

Review of Viscosity Modifier Lubricant Additives

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Abstract

This article reviews viscosity modifiers, additives that increase the viscosity of lubricating oils. Viscosity modifiers are high molecular weight polymers whose functionality is derived from their thickening efficiency, viscosity-temperature relationship, and shear stability. There are now many different additive chemistries and architectures available, all of which have advantages and disadvantages, and affect solution viscosity through different mechanisms. Understanding these mechanisms and how they impart additive function is critical to the development of new viscosity modifiers that enable lubricants to function more efficiently over a wide range of temperatures.

1 Introduction

The viscosity of fluids decreases rapidly as temperature increases. This is a serious concern for lubricants, which usually experience a range of temperatures during use. If the viscosity of a lubricant is too low at a high temperature, the fluid may no longer be able to provide sufficient load support, leading to surface contact. However, if the lubricant is replaced by a much more viscous fluid to ensure the lubricating film is sufficiently thick at high temperatures, then there is likely to be poor efficiency at low temperatures due to viscous friction. This issue is addressed using multi-grade fluids, which contain polymeric additives called viscosity modifiers (VM)s. The purpose of a VM is to thicken a low viscosity base fluid to a useful viscosity at high temperatures while not increasing the viscosity too much at low temperatures. This is illustrated in Fig. 1 by the comparison of two single-grade oils, SAE 5W and SAE 30, with a multi-grade oil, SAE 5W 30.

The multi-grade oil has high temperature viscosity comparable to the SAE 30 oil while maintaining the viscosity-temperature relationship of the SAE 5W oil.

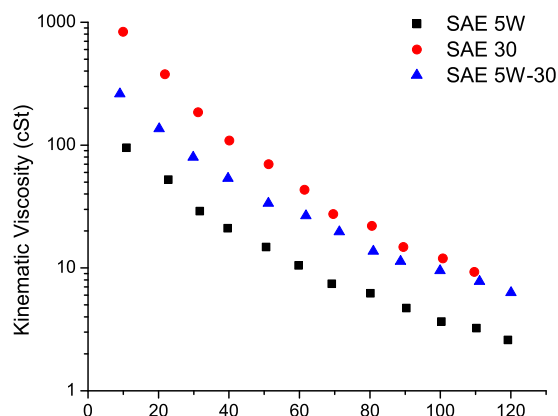


Figure 1: Comparison of two single-grade oils, SAE 5W and SAE 30, with a VM-containing multi-grade fluid, SAE 5W-30. Data obtained from Ref. [1].

Although all VMs are used to change the viscosity-temperature relationship of the oil, there are many different types of VMs that serve somewhat different purposes and perform their function through a variety of mechanisms. VM chemistries include polyalkyl methacrylate (PAMA), olefin copolymer (OCP), polyisobutylene (PIB), and hydrogenated styrene-diene (HSD), with molecular weights typically larger than 10,000 g/mol. All of these polymers will increase viscosity relative to the base oil, but depending on their composition, can have varying effects on the rate of change of viscosity with temperature for the same backbone length. Generally, there are two categories of VMs, thickeners and viscosity index improvers. A viscosity index improver will have a larger effect on solution viscosity at high temperatures than at low temperatures, thereby increasing the Viscosity Index (VI) [2], which is the most commonly used measure of the rate of change of viscosity with temperature. A thickener will increase the viscosity of the solution, but not necessarily increase the VI. The effect of VMs on solution viscosity is typically measured at reference temperatures of 40 and 100°C, although their effect at other temperatures is often relevant, depending on the application.

The mechanisms by which VMs perform their function also depend on chemistry,

both of the VM and the base oil. The most commonly-cited mechanism of VM function is coil expansion, where the polymer coil expands with temperature such that it has a larger effect on viscosity at higher temperatures. However, at this point, it is known that VM polymers do not expand equally, and for some chemistries additional mechanisms are believed to contribute. Understanding these mechanisms is an active field of study and is extremely important to enabling the development of new VM chemistries. Such developments will be needed to enable current trends in lubricated component design and lubrication engineering, e.g., use of ultra-low viscosity engine oils for improved fuel efficiency.

This review paper provides an overview of VMs that should be accessible to a tribologist who has heard some of the terminology but is not an expert, while also providing a robust summary of the topic for detailed study. The review will start with a description of the function of VMs in solution, including the three properties by which their performance is evaluated: thickening efficiency, viscosity-temperature relationship, and shear stability. The metrics used to quantify these properties are presented along with general trends related to the effects of polymer molecular weight and concentration. Then, the most common VM chemistries are described, including their basic synthesis, properties, and typical applications. The effect of chemistry on performance metrics is discussed. Next, the mechanisms by which VMs are believed to change the viscosity of a solution are reviewed. Finally, the use of polymer VMs as multi-functional additives that impart benefits beyond rheological control is discussed. Throughout the review, we will attempt to clarify concepts about VM function and explicitly define VM terminology. We will also highlight the critically important connections between polymer chemistry, mechanisms by which VM polymers influence viscosity, and the behavior of VMs in practical applications.

2 VM Function

The three key features of VM function are thickening efficiency, the viscosity-temperature relationship and shear stability (although some VMs can provide other benefits, as dis-

cussed in Sect. 5). No current VM polymer is able to deliver optimum performance in all three areas, so the choice of VM depends on which properties are most important for a given application. Thickening efficiency describes the amount of polymer that has to be used in a given lubricant formulation and is quantified as the polymer treat rate required to reach a desired viscosity. Here we use the definition of thickening efficiency as the polymer treat rate to achieve a given kinematic viscosity at 100°C [3]. Polymers are expensive relative to base oil, so it is desirable to use as little polymer as possible, i.e. to maximize thickening efficiency [1]. The second key feature of VMs is to change the viscosity-temperature relationship of the solution, as illustrated in Fig. 1. There are multiple ways to quantify this change, as well as theories to correlate it to properties of the VM polymers. Lastly, the shear stability of a VM should be considered. Shear stability is a measure of a solution’s resistance to temporary or permanent viscosity loss at high shear rates. In the following subsections, the viscosity-temperature relationship and shear stability are discussed in terms of how these properties are measured and quantified, and general trends with respect to polymer molecular weight and concentration.

2.1 Viscosity-Temperature Relationship

The most commonly used metric for quantifying the viscosity-temperature relationship of a solution is VI, defined by ASTM D2270 [2] as:

$$VI = 100 \frac{(L - U)}{(L - H)} \quad (1)$$

where U is the kinematic viscosity of the test oil at 40°C, and L and H are the viscosities of reference oils at 40°C with VIs of 0 and 100, respectively, having the same viscosity as the test oil at 100°C. In general, larger VI means a smaller decrease of viscosity with temperature. However, there are a number of limitations associated with the definition of VI [4]. One example is “VI droop,” which describes the observation that the lowest viscosity oils often have a lower VI than the higher viscosity products within a given base oil family [5]. There are also issues with calculating the VI of oils with very low viscosities

for which there are no available reference fluids to calculate the parameters in Eq. 1. To address these limitations, alternative metrics have been proposed, including the dynamic viscosity index (DVI) and the proportional viscosity index (PVI) [4], but they have not been widely adopted.

Another parameter used to quantify the viscosity-temperature relationship is the Q factor, which is defined as:

$$Q = \frac{\eta_{sp}(100^{\circ}\text{C})}{\eta_{sp}(40^{\circ}\text{C})} \quad (2)$$

$$\eta_{sp} = \frac{\eta - \eta_0}{\eta_0} \quad (3)$$

where η_{sp} is the specific viscosity, η is the viscosity of the solution, and η_0 is the viscosity of the solvent. This factor is used primarily to differentiate between thickeners and VI improvers. Specifically, $0 < Q \leq 1$ indicates the thickening power of the VM is less significant at high temperature, so the VM is a thickener, while $Q > 1$ indicates the thickening power of the VM is much more prominent at higher temperatures, as expected for a VI improver [6, 7]. Although both larger Q factor and larger VI indicate a better viscosity-temperature relationship, it has been found that there is no direct correlation between Q and VI in most cases [8].

The effect of VMs on the temperature-viscosity relationship of a solution is dependent on many different factors, including the chemistry, molecular weight, and concentration of the polymer. In general, increasing both polymer concentration and molecular weight will result in a better viscosity-temperature relationship. A polymer's contribution to the viscosity of a solution is quantified by intrinsic viscosity, $[\eta]$. This parameter is related to molecular weight by the Mark-Houwink equation:

$$[\eta] = KM^a \quad (4)$$

where M is the viscosity average molecular weight, often approximated by the weight average molecular weight, and K and a are constants that depend on the polymer and solvent. The constant a is typically between 0.5 and 0.8 for flexible random coils in a

good solvent [9]. The effect of concentration on the intrinsic viscosity is described by the Huggins and Kramer equations, Eqs. 5 and 6, respectively.

$$\frac{\eta_{sp}}{c} = [\eta] + k'[\eta]^2 c \quad (5)$$

$$\frac{\ln(\eta_r)}{c} = [\eta] - k''[\eta]^2 c \quad (6)$$

In these expressions, $\eta_r = \eta/\eta_0$ is the reduced viscosity, c is concentration, and k' and k'' are constants. These equations imply a monotonic increase of solution viscosity with molecular weight and concentration, as is typically observed for VMs [10–12].

The constants in the equations above depend on the chemistry of the polymer and solvent and have been reported for many VM polymers [13]. However, the theory does not account for all possible mechanisms of thickening (see Sect. 4) and so may not be useful as a predictive tool in some cases. For example, the effect of concentration is complicated by the fact that increasing concentration might, in some cases, lead to a change in the thickening mechanism from that of individual polymer molecules to the collective action of multiple associated polymers [14]. The effect of molecular weight depends on chemistry as well since it has been shown that the relevant weight is that of the polymer backbone, as opposed to the overall molecular weight of the polymer [15]. Therefore, although molecular weight and concentration will increase viscosity in general, the specific viscosity-temperature relationship expected for a given polymer depends on chemistry, as discussed in Sect. 3.

2.2 Shear Stability

VM polymers experience high shear rates in some components that can result in a temporary or permanent decrease in viscosity, often called shear thinning. A polymer solution's resistance to thinning is referred to as its shear stability. Temporary viscosity loss is caused by shear-induced configurational changes in the polymers. In this case, when the shear rates are decreased, the viscosity of the fluid returns to its original value. Permanent viscosity loss is due to scission of the polymer chains during shear and is a non-reversible

process. A schematic illustration of the concepts of permanent and temporary viscosity loss is shown in Fig. 2.

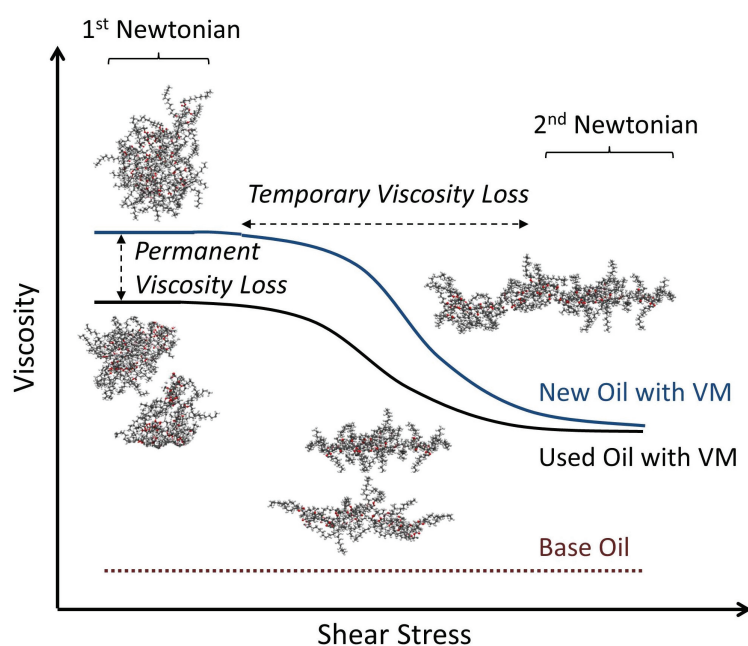


Figure 2: Illustration of temporary and permanent viscosity loss where the insets show the corresponding elongation and scission of a model PAMA molecule from an atomistic simulation. Figure adapted from Ref. [16].

Permanent viscosity loss is due to scission of polymer chains. This is often due to the chains being subject to high shear stresses, but can also be the result of elongation or stretching induced by the geometry of the flow. Chain scission is typically observed at strain rates above approximately 10^6 1/s for engine oil VMs [16]. It should be noted that, although viscosity loss is often reported as a function of shear rate, it is known to be actually determined by the shear stress, as opposed to shear strain rate [17]. Gel permeation chromatography (GPC) data showed that chain scission occurred near the middle of linear polymer chains [14]. Therefore, permanent viscosity loss is also a self-limiting process, because once the polymers are broken down to sufficiently low molecular weight products, there will be no or little further degradation. As a result, viscosity loss is typically characterized by a rapid initial decrease as the bigger molecules break, followed by a slower loss and finally a plateau as the critical molecular weight is reached [15].

The ability of a polymer solution to withstand permanent viscosity loss may be quan-

tified by two parameters: permanent viscosity loss (PVL) and permanent shear stability index (PSSI). The first parameter is a measure of the decrease in viscosity of the polymer solution due to shear:

$$\text{PVL} = \frac{KV_{\text{fresh}} - KV_{\text{sheared}}}{KV_{\text{fresh}}} \quad (7)$$

where KV is the kinematic viscosity at 100°C of the solution before (fresh) and after (sheared) shear. The permanent shear stability index describes the decrease in the polymer's thickening effect:

$$\text{PSSI} = \frac{KV_{\text{fresh}} - KV_{\text{sheared}}}{KV_{\text{fresh}} - KV_{\text{base}}} \quad (8)$$

where KV_{base} is the kinetic viscosity of the base oil at 100°C. A recent study suggested that PSSI may be a better way to describe permanent viscosity loss because it could, under some conditions, be related theoretically to polymer concentration and molecular weight [18].

There are several different bench or rig tests that can be used to measure permanent viscosity loss. First, in the ASTM D7109 Standard Test Method for Shear Stability of Polymer Containing Fluids Using a European Diesel Injector Apparatus at 30 and 90 Cycles, the polymer-containing fluid is passed through a diesel injector nozzle at high pressure that causes the polymer molecules to degrade [19]. This test is often also called the Kurt Orbahn Test. Second, the fluid is degraded by exposure to sonic shear in the ASTM D2603 Standard Test Method for Sonic Shear Stability of Polymer-Containing Oils [20]. Lastly, the Society of Automotive Engineers gear lubricant shear stability requirements are based on the CEC L45-A-99 method, also called the KRL Tapered Roller Bearing Test [21]. Of these three, the KRL test is the most severe, followed by the sonic shear test and then the fuel injector test [22]. In general, reported shear stability will vary based on which method is used to measure it [23], so understanding the conditions of each test is important.

Solution viscosity can also be affected by temporary viscosity loss. Depending on the mechanism of thickening, temporary shear thinning can occur through alignment of polymer chains with the flow direction or, in the case of associative thickening (discussed

in Sect. 4.2), through the disruption of micelles due to high shear. Either of these limit the polymers' ability to resist shear and in turn decreases viscosity. At low shear stress, this effect is small and fluids exhibit Newtonian behavior. Also, at very high shear stress, when the polymers are maximally aligned, the viscosity no longer decreases with increasing shear stress, and a second Newtonian is observed. At intermediate shear stresses, the viscosity decreases with increasing shear. The decrease in viscosity typically occurs above approximately 10^4 1/s for engine oil VMs [16]. This process, illustrated in Fig. 2, is reversible such that the viscosity returns to its original value when the shear rate is decreased.

Temporary viscosity loss of fluids is typically measured in high-temperature / high-shear viscometers (HTHS) and viscosities measured at 150°C using that technique are typically called HTHS viscosities [15]. Such measurements are often performed using a tapered bearing simulator or high pressure capillary viscometer. Recently, researchers have used a ultrahigh shear rate viscometer (USV) to characterize both temporary and permanent viscosity loss. This instrument has the advantage of well-defined, controllable high shear conditions [18]. Single measurements with the USV have a very short shear duration and so enable characterization of temporary viscosity loss, while repeated measurements capture the effects of permanent viscosity loss [16].

Temporary viscosity loss can be quantified as the Temporary Viscosity Loss (TVL) or Temporary Shear Stability Index (TSSI), which have the same form as Eqs. 7 and 8, except the fresh and sheared oil viscosity terms are replaced by low and high shear viscosities, respectively [15]. There are also rheology models that describe shear thinning behavior, as well as the effects of pressure and temperature on viscosity [24]. However, it should be noted that high pressure viscosity cannot be measured using the instruments described in the previous paragraph; instead, a high-pressure Couette rheometer or high-pressure falling-body viscometer may be used. The former allows viscosity to be measured at a range of shear rates at moderate pressures (typically up to 450 MPa) while the latter enables much higher pressures (up to 1.4 GPa) without shear [25]. Viscosity data over a wide range of temperatures, pressures and shear rates obtained using these instruments

can be described by some rheological models. One accurate model is a modified version of the Yasutomi equation [26], which has been shown to be able to accurately capture the viscosities of OCP, PAMA and HSD VM solutions over a range of pressures (up to 800 MPa) and temperatures (40 to 100°C) [27]. While typically VMs are chosen based on their response to temperature and shear, the effect of a polymer on the pressure-dependence of a fluid cannot be neglected since this property may affect load carrying capacity and viscous friction in lubricated contacts.

In general, a significant factor in determining a polymer's resistance to both permanent and temporary viscosity loss is molecular weight, where lower molecular weight polymers are, in general, more shear stable. However, it should be noted that, although most trends are reported in terms of molecular weight, the length of the polymer backbone is actually more important in determining polymer scission than molecular weight [15, 16]. This suggests that smaller polymers maximize shear stability. Unfortunately, while lower molecular weight (shorter backbone) polymers are more shear stable, they typically also have less thickening power, which presents a challenge when trying to maximize thickening while minimizing permanent viscosity loss [28]. In addition, polymer architecture plays an important role in determining shear stability, and this will be discussed in the context of specific VM chemistries in Sect. 3. Overall, many of the same factors affect permanent and temporary viscosity loss, but no direct correlation has been found between the two types of shear stability for different polymers in journal bearing tests [29, 30].

3 Chemistry

A wide variety of polymers have been explored as viscosity modifiers. The most common commercially used chemistries include PAMA, OCP, PIB, and HSD, as illustrated in Fig. 3. In general, hydrocarbon polymers such as OCP, PIB, and HSD are known to exhibit high thickening efficiency, while esters such as PAMAs provide better viscosity-temperature relationship [3]. However, the overall function of these polymers depends on both their chemistry and architecture. In this section, we will discuss several aspects of these chemistries, such as composition, general synthesis techniques, properties of the

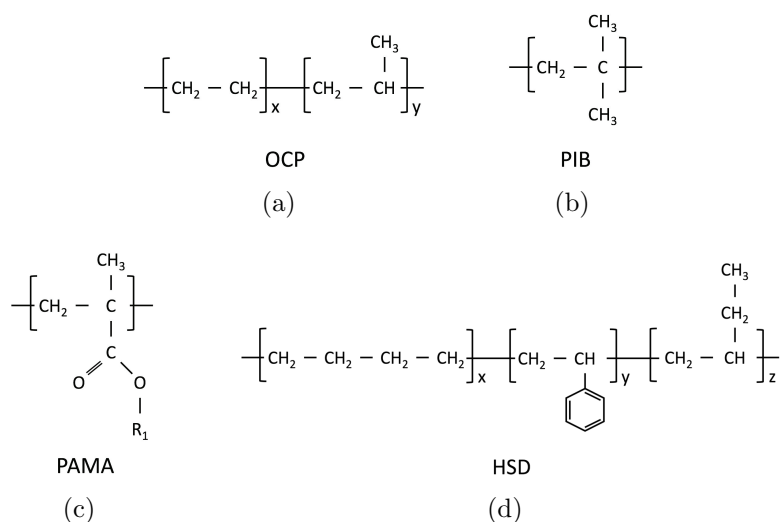


Figure 3: Chemical structures of some commonly used VMs.

polymer, and commercial applications of the VMs. A detailed discussion of synthesis methods is not included.

3.1 Olefin Copolymers

OCP VMs are primarily made of ethylene and propylene monomer units and synthesized via Ziegler-Natta vanadium-based [31] or metallocene catalysis [32, 33]. Variations in OCP chemistry are also commercially available, i.e. ethylene-propylene-diene monomer (EPDM) that include additional diene monomers. The ratio of ethylene-propylene monomers is important as it impacts the properties of the polymer. High ethylene content provides superior thickening efficiency. However polymers with high ethylene content are susceptible to crystallization at low temperatures, which result in poor solubility [10, 15]. Additionally, at low temperatures, the ethylene groups can interact with waxes in mineral oils and adversely effect low temperature flow [34, 35]. A high propylene content, on the other hand, decreases oxidative stability [15, 34]. Due to these characteristics, the ethylene-propylene ratio in OCPs is a compromise between thickening efficiency and low temperature solubility [10, 15, 34]. The thickening efficiency of OCPs is also sensitive to the distribution of monomers in the polymer chain [1, 34]. Large sections of ethylene blocks result in microcrystalline regions that have undesir-

able low-temperature properties. To maximize thickening efficiency and minimize low temperature solubility issues, OCPs are prepared using methods that capitalize on the random distribution of monomer units [15]. Tapered compositions (copolymer with A-A/B-B composition, where A represents a block of monomer “A”, B represents a block of monomer “B”, and A/B represents the segment containing both “A” and “B” monomers) have also been explored and resulted in improved thickening power [36, 37]. The effectiveness of OCPs as VMs can be increased by increasing the molecular weight of the polymer or concentration of the polymer in solution [10, 35, 38]. However, increasing the molecular weight results in long linear chains that have poor shear stability [35]. Overall, OCPs are good cost effective VMs that are used in applications such as gasoline and diesel engines. Unfortunately, poor low temperature solubility and shear stability exclude their use from most other types of lubricants.

3.2 Polyalkyl Methacrylate

PAMA is traditionally synthesized through free radical polymerization of alkyl methacrylate monomers. Commercial PAMA VMs have also been successfully synthesized through living free radical polymerization from alkyl methacrylate monomers to form block and star-shaped structures [39, 40]. Alkyl methacrylate monomers are available in different alkyl group chain lengths and result in polymers with diverse physical and chemical properties. For example, polymers with smaller side chains ($< C_7$) have poor solubility in oil, and solubility increases as the side chain length is increased ($> C_7$). PAMA VMs typically consist of mixtures of monomers with different side chain lengths, where the combination provides flexibility to create polymers with varying solubility, thickening efficiency, and viscosity index [35]. PAMA VMs are also available in several architectures, such as random, block, and star-shaped copolymers. PAMAs are effective VI improvers because they contribute more to viscosity at higher temperatures and minimally affect viscosity at lower temperature [35]. This property is directly influenced by the solubility of the polymer, where studies show that PAMAs are (relatively) poorly soluble in the oil at low temperatures and stay in a coiled form, therefore contributing little to viscosity.

However, as temperature is increased, the solubility of the polymer improves and the polymer expands, thus providing a larger contribution to solution viscosity [15, 41, 42]. These polymers are used in the formulation of multi-grade lubricating oils. PAMA VMs are commercially available in various compositions and molecular weights. Typically, the larger molecular weight PAMAs contribute more to VI improvement. However, high molecular weight PAMAs have poor shear stability compared to low molecular weight PAMAs [11, 35]. Overall, PAMAs have exceptional low temperature rheology, good thermal stability, chemical stability, and are soluble in refined and synthetic oils, but as with all polymers, they are still susceptible to mechanical shear [35, 38]. Compared to OCPs, PAMAs have good low temperature performance, thus prompting their extensive use in automotive engine oils, gear oils, automatic transmission fluids, hydraulic fluids, and industrial oils [38].

3.3 Hydrogenated Styrene-Diene

HSD VMs are synthesized with either butadiene or isoprene as the diene monomers [43]. Styrene-diene polymers are synthesized through anionic solution polymerization to form random, block, or star-shaped viscosity modifiers [43]. After the polymerization process, the diene monomers are hydrogenated to form HSD polymers [15]. While styrene monomers improve the thermal, oxidative, and shear stability of the polymer, the styrene blocks are oil insoluble over most of the relevant temperature range [15]. The solubility of HSD polymers is influenced by the diene blocks. For maximum solubility and thickening efficiency, a high ratio of diene monomers should be present in the polymer. However, in the case of hydrogenated styrene-butadiene (HSB) synthesized with 1,4-butadiene configuration, large blocks of hydrogenated 1,4-butadiene chains are vulnerable to crystallization at low temperature and exhibit properties similar to linear polyethylene chains [44]. To prevent this, HSB polymers usually contain butadiene monomers with both 1,4- and 1,2-configurations. Advancements in HSD VM chemistry have led to the development and commercialization of radial isoprene polymers, which have a star-shaped architecture [15, 38]. These polymers have a divinylbenzene core and polyisoprene arms [35]. Option-

ally, the arms can also be copolymerized with additional monomers [35]. Overall, radial isoprene polymers have better shear stability than other HSD polymers due to its star-shaped architecture [38]. In general, HSDs are commonly used in engine oil applications [15].

3.4 Polyisobutene

PIBs are made from a mixture of butene isomers that primarily consist of isobutylene and are synthesized through a Lewis acid-catalyzed cationic polymerization process. In the past, PIBs were widely used as synthetic base fluid in a number of applications due to properties such as clean burning, non-staining, low smoke, low toxicity, and low deposit formation [45]. They were used in applications, such as two-stroke engine oils, compressor fluids, gear oils, metal working fluids, and greases, and as a thickener [12, 45]. This was possible due to their availability in various viscosity grades. At low treat rates, the high viscosity grade PIBs were used as viscosity modifiers that provided viscosity adjustments to low-viscosity base stocks [45]. However their popularity decreased due to poor oxidative and mechanical stability [1]. Currently, PIBs are still used in two-stroke engine oils, gear oils, and hydraulic fluids [38].

3.5 Advancements in VM Chemistry

Developments in VM polymer chemistry have continued optimization of their performance, i.e., thickening efficiency, viscosity-temperature relationship, and shear stability. This includes development of polymer blends containing more than one of the chemistries described in the above sections, compositional modifications that extend VMs beyond the above-mentioned traditional chemistries, and exploration of novel polymer architectures that impart significantly improved performance compared to simple linear chains.

PAMA-OCP VM is a polymer blend used in gasoline and diesel engine oils. PAMAs and OCPs are incompatible as mixtures; however PAMA-OCP blends can be created by adding a small amount of grafted PAMA on OCP as a compatibilizer [46–48]. The PAMA-OCP blend produces a VM that imparts properties of both PAMA and OCP

molecules, where PAMA provides good VI and low temperature rheology, while OCP provides thickening efficiency [49].

Modifications to a VMs composition have also been explored [50–52]. Such studies showed that compositional modifications have the ability to not only improve thickening efficiency, but also to enhance properties such as shear, thermal, and oxidative stability. In one study, terpolymers of styrene, dodecyl methacrylate, and octadecyl methacrylate were tested as VMs [50]. The authors showed that the terpolymers had VIs comparable to methacrylate additives and better thermal and shear stability compared to conventional methacrylates. They found that the shear stability of the polymer improved with increased styrene content, however increasing the styrene content decreased viscosity and VI. It has also been shown that styrene, dodecyl methacrylate, and octadecyl methacrylate terpolymer have better thermal stability compared to other methacrylate-based terpolymers [52].

The influence of polymer architecture on rheology is also widely explored in literature [3, 28, 53–56]. Advancements in polymer architecture have moved from linear structures to branched [28, 53, 54], comb [3], and star-shaped [1, 55, 56] polymers. Studies show that these architectures provide good thickening efficiency and shear stability. References [28, 53] explored the effects of high molecular weight, highly branched polyethylene architectures on thickening efficiency and shear stability. These studies showed that hyperbranched dendrite structures improve shear stability but have poor thickening efficiency compared to linear polyethylene structures [53]. However, the thickening efficiency of high molecular weight highly branched polyethylene can be improved through cross-linking [28]. In another study, a novel polymer with comb architecture was created by combining linear polyalphaolefins and PAMA [3]. Overall, the comb polymer showed improved temperature-viscosity relationship, low temperature viscosity properties, and reduced fuel consumption [3].

Star-shaped architectures are also widely used since they are high molecular weight polymers with good thickening efficiency and shear stability. A comparison between linear and star-branched PAMA revealed that the latter provides superior thickening efficiency

than the former and that, at a given shear stability index, star-branched PAMA solutions had higher VI than solutions with linear PAMA [56]. GPC measurements suggested the improved shear stability of star polymers is attributable to the breaking of chemical bonds near the core of the star, as opposed to in the middle of a linear chain [14]. Ultimately, however, under severe degradation conditions, star polymers exhibit equivalent shear stability to linear polymers of comparable degraded molecular weight. Such architectures are most commonly found in PAMAs, but have been applied to other chemistries as well; for example, compared to linear random and block HSD, star-branched structures exhibited improved thickening efficiency and shear stability [57].

4 Mechanisms Behind Functionality

A number of mechanisms have been proposed to explain how VM polymers improve the viscosity of a solution at high temperature. The most commonly cited mechanism is coil expansion, which describes the increase of viscosity with temperature due to expansion of polymer coils [41]. This mechanism is characteristic of esters such as PAMA. Other polymers, such as HSB, are believed to increase viscosity through association/aggregation of the polymers, leading to the formation of micelles [58]. In addition, polymers may affect the viscosity of a solution through secondary mechanisms, including the formation of knots and through their effect on adjacent solvent molecules. Lastly, it should be noted that even polymers that do not exhibit any of these mechanisms can improve VI, due to the definition of that parameter (Eq. 1) [42]. Regardless, it is often beneficial to use a polymer that can provide additional thickening through one of the above mechanisms. Therefore, understanding these mechanisms is important as it may lead to the design of novel VMs with optimal performance.

4.1 Coil Expansion

Coil expansion was originally proposed in 1958 and suggested that a polymer remains in a coiled conformation at lower temperature and then expands due to increased solubility at higher temperatures resulting in higher viscosity [41]. The concept of the coil expansion

theory, in which polymer coil size increases with temperature, is illustrated in Fig. 4. A simple relationship between viscosity and polymer size is given by the Einstein equation, which is based on an approximation of polymers as equivalent hydrodynamic solid spheres:

$$V_e = \frac{[\eta]M}{2.5N} \quad (9)$$

where V_e is hydrodynamic volume and N is Avogadro's number. This expression was extended to explicitly relate viscosity to hydrodynamic radius in the Flory-Fox equation [27]:

$$R_h = \frac{1}{\sqrt{6}} \left(\frac{[\eta]M}{\phi_0} \right)^{1/3} \quad (10)$$

where R_h is the hydrodynamic radius of the polymer and $\phi_0 \approx 2.5 \times 10^{23} \text{ mol}^{-1}$ is the universal Flory constant; the other variables are the same as defined in previous sections. This model predicts a monotonic relationship between the size of the polymer and its contribution to solution viscosity. Therefore, if the size of a polymer coil increases with temperature, the polymer will have a greater effect on viscosity at high temperatures than at low temperatures; this is the ideal behavior of a VI improver.

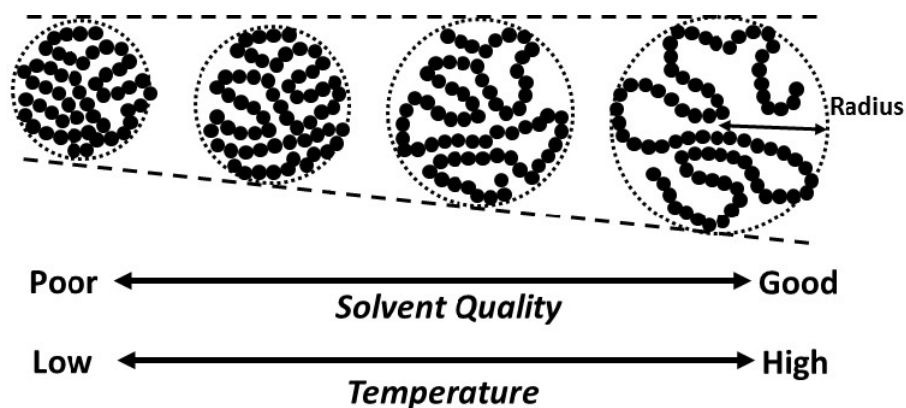


Figure 4: Illustration of the coil expansion mechanism: A VM polymer coil expands as temperature and solvent quality increases. Reproduced with permission from Covitch and Trickett [42].

The size of a polymer coil can be measured using direct experimental techniques, extracted indirectly from experimental measurements of solution viscosity, or calculated using atomistic simulations. Direct experimental techniques that have been used to char-

acterize VM polymers are dynamic light scattering (DLS) and small-angle neutron scattering (SANS). DLS is a technique where light is passed through a solution. Fluctuations in the intensity of the scattered light occur due to the Brownian motion of the macromolecules and intramolecular motion. Slower fluctuations correspond to large molecules with slower diffusion rates [59, 60]. Using the diffusion coefficient, the hydrodynamic radius, R_h , of a polymer is estimated using the Stokes-Einstein equation [61–63]. SANS uses neutron scattering to measure the size and shape of polymer conformations. The scattering of the neutron either occurs through interactions with the nucleus or unpaired electrons [64]. The scattering intensity is then used to create Guinier plots which are fit to mathematical models to measure a polymer’s radius of gyration, R_g [42, 63–66]. Coil size can also be obtained indirectly from measurements of viscosity [8, 27, 67]. Specifically, the viscosity of a solution is measured as a function of polymer concentration. The intercept of a linear fit to this data is the intrinsic viscosity (see Eqs. 5 and 6) which can then be used in Eq. 10 to calculate R_h . Recently molecular dynamics simulations (MD) have also been used to quantify the coil size of VM polymers [63, 68–70]. In MD, the exact positions of atoms are known, so R_g is calculated as the distance between each atom in a molecule and the molecule’s center of mass:

$$R_g = \sqrt{\frac{1}{M} \sum_i m_i (\mathbf{r}_i - \mathbf{r}_{cm})^2} \quad (11)$$

where M is the total mass of the molecule, i is the atom index, m_i is the mass of atom i , \mathbf{r}_i is the position of atom i , and \mathbf{r}_{cm} is the position of the center of mass of the molecule.

All of these approaches allow the coil size mechanism to be tested for different VM polymers. Such analyses have proven that not all polymers expand with temperature. For example, Fig. 5 shows a comparison between the coil sizes of PAMA and OCP as functions of temperature obtained from direct and indirect measurements [27, 42]. In both cases, only the PAMA expands with temperature. This stark contrast between the behavior of OCP and PAMA has also been demonstrated in MD simulations, which further showed that oxygen atoms in PAMA are critical to expansion behavior [68]. The

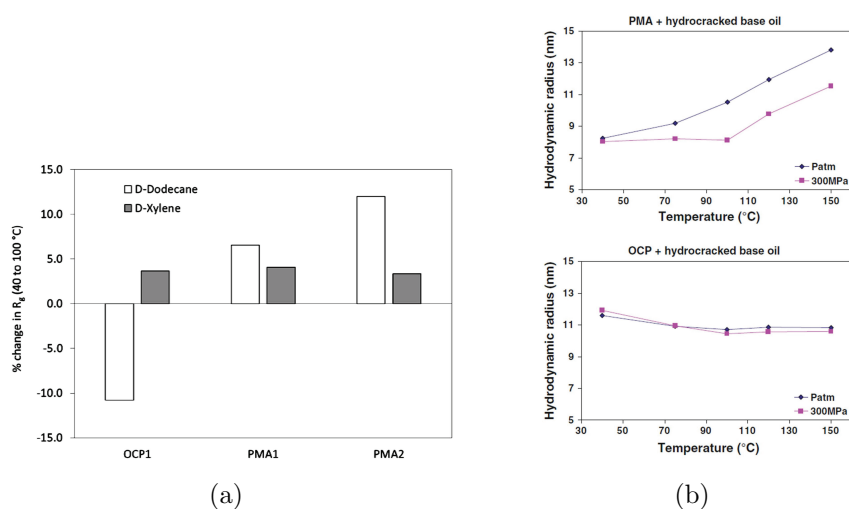


Figure 5: Change in coil size with temperature measured (a) directly using SANS (figure reproduced with permission from Covitch and Trickett [42]), and (b) indirectly using viscosity data (Figure reproduced with permission from Mary et al. [27]; Copyright 2013 by Springer), showing expansion of PAMA but not OCP

absence of coil expansion has been shown for OCP, as well as other hydrocarbon-based polymers [8, 67, 70]. Regardless, coil expansion will improve the viscosity-temperature relationship. Therefore, although coil expansion is not necessary for VMs to perform their function, it is beneficial.

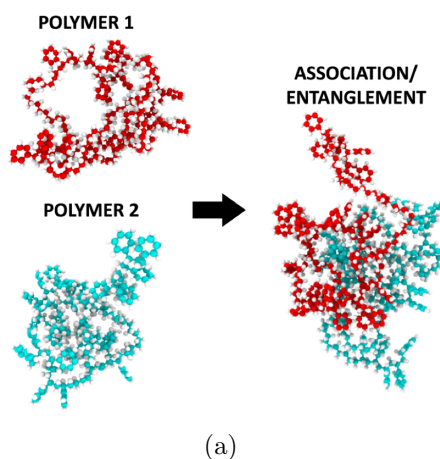


Figure 6: Schematic illustrating the concept of polymer association or entanglement.

4.2 Association and Entanglement

Another means by which VMs may increase the viscosity of a solution is through the interaction of multiple polymer chains, as illustrated schematically in Fig. 6. This mechanism can be referred to as association, aggregation, entanglement or micelle formation. There are subtle differences between the meaning of these terms, for example, entanglement is the inter-penetration of polymer chains [71] while association is the formation of transient cross-links between polymer chains [72]. However, they are used somewhat generically in the VM literature to indicate an increase in viscosity through the collective action of multiple polymers [1, 14, 15, 28, 53, 73, 74]. Polymers that act via this mechanism are sometimes referred to as “associative thickeners” [15].

In general, solution viscosity is expected to increase with polymer concentration. However, the rate of that increase depends on whether the polymers are acting as individual chains or as aggregates of multiple chains, which depends on concentration. Polymer solutions can be classified as dilute or semi-dilute, where the transition between the two is called the critical concentration, C^* [75]. The parameters of Eqs. 5 and 6 will be different for solutions below and above the critical concentration, such that the rate of increase of viscosity with concentration is larger for concentrations above C^* . The critical concentration of a polymer can be approximated from measurements of solution viscosity as a function of concentration [76] or calculated from the polymer’s molecular weight and measured/estimated radius of gyration [27]. Critical concentrations are dependent on polymer molecular weight, solvent type and temperature.

In addition to concentration, the occurrence of associative thickening is dependent on polymer chemistry. Specifically, association will be more significant for molecules containing attractive groups, such as charged polymers, block copolymers in some solvents, and polymers with hydrogen bonding [77–80]. The VM polymer for which the associative thickening mechanism is most often cited is HSD, which is a block copolymer that forms micelles due to the different solubilities of the blocks to the solvent [58]. The polystyrene blocks are oil insoluble over most of the relevant range of engine operating temperatures

[15], so the molecules orient themselves such that the central core consists of immiscible styrene blocks surrounded by soluble diene blocks, leading to the formation of a micelle structure [73, 74].

The aggregation of polymers can be detected indirectly from measurements of the distribution of polymer molecular weights, using techniques such as those discussed in the previous subsection. For example, two distinct peaks in the molecular weight distribution of HSD in n-heptane measured by DLS indicated the presence of multi-polymer aggregates as well as isolated polymers [74, 76]. Molecular-scale simulations offer another way to study the interactions between polymers in solution. In model-based studies, association or entanglement has been calculated from the number and duration of “contacts” between adjacent polymers [70, 81, 82]. In general, the topic of polymer association and entanglement is a robust and well-studied topic within polymer physics (see, for example, [83–88]). However, few such studies are specifically focused on VMs and it is more typical to infer an association mechanism based on observed thickening behavior.

4.3 Other Thickening Mechanisms

Although the two mechanisms discussed in the previous sections, i.e. coil expansion and association/entanglement, are the most commonly cited in the VM literature, there are other ways in which polymers may affect the viscosity of a solution. First, it has been proposed that polymers can “self-entangle” to create knots. These knots then restrict the polymer’s ability to uncoil when subject to shear, thereby increasing viscosity [89]. There is no direct experimental evidence of the effect of polymer knots on solution rheology, and this has not been specifically cited as a mechanism for VMs. However, a recent simulation study characterized a similar phenomenon, self-association, by counting the number of atom pairs in contact within individual HSB polymers [69], which suggests that this mechanism may contribute to overall thickening in some cases.

All thickening mechanisms discussed so far have been focused on viscosity increase due to behaviors exhibited by the polymers themselves. However, it has also been proposed that polymers can increase viscosity indirectly through their effect on nearby solvent

molecules. Specifically, the polymer causes a disturbance to the velocity field through the forces it exerts on the solvent, which increases viscosity [89–91]. Like self-entanglement, this mechanism is difficult to measure experimentally, but simulations have provided some support. Specifically, a recent modeling study showed that solvent molecules close to a PIB polymer may be less aligned with the flow direction than the solvent molecules further away from the PIB [70].

It is unlikely that these other mechanisms play a major role in VM thickening, particularly in cases where coil expansion or association/entanglement are present. However, for polymers that do not exhibit expansion or association, secondary thickening mechanisms may be important, which suggests that they could be leveraged in future VM designs to further improve performance.

5 VMs as Multi-Functional Additives

Although VMs are used in lubricant formulations primarily to improve the high temperature viscosity of the solution, they have also been shown to provide additional benefits as friction modifiers, pour point depressants, and dispersants. VM polymers that perform one or more of these additional functions are known as multi-functional viscosity modifiers.

One commonly studied secondary role of VMs is their ability to reduce friction and/or wear, i.e., to act as friction modifiers [92]. The beneficial effect of VMs in boundary lubrication was observed in early studies as larger than expected decreases in friction and wear with VM solutions that was not associated with an increase in viscosity [93, 94]. Since then, this behavior has been shown to be due to the formation of boundary films through the physical adsorption of the polymers on polar surfaces [95]. The films consist of dense, viscous layers of polymers whose thickness can be correlated to the polymer's characteristic coil size [96]. The viscous polymer layer at the contact inlet leads to a thicker film in boundary lubrication and, in turn, reduced friction [97].

Improved tribological behavior in boundary lubrication has been observed for multiple VM chemistries, including OCP, PIB and PAMA, but many of the studies have focused

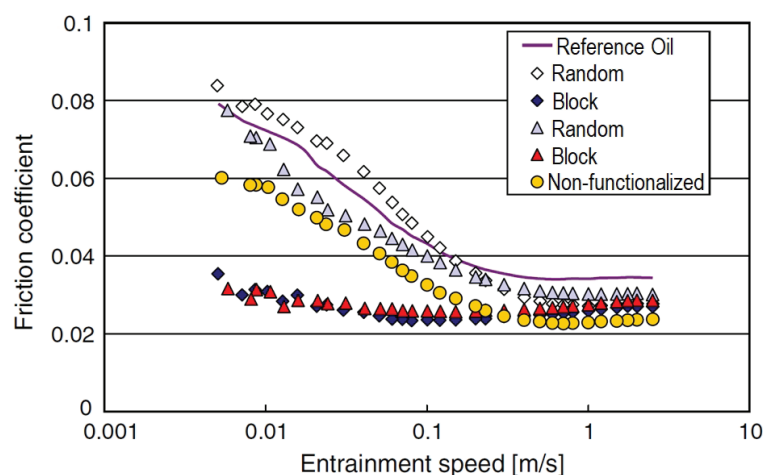


Figure 7: Comparison of friction reduction by VMs illustrating the beneficial effect of a block structure and functionalization (figure reproduced with permission from Fan et al. [98], copyright 2007 by Springer). Legend adapted from the the original paper for clarity.

on PAMA because its versatile architecture enables investigation of the effects of specific features. Such studies have shown that structure, functionalization and molecular weight are key factors in determining the effectiveness of a VM boundary layer. Examples of the effects of block structure and functionalization on friction are shown in Fig. 7 [98]. Three guidelines for polymer friction modifiers were proposed in Ref. [95]: functional groups must be present to enable the polymer to adsorb on polar metal surfaces, block structures are preferred over functional groups statistically distributed over the polymer, and medium to high molecular weight polymers will form the thickest boundary films. However, low molecular weight polymers have also been shown to be beneficial in boundary lubrication [99, 100]. It has also been shown that VMs can influence the thickness of a boundary film formed by traditional additives, such as zinc dialkyldithiophosphate (ZDDP) [101]. However, while VMs typically complement the function of other additives, they can also adversely affect the performance of some dispersants or corrosion inhibitors, possibly because these additives compete for surface adsorption sites [102]. Current ongoing research is focused on the design of novel VMs that can either complement or potentially replace traditional friction modifiers in lubricant formulations [99, 103].

Another secondary function of VMs is as a pour point depressant. The pour point is the lowest temperature at which an oil will pour when cooled under defined conditions

[104] and pour point depressants (PPDs) decrease this temperature by interfering with the growth of wax crystals. Polyacrylates and polymethacrylates are some commonly used PPD chemistries, among others. By incorporating specific monomers into PAMA chemistries, PAMA VMs can also act as pour point depressants, so they both increase the VI and decrease the pour point [11, 105–108]. This is achieved by formulating PAMA VMs that contain long alkyl group monomers (C_{14} or higher). The long alkyl chains will co-crystallize with the wax and avoid association of the wax particles, therefore keeping the oil fluid [38]. Multi-functional PAMA VMs are different from traditional polymethacrylate PPDs in that PPDs typically contain short backbones with long side chains, while VMs consist of long backbones with short side chains (relative to PPDs). Note that, although these PAMA VMs have PPD activity, a secondary PPD is often added to the lubricant formulation to more effectively treat the particular formulation.

VMs can also function as dispersants [109–115]. Dispersants are used to disperse or suspend deposit-forming contaminants such as soot and sludge which cause issues including increased viscosity, abrasive wear, and plugging of filters. Traditionally, dispersants have a polar head group and non-polar tail group, where the polar head group associates with polar contaminants and keeps them suspended in the oil, while the tail group creates a barrier that separates small groups of contaminants from forming larger aggregates [116]. Dispersant VMs are created by incorporating polar functional groups, such as amines, alcohols, or amides, onto the backbone of VM polymers. This enables the polymer to function as both viscosity modifier and dispersant. Lastly, studies have shown that dispersant VMs can be functionalized further to provide antioxidant and anti-wear properties [110, 117, 118], thus making them truly multi-functional additives.

6 Summary and Outlook

As alluded to several times in this review, one of the challenges in the field is that the terminology is confusing or simply not used correctly. For example, it is common to hear any VM referred to as a viscosity index improver, regardless of whether it actually improves VI. Even for additives that actually increase VI, their effect is likely to be

described as increasing the viscosity of the solution more at higher temperatures than at lower temperatures. This is not necessarily true, since VI can increase even if the magnitude of the viscosity change is larger at lower temperatures, as is often the case. Consistent use of nomenclature would greatly benefit this field because it could facilitate communication between polymer chemists who have the ability to create novel VMs and the engineers who use those VMs and understand the requirements for these additives in terms of lubricant function.

Another key message of this review is that VM functionality is directly correlated to the properties of the polymers themselves, specifically their size, chemical composition and structure. These properties also determine how a VM polymer will affect the viscosity of a solution. While coil expansion is often cited as *the* mechanism for VMs, it is now well established that only some polymers, among VMs only PAMAs, are likely to actually expand with temperature. The research community may continue to explore ways to increase coil expansion with novel PAMA architectures. However, based on the understanding that other mechanisms are involved, particularly for hydrocarbon-based VMs, new breakthroughs may be possible through research focused on enhancing other thickening mechanisms.

Many studies whose goal is to optimize VMs are specifically focused on the viscosity-temperature relationship. However, as described in this review, VM function also includes thickening efficiency, shear stability and other potential benefits a VM may provide to a lubricating fluid. No current VM polymer can provide optimal function in all of these areas. Furthermore, some properties have an opposite effect on different functions, e.g. increasing backbone molecular weight improves the viscosity-temperature relationship but adversely affects shear stability. Therefore, it is important to understand the interrelated effects of polymer properties on multiple VM functions so that the best VM for a given application can be selected, or new polymers can be designed to better optimize multiple performance metrics.

The need for optimized VMs will continue to become more important as lubricants are asked to provide better performance under a wider range of operating conditions. One

trend driving this is the desire for improved fuel efficiency, which is leading to the use of ultra low-viscosity engine oils. The lighter base oils used in these formulations are more efficient at lower temperatures, but can become too thin during operation at high temperature. VMs must be available to address this issue. This goal can be achieved through clear communication within the research community using consistent nomenclature and based on a better understanding of fundamental mechanisms.

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