubility of the prepared copolymers was found inversely proportional to their molecular weight. *Elsayed (2006)* employed four different esters and carried out free radical copolymerization using different monomers (vinyl acetate, maleic anhydride, 1-octene, and 1-tetradecene). The copolymers prepared using vinyl acetate, or octene were found, relatively, more efficient as VI improvers. Effectiveness was found proportional to the alkyl chain length. Those prepared from tetradecene with different alcohols were found to be more effective as pour point depressant than those prepared from dodecene or octane. Effectiveness as pour point depressants was also found proportional to concentration of the additives and also to chain length of the alkyl groups. Maleate copolymers proved to be efficient as viscosity index improvers according to *Ahmed (2008)*.

In this work a group of copolymers based on polyacrylates were prepared and evaluated as viscosity index improvers for lube oil. Polyacrylates have been chosen since they are simply prepared compared with other viscosity index improvers, compatible with other additives, of high shear stability, effective as pour point depressants and of relatively low cost.

2. Experimental

2.1. Copolymers preparation and characterization

2.1.1. Materials

In this work Acrylic acid [$\text{H}_2\text{C}=\text{CH}-\text{COOH}$] was esterified using a number of alcohols, Octyl Alcohol [$\text{CH}_3(\text{CH}_2)_7\text{OH}$], Decyl Alcohol [$\text{CH}_3(\text{CH}_2)_8\text{CH}_2\text{OH}$], Dodecyl Alcohol (Dodecanol) [$\text{CH}_3-(\text{CH}_2)_{11}-\text{OH}$], Tetradecyl alcohol (Tetradecanol) [$\text{CH}_3-(\text{CH}_2)_{13}-\text{OH}$], Hexadecyl alcohol (Hexadecanol) [$\text{CH}_3-(\text{CH}_2)_{15}-\text{OH}$]. Benzoyl peroxide [$(\text{C}_6\text{H}_5\text{CO})_2\text{O}_2$] was used as an initiator. Hydroquinone (1, 4-Dihydroxybenzene; p-Dihydroxybenzene; or 1,4-Benzenediol) [$\text{C}_6\text{H}_4(\text{OH})_2$], Catalysts: p-Toluene Sulfonic Acid (PTSA) monohydrate [$\text{CH}_3\text{C}_6\text{H}_4\text{SO}_3\text{H} \cdot \text{H}_2\text{O}$] were used as inhibitor. Solvents have been selected and used according to the process, materials, and reaction conditions (Table 1). Free radical initiators are used to initiate the polymerization process. The initiators were either oxygen-based or nitrogen-based thermally unstable compounds. Their decomposition could yield two free radicals (*Rudnick, 2003*). Acrylic acid is very active, it can undergo polymerization even in absence of any initiators, hence; inhibitors are needed to inhibit its polymerization. After esterification, the esters need to be purified. Sodium hydroxide (NaOH) was used to remove the unreacted acid. Anhydrous Calcium chloride (CaCl_2) and anhydrous Sodium sulfate (Na_2SO_4) were used to dry the final product. All materials are from Aldrich Chemical Co. Ltd. (U.K.).

Table 1
The employed solvents and their boiling points.

Solvent	Source	b.p.(°C)
Xylene	Aldrich Chemical Co. Ltd. (U.K.)	138
Toluene	Aldrich Chemical Co. Ltd. (U.K.)	110
Benzene	Aldrich Chemical Co. Ltd. (U.K.)	80–81
Methanol	Aldrich Chemical Co. Ltd. (U.K.)	64
Acetone	Aldrich Chemical Co. Ltd. (U.K.)	56
Ethanol	Aldrich Chemical Co. Ltd. (U.K.)	78–79

2.1.2. Procedures

Polyacrylates viscosity index improvers have been prepared in several steps, starting from esterification of acrylic acid with alcohols, purification of produced esters, identification of the purified esters, polymerization of the esters, and finally characterization of the produced polymers via solubility test and molecular weight determination.

2.1.2.1. Esterification of acrylic acid with different types of alcohols. Esterification has been carried out by reacting one mole of acrylic acid with one mole of the selected alcohol (octyl, decyl, dodecyl, tetradecyl, and hexadecyl). The reactions were carried out in a resin kettle in presence of 0.5% p-toluene sulfonic acid as a catalyst, 0.25% hydroquinone as inhibitor, for the polymerization of acrylic acid, and xylene as a solvent. Esterification reactions were carried out under a slow stream of deoxygenated nitrogen and were agitated using a mechanical stirrer at 500 rpm. The reactants which were mixed with an equal weight of xylene were heated gradually from the room temperature up to $130\text{ }^\circ\text{C} \pm 5\text{ }^\circ\text{C}$ (*Sadykhov et al., 1974*). The extent of reaction was followed by monitoring the amount of liberated water.

2.1.2.2. Purification of the prepared esters. A suitable amount of charcoal was added to the esters and allowed to reflux for 4 h and then filtered. The filtrate was taken and washed by 0.5 N sodium hydroxide in separating funnel and shake well. The entire process was repeated several times to ensure complete removal of the unreacted acid. The purified ester was then washed several times with distilled water to remove any traces of sodium hydroxide then the ester was left overnight on calcium chloride anhydrous for drying. It was then removed by filtration, xylene was removed by distillation. The ester was then ready to use in copolymerization process.

2.1.2.3. Identification of the purified esters. The infrared spectra obtained using an F.T.I.R [Fourier Transform Infra Red] spectrometer model type Mattson-Infinity Series Bench top 961 have been employed for identification of the purified esters before going ahead for copolymerizing them.

2.1.2.4. Copolymerization of the produced esters. Polymeric additives were prepared by free radical copolymerization of equimolar quantities of the prepared esters. The reaction was carried out in a four-necked round bottom flask equipped with a stirrer, efficient condenser, thermometer, and an inlet for introduction of dry nitrogen. Drying of nitrogen took place by passing it through a silica gel bed. The process was carried out by adding in the flask one mole of each of the selected esters together with the desired weight of initiator (benzoyl peroxide). The mixture was heated to $60\text{ }^\circ\text{C} \pm 5\text{ }^\circ\text{C}$ for 8 h in the presence of toluene as a solvent. At the end of the reaction, the temperature was allowed to reduce to the room temperature, and the reaction mixture was then poured drop by drop in cooled methanol with continuous stirring. The mixture was filtered off and dried. Constituents of the prepared polymers and their designation are shown in Table 2.

2.1.2.5. Characterization of the prepared copolymers. Solubility of the prepared copolymers in lube oil was investigated before testing their effectiveness as viscosity index improvers. The solubility test took place by dissolving 1 g of the polymer in 100 g of additive free base oil (SAE 30). The (1 g/100 g) mixture has been allowed to stand overnight. This time was enough to produce the required swelling for the polymer. The mixture was agitated by a Teflon covered magnetic stirrer for 20 min at $60\text{ }^\circ\text{C}$ to disintegrate the gel. To test homogeneity and thermodynamic stability of the mixture, viscosity of five different samples from

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