THE EFFECT OF MOLECULAR WEIGHT OF VISCOSITY INDEX IMPROVER ON VISCOSITY LOSSES OF MULTIGRADE CRANKCASE OILS

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Abstract

The aim of this investigation work focuses on the effect of molecular weight of polymer type- viscosity index improvers- on the permanent and temporary viscosity losses of formulating multigrade crankcase oils. To achieve this goal, four members of a family of polyalkylmethacrylate-based viscosity index improvers having different molecular weights are used to formulate the tested model oils. Permanent and temporary viscosity loss parameters are produced by measuring the viscosity of polymer-oil blend before and after mechanical degradation at low and high shear rates. Viscosity Loss Trapezoid technique is used to interpret the dependency of molecular weight of viscosity index improvers on viscosity loss parameters, which lead to certain exceptions in regard to the molecular weight distribution of polymer additives.

Keywords

Lubricating oils – shear stability - Viscosity Loss Trapezoid.

Introduction

Over the last five decades, high molecular weight polymeric materials have been used to modify the viscosity-temperature characteristics of mineral oils to make engine oils, which can operate satisfactorily over a wide range of temperatures. Polymers improve the viscometric properties by causing minimal increase in engine oil viscosity at low temperatures to improve cold starting and considerable increase at high temperatures to provide adequate lubrication at high temperatures (1,2).

When oils containing polymers are subjected to severe shear conditions such as in the engine, the random coil is severely distorted. In extreme cases, bond energies can be exceeded and the polymer will break. This can happen in a variety of areas in equipment, for example between the piston rings and cylinder wall or between the gear teeth of an axle or across the pressure relief valves of hydraulic system (3). Observations made by several workers, including Hillman et al. (4), using gel permeation chromatography (GPC) indicate that high molecular weight polymers are degraded and intermediate molecular weight polymers are produced, which are less effective thickeners, with the result that the viscosity of the oil decreases. This viscosity loss caused by polymer degradation is known as permanent viscosity loss.

All polymer solutions are non-newtonian, that is, shear stress is not directly proportional to shear rate. There are several types of non-newtonian behaviour, but viscosity index improvers, specially, at high temperatures exhibit only one; pseudoplasticity or shear thinning (5). When oil is subjected to shear stress/rate, polymer molecules are distorted. The size, shape and alignment with the field of flow of these elongated structures are such that the polymer contributes less to viscosity than does the spherical, random coil configuration that exists at low shear stress/rate. The higher the shear rates the lower the viscosity until a stable

region is reached. As long as the shear stress does not break the molecule, the process is completely reversible, i.e. when the shear stress is removed, the viscosity returns to the original value and the viscosity loss is called temporary viscosity loss (6).

Rosenberg (7) observed that there was no correlation between permanent and temporary viscosity losses when he examined a wide variety of engine oils in a journal-bearing dig. Although much work has been done on the isolated effects of permanent or temporary viscosity losses. Little work has focused on the combined permanent and temporary viscosity loss. Alexander (8) has reviewed some literature on this subject. Over the last few years, T.W. Selby (9) proposed a new technique to combine both temporary and permanent viscosity loss which, is called Viscosity Loss Trapezoid (VLT) . In the present work, this technique is used to indicate the influence of viscosity index improvers molecular weight on both permanent and temporary viscosity losses.

Viscosity Loss Trapezoid technique (VLT)

Determination of VLT requires the measurements of four viscometric values. Two of these are obtained after the tested oil has been degraded at high and low shear rates, and two before that, also at the same low and high shear rates. In the determination of a given trapezoid, all viscometric measurements are made at a chosen temperature, normally, 100 ^{0}C is a standard temperature used to determine shear stability parameters of multigdrade oils. All viscosity measurements must be made under steady state conditions for both temperature and shear rates.

The four viscosity measures of the oils used to predict the TVL are:

V_l the low shear rate viscosity of the fresh oil,

V_h the high shear rate viscosity of the fresh oil,

V_{ld} the low shear rate viscosity of oil after shearing forces degradation,

V_{hd} the high shear rate viscosity of oil after shearing forces degradation

The above viscosity measurement are used to determine the familiar viscosity loss parameters which are :

Permanent Viscosity Loss $PVL = V_l - V_{ld}$ (1)
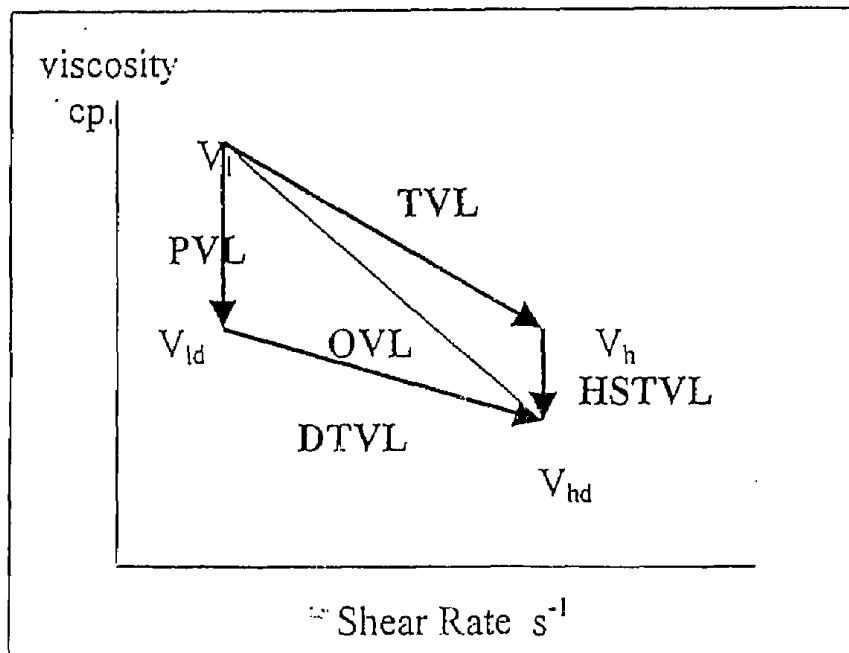
Temporary Viscosity Loss $TVL = V_l - V_h$ (2)

T.W.Selby (10, 11) introduced three relatively unfamiliar viscosity losses, they are:

High shear permanent viscosity loss HSPVL $= V_h - V_{hd}$ (3)

Degraded temporary viscosity loss DTVL $= V_{ld} - V_{hd}$ (4)

Overall viscosity loss OVL $= V_l - V_{hd}$ (5)

The following figure gives an example of VLT reflecting the above values.

It is clear that the value of OVL is equivalent to the sum of TVL and HSPVL and the sum of PVL and DTVL .

Experimental work

a- Model oils formation

Four model oils are formulated by using available four different molecular weight polyalkylmethacrylate additives as viscosity index improvers. The polymers are blended into highly refined mineral oils at a level sufficient to formulate model oils with a kinematics viscosity of approximately 14.5 cSt at 100 ^{0}C. (the value contribute formulated oils reflecting SEA 40 classification range for engine crankcase oils). Table (1) indicates the molecular weight of each polymer together with its concentration in formulated oil and the kinematics viscosity at 100 ^{0}C for base oil and polymer – oil blend.

b- Mechanical shear degradation

The all tested oils are subjected to mechanical shear degradation by using Diesel Injection Rig according to ASTM standard method (3945 – 80) . In this test method oil is subjected to a shearing process at standard cycle frequency of 30 cycles. The viscosity at low and high shear rate for all tested oils are measured before and after the degraded test at 100 ^{0}C.

c- Viscosity measurements

As noted, the viscosity of formulated oils must be measured both at low and high shear rates before and after degradation.

Rotational viscometry at low shear rate is chosen in preference to the more common and more precise kinematics (capillary) viscometry. Since

kinematics viscosity is a function of dynamic viscosity and density, it is preferable to avoid density effects among oils by using instrument capable of measuring viscosity in absolute unit (millie Pascal second) directly. Accordingly, low shear rate data is obtained, in this research work, by using Haake Rotary Viscometer at fixed shear rate 10^2s^{-1}.

At high shear rate, only rotational viscometry with constant shear rates should be used. In contrast, capillary viscometer has a widely varying shear gradient across the annular shearing zone particularly at high shear rate/stress, which distorts the viscosity loss comparison. Haake Rotary Viscometer with adjusted shear rate $4*10^4 \text{ s}^{-1}$ is used.

Results and Discussion

Tables 2 and 3 give the viscosity measurements of base and blended oils at low and high shear rates respectively. The viscosity loss trapezoid for base oil and each polymer-oil blends are established. Figures 1 to 5 collect the formed viscosity loss trapezoids. The various values of viscosity losses are determined by using the equations 1 to 5. The results are collected in table 4.

Figure 1 shows that the VLT for the highly refined base oil, used as a base stock, is a straight line – a collapsed trapezoid. Such observation indicates the high degree of precision of VLT technique when using Haake rotary viscometer and shows that there is no component of the base oil, which can be degraded or oriented. This collapsed trapezoid proof that the base oil is truly Newtonian over the tested ranges of shear rates and temperature.

Figure 2 represents VLT of the higher molecular weight polymer, M1, It is evident that this polymer gives the considerable viscosity to the base oil

at relatively low concentration. Both PVL and TVL are higher than the other polymers. OVL, which is the combination between the PVL and DTVL, shows the biggest value.

VLTs for both polymers M2 and M3, the intermediate molecular weight polymers, are summarized in the figures 3 and 4. Regarding the areas of VLTs it is clear that these areas decrease by decreasing molecular weight of polymer with a considerable reduction of all viscosity loss parameters.

VLT for the lower molecular weight tested viscosity index improvers, M4, is shown in figure 5. It is obvious that both viscosity loss values and VLT area of polymer M4 are reduced in comparison with the other tested polymers. The previous observations confirm the trend of reducing all viscosity loss values with decreasing the polymer molecular weight.

The less trapezoid area is associated with great resistance to PVL and a more horizontal configuration of the trapezoid is associated with low TVL, indicated fewer macromolecules subjected to orientation, whether by concentration or lower molecular weight. Thus, PVL is identified with a reduction in the length or complexity of a macromolecule in oil solution. The effect is shown as the breaking of the linear polymer backbone or the shearing of the long side-chain in case of non-linear viscosity index improvers. It can also be recognized that the reduction of length of the viscosity index improvers molecules by the occurrence of PVL is accompanied by a decrease in TVL as shown by the smaller value of DTVL. Considering HSPVL, degradation at high shear rate removed some of the viscosity loss by the orientation effect of degraded macromolecules.

Conclusion:

It is evident that the relationship between original and degraded molecular weight of tested polyalkylmethacrylate and viscosity loss parameters is reciprocal. The changes of molecular weight indicate the expected degree of change in the viscosity loss parameters. So it can be concluded that the viscosity loss parameter values should be capable of approximately anticipating the molecular weight distribution before and after shear degradation. VLT technique is simple and gives clear information about all-viscous influence of viscosity index improvers.

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Table 1 Molecular weight of polymer additives and Ubbelohde kin. Viscosity of oil / polymer blends

Base oil and Polymer	Molecular weight	Polymer % added to base oil	Kin. Viscosity at 100°C cSt
base oil	---	---	5.32
M1	490000	3.4	14.57
M2	133000	7.13	14.48
M3	70000	10.15	14.54
M4	45000	15.54	14.51

Table 2 Viscosity at low and high shear rates for undegraded
and degraded oil blends

Polymer Types and base oil	Low sheer viscosity of Non-degraded oil V_l (cp)	High sheer viscosity of Non-degraded oil V_h(cp)	Low sheer viscosity of Degraded oil V_{ld}(cp)	High sheer viscosity of Degraded oil V_{hd}(cp)
Base oil	4.45	4.43	4.46	4.45
M1	11.93	9.52	9.87	9.03
M2	11.92	10.55	10.95	10.19
M3	12.07	11.13	11.46	10.87
M4	12.06	11.51	11.64	11.32

Table 3 Viscosity loss parameters of formulated tested oils

Polymer Types	Permanent Viscosity Loss PVL	Temporary viscosity loss TVL	High shear permanent viscosity loss HSPVL	Degraded temporary viscosity loss DTVL	Over all viscosity loss OVL
M1	2.06	2.41	0.49	0.84	2.9
M2	0.97	1.37	0.36	0.76	1.73
M3	0.61	0.94	0.26	0.59	1.2
M4	0.42	0.55	0.19	0.32	0.74

figure 1: Viscosity Loss Trapesoid for base oil
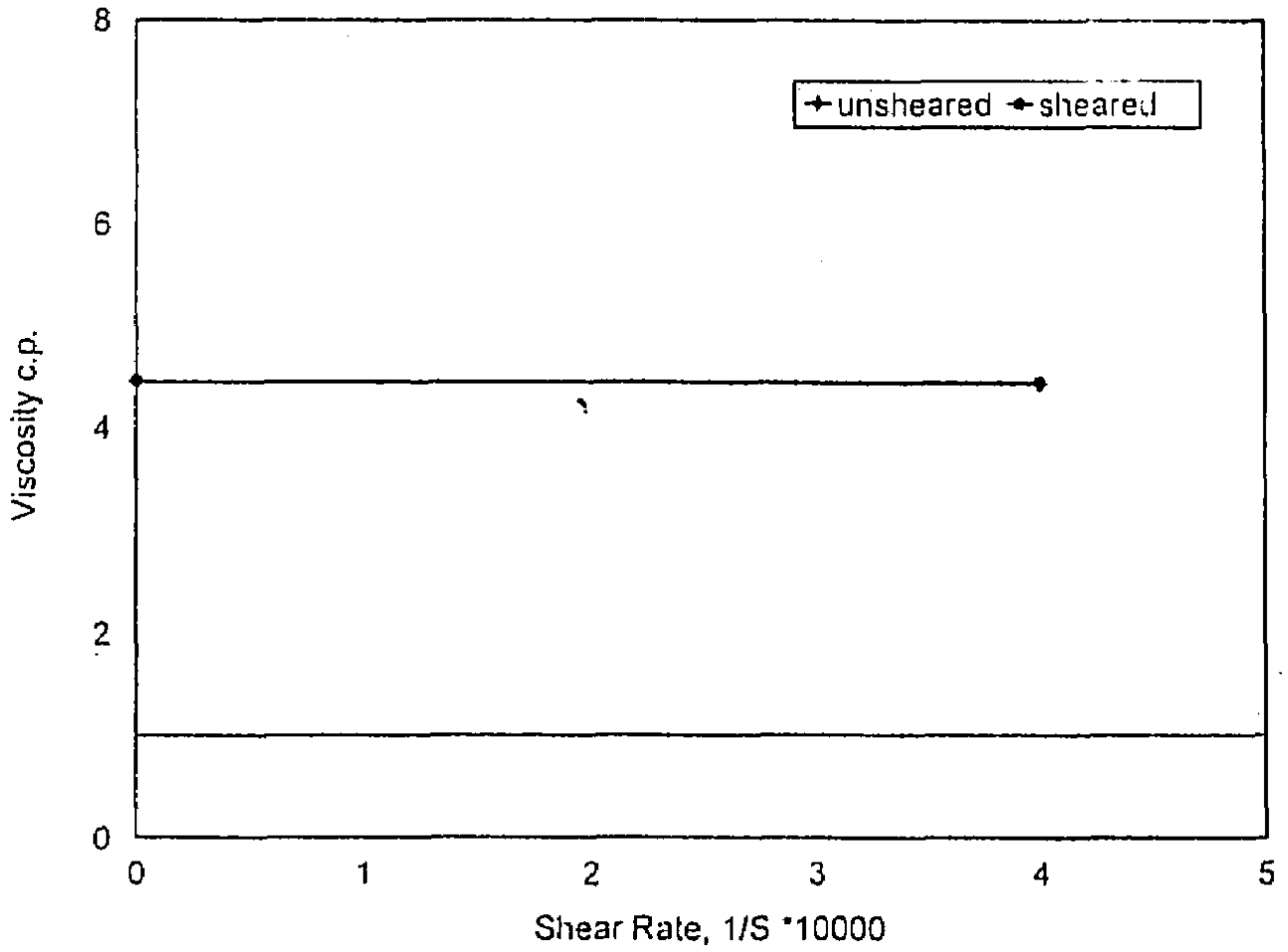
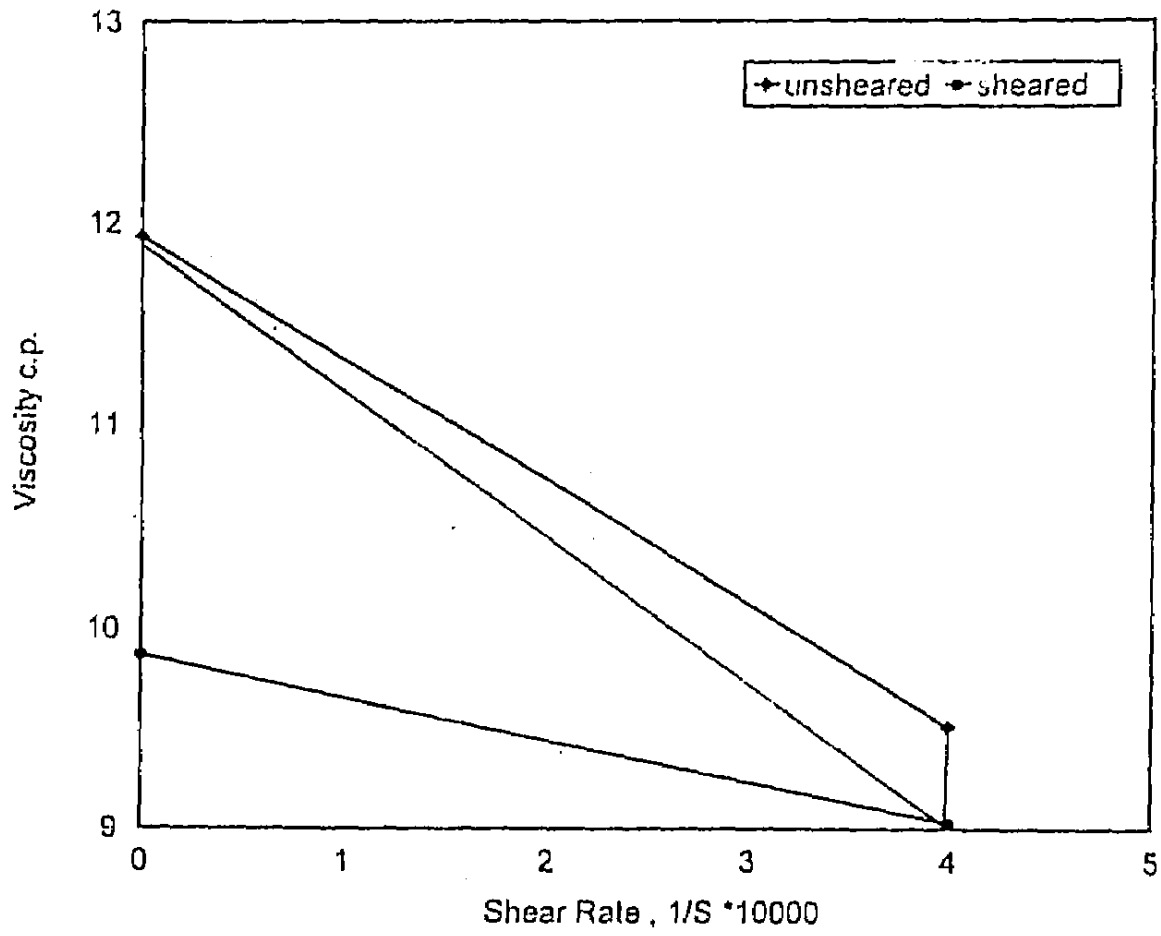figure2: Viscosity Loss Trapesoid for Polymer M1

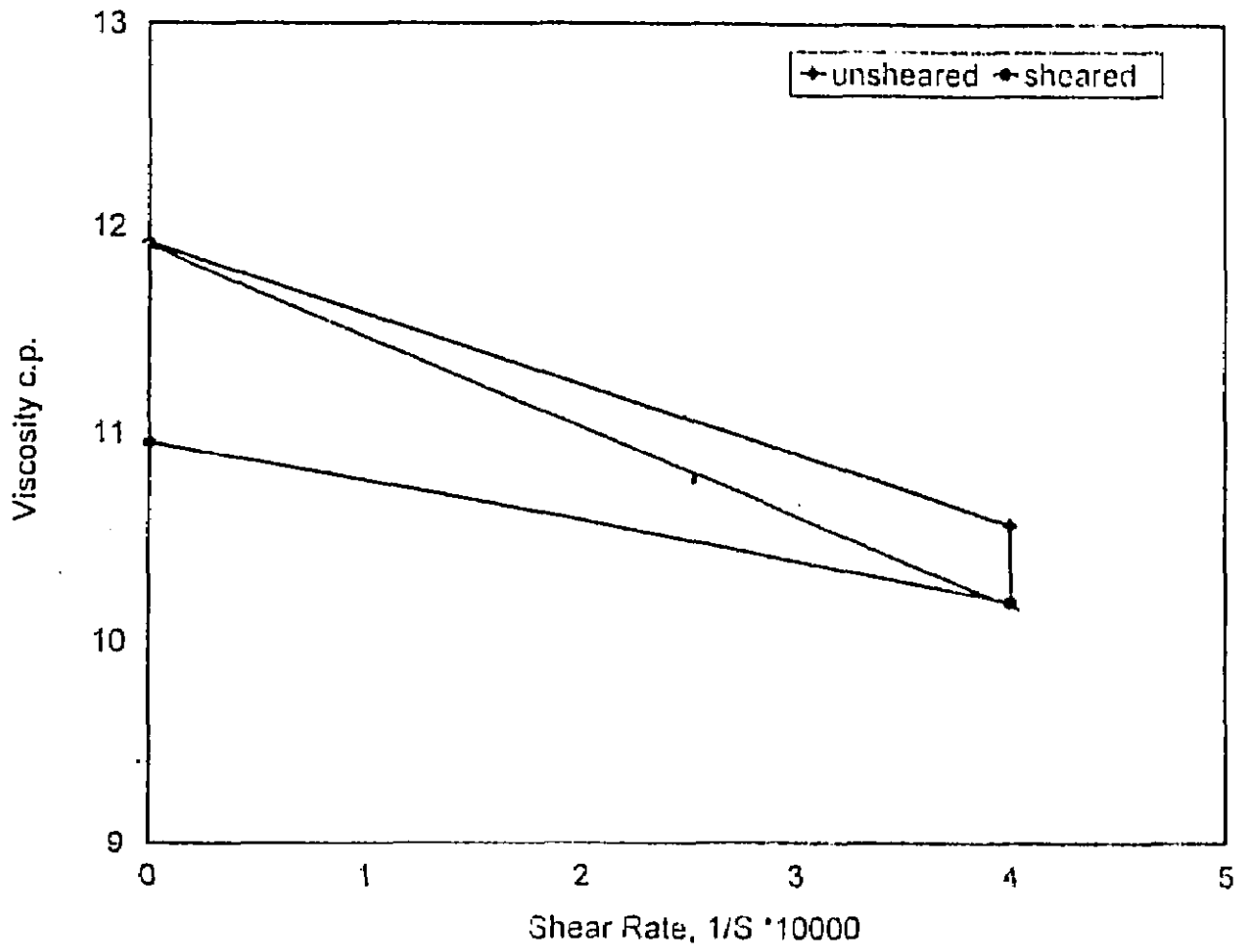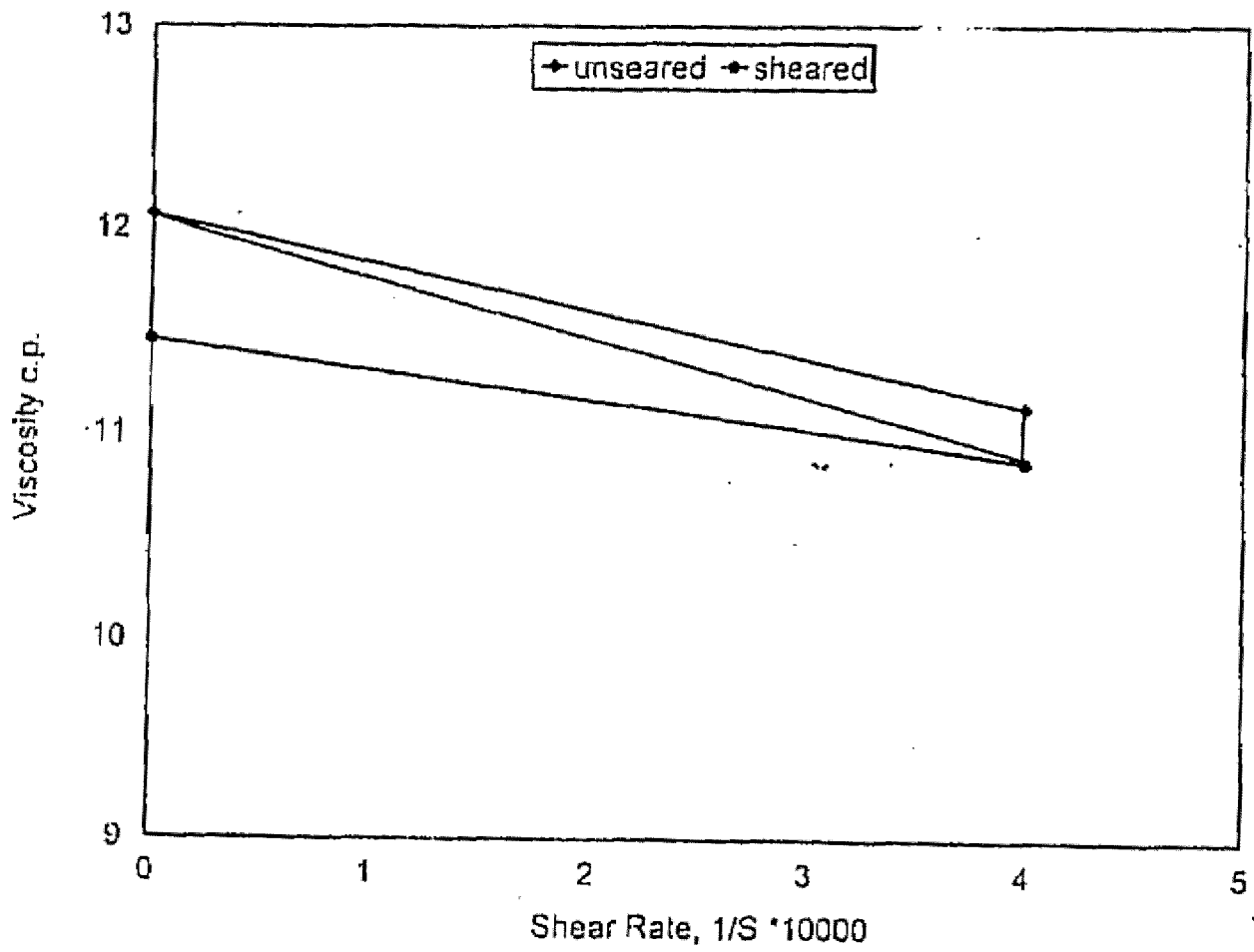figure 3: Viscosity Loss Trapesoid for Polymer M2

figure 4: Viscosity Loss Trapesoid for Polymer M3

figure 5: Viscosity Loss Trapesoid for Polymer M4