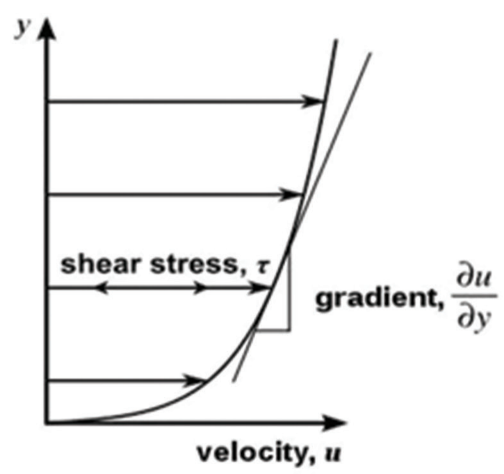
APPLICATIONS, TESTS, AND MEASURES OF VISCOSITY LOSS IN SHEAR STABILITY OF MULTI-GRADE, POLYMER-THICKENED LUBRICANTS

Lubricants are substances or fluids that are used to reduce the friction between mechanical components that come in contact [1]. Lubricants serve many different purposes, a leading one being their usage in vehicles. Lubricants are vital in automobiles due to the importance of properly lubricating engines as they operate at high speeds and temperatures. When mechanical components of an engine rub against each other, a great amount of friction and heat can be generated. With the use of lubricants, an engine can function for a prolonged period of time. A well-lubricated engine experiences a reduction in friction from wear and tear due to contact stresses between the moving surfaces [2]. This reduction increases efficiency and fuel economy. Therefore, the automobile user saves money and gas as the engine is properly lubricated. Conversely, devoid of the lubricant, the engine parts can be damaged and fused due to high contact temperatures generated by the frictional heating of the moving components.

In order to lubricate and lubricate effectively, the lubricant needs to have an acceptable and preferably optimized viscosity, which is a measure of the fluid's ability to flow. Viscosity is a function of temperature. In this regard lubricants can be classified into two types: single-grade and multi-grade [3]. Both types contain packages of performance additives such as detergents, dispersants, antioxidants and anti-wear agents depending on the application. Single-grade lubricants have a viscosity optimized for a particular temperature range, usually summer and winter grades. They have to be changed with each season in temperate climates. Multi-grade lubricants work well at both high and low temperatures since they are thinner at low and thicker at high temperatures, relative to single-grade lubricants [4]. Multi-grade lubricants are made with either special, and usually expensive, synthetic base fluids, or more commonly with mineral oils thickened with oil-soluble polymers. Multi-grade, polymer-thickened lubricants are composed of polymer thickeners and a light base stock lubricating oil. The polymer in the lubricant thickens the fluid, increasing the viscosity. An important property to consider when manufacturing multi-grade, polymer-thickened lubricants is their shear stability since different kinds of formulated lubricants are used depending on the vehicle component being lubricated and the shears encountered in it. The type of polymer, its molecular weight, and its treat rate is selected to meet initial, fresh oil viscosity grade requirements and also to account for any degradation of the polymer chains so that the oil "stays in-grade" during service or testing. This degradation of the polymer results in the loss of viscosity at the operating conditions and temperatures at which the engine functions and reduces the strength of the oil films formed between the components of the engine. In addition, the loss of viscosity affects the ability of the lubricant to remain in high load areas and reduces the strength of the oil film. Minimizing shear degradation is critical to minimizing the viscosity loss of the lubricants. It is also essential to provide the oil's contribution to fuel economy while still maintaining an adequate oil film strength as those are critical parameters of a lubricant. Manufacturers of multi-grade, polymer-thickened lubricants test their engine protecting performance by subjecting them to extensive performance tests including tests to determine their viscosity loss and shear stability.



Viscosity, $\tau = \mu \frac{du}{dy}$

Where,

μ = Dynamic viscosity

τ = Shear stress= F/A

$\frac{du}{dy}$ = Rate of shear deformation

Figure 1. Graphical definition of viscosity.

Shear stability is a measure of how resistant an oil or lubricant is to change in its viscosity under applied mechanical stresses and shears such as those generated during the operation of a running engine [5]. Viscosity is defined as the ratio between applied shear stress and rate of shear (Figure 1). It is also called the coefficient of viscosity or dynamic viscosity. The shear rate is defined as the velocity gradient perpendicular to the direction of flow. In the example of a lubricant in a mechanical system, such as piston rings and piston walls, or journal bearings, the shear rate is the difference in velocity at the two surfaces divided by the distance between the two surfaces. The unit of shear rate is inverse time, typically s-1. Shear stress is the force per unit area in the direction for the flow. When a mechanical stress is induced, for example by the operation of a running engine, thinning of the lubricant may occur. This thinning results from the reduction of viscosity. As this thinning occurs, the engine is more susceptible to corruption and damage. When the lubricant can no longer control the heat generated by friction, and the surrounding high temperatures, the engine can no longer function properly.

There are two mechanisms for shear loss in polymer-thickened lubricants. One is permanent viscosity loss (PVL) due to the polymers breaking into smaller polymers. PVL can also occur from thermal degradation or oxidation [6], but this usually does not significantly contribute to viscosity loss as the polymers degrade from the ends. In mechanical shearing, the breakage occurs towards the middle of the polymer chain length causing a significant viscosity loss. In automotive engines, this typically occurs in the pistons and bearings. The other mechanism for viscosity loss is temporary viscosity loss (TVL) which occurs under high shear rates and as the name implies is reversible with the viscosity returning to a higher value when the shear rate is lowered [7]. TVL occurs when polymers are stretched but not broken under the applied shear stresses. Oil viscosities can be tested with High Temperature High Shear (HTHS) viscosity measurements and these values are then included in engine oil specifications. The amount or treat rate of polymer added to any engine oil dictates the degree of PVL or TVL. For example, synthetic engine oils tend to have naturally higher viscosity indexes (a measure of the rate of change of viscosity vs. temperature where a higher index indicates a lower slope) so they require less and sometimes no polymer to achieve their multi-grade viscosity ratings. HTHS viscosity are measured with methods such as ASTM D4683 (Tapered Bearing Simulator), D4741/CEC L-36-90 (Tapered Plug Viscometer), D5481 (Multicell Capillary Viscometer) or with an ultrahigh shear rate viscometer (USV) [14]. The minimum SAE J300 -2015 HTHS ratings for engine oils are:

Table 1. SAE J300 -2015 HTHS ratings for engine oils.

SAE Viscosity Grade	High Temperature High Shear Rate @150^{0}C (mPa·s)
8	1.7
12	2
16	2.3
20	2.6
30	2.9
40 - Winter (0W-40, 5W-40, 10W-40 grades)	3.5
40 – Heavy Duty (15W-40, 20W-40, 25W-40 40 grades)	3.7
50	3.7
60	3.7

Three methods, Kinematic viscosity (KV) loss, percent loss, and PSSI are often used to evaluate the PVL performance of multi-grade, polymer-thickened lubricants. Kinematic viscosity (KV), is a measure of a fluid's resistance to flow under gravitational forces. It is measured as the ratio of dynamic viscosity to fluid mass density [8]. Kinematic viscosity is measured by calculating the time it takes for oil to travel through an orifice of a capillary with the force of gravity acting upon it. A capillary tube viscometer is an instrument used to measure the kinematic viscosity of a fluid.

A prominent procedure for analyzing kinematic viscosity measurements is ASTM D445 which requires the use of a calibrated viscometer. The kinematic viscosity loss of various fluids is measured using a procedure such as ASTM D445 with a viscometer in a temperature-controlled environment. The kinematic viscosity of oils and lubricants can be lost in environments with high temperatures. To enhance the performance of a lubricant and to be economically efficient, it is preferable to limit the number of polymers needed to make a good lubricant [8]. Therefore, quantifying the effects of molecular weight, molecular weight distribution, and thickening efficiency are important. The thickening efficiency is defined by the amount of polymer needed to increase kinematic viscosity and is often recorded as the kinematic viscosity of a blend of a polymer-containing product at a certain weight percent in a standard base oil. For shear stability, most oil and lubricant analysis measure and report the kinematic viscosity before and after shearing occurs.

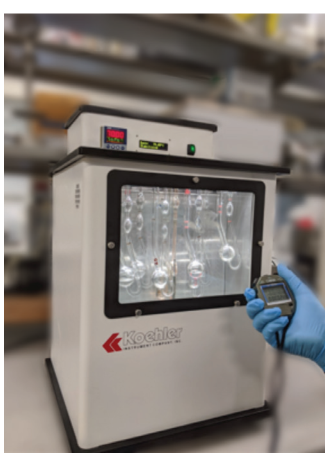


Figure 2. Capillary tube viscometer.

Another measure of viscosity loss is percent loss. The percent loss of viscosity is defined as:

(1)

$$Percent\ Viscosity\ Loss = \frac{Permanent\ shear\ loss}{Viscosity\ before\ shear} = \frac{(V_i - V_f)}{V_i} * 100$$

where Vi is the initial KV of the lubricant with polymer, and V_f is the KV of the lubricant after shearing. The percent loss of viscosity measured in lubricants dictates the performance of the lubricants. A significant percent loss indicates to the manufacturing company that their lubricant may not be a good performer [10].

Permanent shear stability index (PSSI) is another type of viscosity loss indicator that can be measured. The SSI is defined as:

(2)

$$PSSI = \frac{Permanent\ shear\ loss}{Contribution\ of\ viscosity\ modifier} = \frac{(V_i - V_f)}{(V_i - V_o)} * 100\%$$

where V_o is the KV of the base oil before addition of polymer. PSSI is a measure of the loss of viscosity due to shearing contributed by an additive [11]. It is affected by the base fluid, the chemistry and concentration of the additive, and the presence of other additives. The PSSI is a measure of the effectiveness of the polymer additives in maintaining their contribution to the final fluid blend viscosity. The property is important to the suppliers of the polymers and to the lubricant formulators who use them. The percent viscosity loss is the important measure for the lubricant supplier and end user.

The three previously mentioned properties require some kind of shear procedure. Sonic shear, diesel injector shear, KRL, and Sequence VIII (L-38) and are examples of laboratory bench test also used to evaluate the performance of multi-grade lubricants. Sonic shear tests are often used in the hydraulic fluid industry. They can also be applied to transmission fluids and tractor fluids [7]. ASTM D2603, Sonic Shear for Polymer-Containing Oils, and ASTM D5621, Sonic Shear for Hydraulic Fluids, are the two test methods commonly used in the industry. A sonic oscillator is used to irradiate or shear the lubricant sample for a certain amount time at power levels calibrated with specified Reference Fluids in both methods. The viscosity change between the initial and sheared lubricant is then measured [11]. ASTM D2603 can be run at different severity levels. At its lower levels, using Reference Fluid A, the test is known to be polymer chemistry dependent, and so is mostly used for polymer manufacturing and their specifications. At higher shear levels, using Reference Fluid B, it is less polymer dependent and in ASTM D5621, which also uses Reference Fluid B and shears for a longer time, no polymer chemistry dependence is observed.

The diesel injector shear test or ASTM D6278 and CEC L-14-A uses a high shear nozzle or diesel injector apparatus to evaluate the percent viscosity loss of polymer-thickened lubricants due to shearing [12]. This test method is mostly used for quality control. The oils are passed through the shearing injector 30 times, or cycles, and the severity of the test is comparable to the shearing severity found in passenger cars. A 90-cycle version of the test, ASTM D7109, is a more severe test and may better approximate shear loss found in heavy duty Diesel engines.

Figure 3. Diesel injector tester.

The KRL (Kegelrollenlager, German for Tapered Rolling Bearing) test is also used to test the shear stability and performance of multi-grade, polymer-thickened lubricants. This test utilizes a tapered rolling bearing in a cup fitted to a four-ball instrument [7]. Load is applied to the bearings as it rotates at a specific speed for a certain period of time. The test usually takes up to 20 hours to complete with the bearings rotating at around 1,450 revolutions per minute. After the test is over, the viscosities before and after the test are compared to calculate the percent viscosity loss. This test method is aggressive and considered to be one of the most severe shear tests as it forces the lubricants to undergo extreme shearing for an extended period of time. The method is relatively severe because it operates in the elastohydrodynamic lubrication regime (EHD) and causes the bearings produce high shear stresses on the fluids. CEC L45-A-99 is one of the procedures that uses the KRL test.

Figure 4. KRL tester and tapered bearing assembly.

Sequence VIII (Roman numeral eight, also known as the Labeco 38 or L-38) is a common test used to specify the allowed viscosity loss of a multi-grade, polymer-thickened passenger car engine lubricants. The Sequence VIII or L-38 is used to test the quality of a lubricating fluid under high-temperature conditions.

Figure 5. Sequence VIII (L-38) test stand.

This test uses a copper/tin/lead rod bearing and measures the presence and extent of corrosion in the bearings [13]. The shear stability is also measured in this test. The test uses a single-cylinder, spark ignition, lubricant test engine with an external lubricant heater circuit. The engine runs a 3150 revolutions per minute for 40 hours with the tested fluid. After the 40 hours are over, the bearings are visually examined to see if there is any corrosion. When there's visible corrosion on the bearings, that means that the quality and the performance of the lubricant tested is poor. Furthermore, the viscosity of an oil sample taken after 10 hours of testing and stripped of any fuel that may have diluted the oil is also measured to calculate percent loss or stay-in-grade kinematic viscosity. To summarize, the severity of permanent shear stability tests can be ranked as follow: KRL > HF sonic shear > 90-cycle fuel injector > (30-cycle fuel injector, low power sonic shear, L-38).

Different kinds of multi-grade, polymer-thickened lubricants are formulated for different applications. Engine oil, also known as motor oil, is a type of multi-grade, polymer-thickened lubricant made from mineral oil base stocks and other additives [14]. The base stock takes up to 70 to 90% of the solution and the additives take up 10 to 30% of the solution. Engine oil is used to lubricate internal combustion engines, to reduce friction in moving parts of the engine, and to clean, cool, and protect the engine. Multi-grade engine oils are formulated with viscosity index improvers (VIIs) to improve the viscosity vs. temperature characteristics (VI). VIIs are polymer additives capable of maintaining fluid viscosities over a greater range of temperatures without losing to much viscosity over the oil service life [15].

VIIs resist thinning of lubricants. Several mechanisms have been proposed to explain how VIIs perform this function. The most widely cited mechanism is coil expansion, which states that increasing temperature increases the solubility of the polymer in the base oil, which results in expansion of the polymer coil and, in turn, increases viscosity. Many polymers used as thickeners do not follow this mechanism and are often referred to as Viscosity Modifiers (VM). They, like all soluble polymers, impede the motion of solvent (oil) molecules and do so relatively more at high temperatures than at low temperatures. With the use of VIIs, regardless whether the engine runs at high or low temperatures, the oil can maintain a good viscosity.

Automatic transmission fluids (ATF) are another kind of multi-grade, polymer-thickened lubricants. ATF's are used in a closed system and are not exposed to outside elements or pollutants [16]. They are composed of base oils, anti-wear additives, corrosion inhibitors, anti-foam, detergents and seal swell additives and agents. Their features and benefits are enhanced, long-term frictional properties, exceptional thermal and oxidation stability, great film-strength and anti-wear properties, exceptional shear stability, and low-temperature fluidity [17]. All ATF's contain friction modifiers, except for those specified for some Ford transmissions and the John Deere J-21A specification. Dexron/Mercon/ATF+4 and multi-vehicle synthetic are some of the various types ATF fluids on the market. Automatic transmission fluids have many performance-enhancing chemicals added to the fluid to meet the demands of each transmission.

Hydraulic fluids are another kind of multi-grade, polymer-thickened lubricants. They are primarily used as a medium to transfer energy in hydraulic systems [18]. Other uses of hydraulic fluids include heat transfer, contamination removal, sealing, and lubrication. Hydraulic fluids help keep proper viscosity across a wide range of temperatures. Hydraulic machines generate excess heat that can overheat the system and damage the components due to low of viscosity. Hydraulic fluids have similar characteristics and properties as other previously mentioned lubricants such as good thermal and shear stability, low chemical corrosiveness, and high anti-wear characteristics [18]. They can be broken down into different categories such as mineral oils, fire-resistant fluids, water/oil emulsions, water glycol, and phosphate esters [19]. Depending on the operating hydraulic system, operating pressures, environment temperatures, and types of pumps, different kinds of hydraulic fluids serve different systems. Mineral oils are excellent for extreme hot or cold temperatures, but they can have a low flash point. When a fire risk is plausible and the system requires a lubricant to high higher flash points, fire-resistant fluids are utilized. In applications where mineral oil hydraulic fluids are used, like excavators and back hoes, the use of single-grade fluids is still common. Mechanical shear is much more severe in these applications than in engine oil applications, so multi-grade polymer-thickened hydraulic fluids require much more shear stable polymers which come at an increased cost. The advantage of all-season use may not be enough to overcome these costs, but it turns out that the higher VI of the multi-grade hydraulic fluids provide improvements in hydraulic efficiency, which over the service life of the fluids more than overcomes the cost difference.

Gear oils are another common type of multi-grade, polymer-thickened lubricants. Their primary usage is in transmissions, transfer cases, and differentials of automobiles [20]. Essentially gear oils can be used wherever a gearbox can be found. They are composed of a base oil, extreme pressure additives, and anti-wear additives. A good gear oil must have great thermal and oxidation stability, extreme pressure properties, and the ability to demulsify to remove water from the system. Gear oils can be made for specific purposes. Depending on which gears and system the lubricant will be applied onto, different additives may be more or less suitable. Various types of gear oil include rust and oxidation inhibitors (R&O), extreme pressure, compound (EP), and synthetic oil [20]. R&O gear oils are designed to reduce corrosion and oxidation in the gearbox. Extreme pressure gear oils are used to handle extreme heat and pressure and contains a few additives. Compound gear oil are formulated with fatty oils to create high viscosities which are suitable for low-speed and high-pressure applications. Synthetic gear oil is used for extreme machine conditions, vary in their viscosities, are more shear stable and can work in both extremely low and high temperatures.

In conclusion, multi-grade, polymer-thickened lubricants are essential to many mechanical systems as they prevent mechanical systems from breaking down due to high shear stress, and frictional heating. Shear stability is an important property and predictor of the performance of multi-grade, polymer-thickened lubricants and viscosity loss is the technique used to measure it. Finally, with the number and variety of multi-grade, polymer-thickened lubricants at hand, it is essential to test each of them to compare their properties and determine which kind will deliver the highest performance in automotive, hydraulic, and machinery operation.

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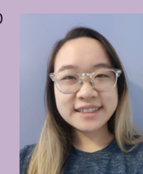

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