

Technical Note

Polymer Additives for Improvement of Viscosity Index

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The viscosity of a liquid is inversely related to the temperature. The main function of a viscosity modifier (or viscosity index improver) is to minimize the viscosity change with temperature. The dependence of viscosity on temperature polymers in oil is expressed using viscosity index (VI). The VI is calculated from the viscosity of the polymer in oil solution at two temperatures, generally 40°C and 100°C. The smaller the difference in viscosity at low and high temperatures, the higher the VI. Most paraffinic oils without a VI improver have a viscosity index of 95 to 105. Multi-grade oils are formulated within a specified viscosity range by adding polymer. Depending on the polymer chosen, the resulting oil can have a viscosity index between 105 and 300. The polymers used are generally polymers with a molecular weight of 10,000 to 150,000 daltons. Common VI improvers include olefin copolymers, polyalkylmethacrylates and styrene-butadiene copolymers. Multi-grade oils are widely used as engine oils, gear oils and transmission fluids.

It is widely accepted in the literature that increasing the temperature of polymer solutions causes the polymer molecules to expand and thicken the solution. This explanation is adequate but incomplete. The interactions at the molecular level must be considered. With increased temperature in the solid state (no oil present), the polymer molecule actually contracts. The reason for the contraction is that heat raises the energy level of the system allowing the molecule to seek a lower energy state. When the polymer is placed in oil at increased temperature, the molecules occupy a greater volume resulting in an increased viscosity.

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A simple explanation of viscosity decreasing with increasing temperature could be given by Eyring's theory of liquid viscosity based on the hole theory of liquids. Using this model and assuming a Boltzmann distribution of energy over all polymer molecules, an explanation of the temperature dependence to the viscosity arises. In its simplest form, the equation can be expressed as

$$\ln(V) = A + B/T$$

where A and B are constants and $\ln(V)$ is the natural log of viscosity.

At elevated temperatures the term B/T approaches zero and does not contribute significantly to the viscosity. However, at low temperatures the term B/T contributes significantly to the viscosity and we see an increase in viscosity.

The basis for explaining the concentration dependence of the viscosity of polymer solution is Einstein's relationship for the viscosity of dilute solutions of spherical particles (polymer coils) called the intrinsic viscosity given by η/η_0 expressed as

$$\eta/\eta_0 = 1 + 2.5\phi$$

where η is the viscosity of the solution, η_0 is the viscosity of the solvent, and ϕ is the volume fraction of polymer molecule coils.

Based on this equation, adding polymer to an oil should increase the viscosity at any temperature. It is well known in thermodynamics that increasing the temperature in the solid state or in solution without the interaction between solvent and polymer decreases the distance from end to end of the polymer coil (decrease of the coil diameter) and therefore decreases the value of ϕ . From this point of view, addition of polymer to oil (assuming no interaction) at any temperature should decrease the viscosity.

Addition of oil to a polymer results in the addition of a new interaction parameter. With the addition of oil, increasing the temperature results in an opposite effect because of the interaction (diffusion) of the oil into the space around the polymer molecules. Initially, the dissolving of polymer results in swelling of the polymer coil

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domains and then swelling of individual molecules which dominate and prevent the decrease of the molecular coil diameter.

There are two assumptions that one can make. The first is that the degree of swelling is governed by the difference in the solubility parameters of the polymer and the solvent (Flory-Huggins parameters) and the temperature.

The second is that, according to Fick's first law of diffusion, in the diffusion of oil molecules into the polymer coil, the diffusive flux is proportional to the squared velocity of the diffusing particles (oil molecules) which increases with temperature.

Combining these assumptions indicates that the swelling of polymer coils should be decreased at low temperature.

It follows that ϕ in Einstein's equations for intrinsic viscosity is higher at high temperatures than at low temperatures. It further follows that when polymer molecules are incorporated into oil both a higher viscosity and a higher VI result.

The use of a polymeric viscosity modifier in oil offsets the thinning of the base oil as the temperature is increased. The result is a relatively stable viscosity over a wide temperature range.