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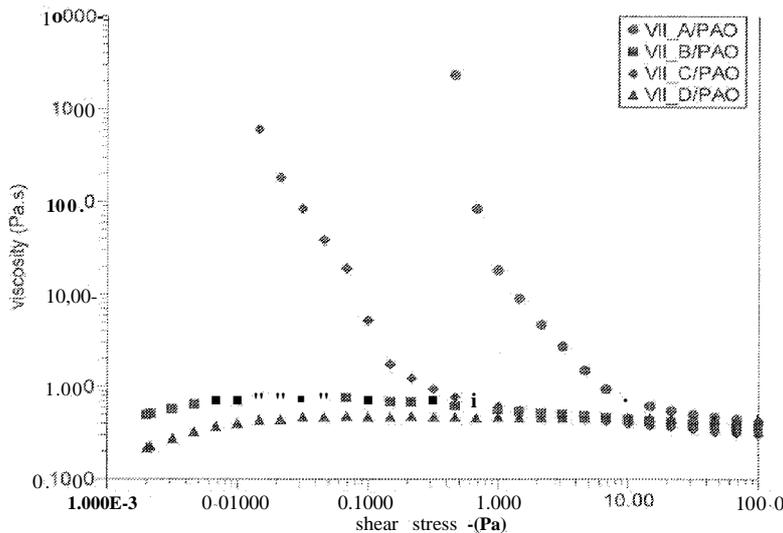

FIGURE 1

(57) **Abstract:** The present disclosure relates to a method to determine the predisposition of a polymer to form network or gel in a lubricating oil which comprises obtaining a composition of a polymer in a diluent, measuring the shear stress as a function of shear rate, determining the yield stress using the Herschel-Bulkley equation and assessing the yield stress, thereby determining the predisposition of the polymer to form a network or gel.

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RHEOLOGICAL METHODS TO DETERMINE THE PREDISPOSITION OF A POLYMER TO FORM NETWORK OR GEL

CROSS REFERENCE TO RELATED APPLICATIONS

[0001]   This application claims priority to U.S. Provisional Application No. 61/540,997 filed on September 29, 201 1, the entire contents of which is hereby incorporated by reference. This application is related to co-pending US applications Serial Number 12/761,880 and Serial Number 12/762,096 which in turn claim the priority to and the benefit from USSN 61/173,528, filed on April 28, 2009, and USSN 61/173,501, filed on April 28, 2009, and USSN 12/569,009, filed on September 29, 2009, all of which are incorporated herein by reference in their entirety. This application is also related to USSN 61/299,816, filed January 29, 2010, and USSN 61/297,621, which are herein incorporated by reference in their entirety.

TECHNICAL FIELD

[0002]   The method of the present disclosure is to screen for polymers having a tendency to form gels. The present disclosure relates to methods to determine the predisposition of a polymer to form networks or gels in diluents such as oils, especially lubricating oils. It has been found according to the present disclosure that a procedure selected from the group of yield stress test and G'/G" crossover test as modified according to this disclosure can be used to determine whether or not a polymer has a tendency to gel.

BACKGROUND OF DISCLOSURE

[0003]   Viscosity Index Improvers (VII) are polymers that influence rheological properties of the lubricating oil by, for example, interactions with components of lubricating oils (e.g., base oil, pour point depressant (PPD), dispersant or detergent inhibitor (DI) package) and/or interactions with itself (polymer-polymer). VII interactions with lubricating oil components (e.g., wax) are well characterized by tests like Mini-Rotary Viscometer (MRV) (ASTM D4684), Pour Point (ASTM D5949, D5950, or D5985), and Scanning Brookfield (ASTM D5133).

[0004]   Viscosity index improvers are typically polymeric molecules that are added to compositions such as a lubricating oil to alter viscosity response of the composition with temperature. With lubricating oils, these molecules thicken the oil at higher temperatures offsetting viscosity losses that would otherwise reduce the lubricating properties and wear protection of the oil and increase boundary friction. At low temperature, however, these polymers may form networks due to polymer entanglements or small crystals. The extent to which such networks are formed depends on the temperature, concentration, and the nature and molecular weight of the polymer. Such networks can "stiffen" the lubricating oil and reduce its flowability, form 'lumps' or 'gels,' or turn the entire solution into a 'frozen' solid (composition that can not be poured).

[0005]   Certain VII having a high amount of continuous ethylene segments dispersed in the polymer backbone can lead to gelation via polymer network formation. Olefin copolymers such as ethylene-propylene copolymers, for example, tend to stiffen due to crystallization of the ethylene segments of the polymer chain. Other, non-crystalline molecules can form gels or become frozen solid when the polymer forms stable entanglements. Certain VII containing styrene blocks also lead to network formation by polymer interactions. Both effects depend on the molecular weight of the polymer and its concentration and temperature of the solution.

[0006]   Polymer interactions are different than wax interactions in base oils and require different measurement technique(s). Methods mentioned above such as Mini-Rotary Viscometer (MRV), Pour Point, and Scanning Brookfield are not sufficiently sensitive or indicative of how polymers such as alpha-olefm copolymers would interact in lubricating oils. There is currently a need for a test that would reliably detect the predisposition of a given polymer to form gels or turn into solids when formulated into a composition.

SUMMARY OF DISCLOSURE

[0007]   One aspect of the present disclosure relates to a method to determine the predisposition of a polymer to form a network or gel in a composition such as a lubricating oil, which comprises (a) obtaining a composition of a polymer in a diluent, (b) measuring the shear stress of the composition as a function of shear rate or measuring the

shear rate of the composition as a function of shear stress, (c) determining the yield stress using the Herschel-Bulkley equation:

$$\tau = \tau_0 + k(r)^n$$
$$where, \tau = Shear\ Stress$$
$$\tau_0 = Yield\ Stress$$
$$k = consistency$$
$$\gamma = shear\ rate$$
$$and\ n = power\ law\ exponent$$

, and

(d) comparing the yield stress, thereby determining the predisposition of the polymer to form a network or gel. The Herschel-Bulkley equation is well-known in the art and explained, for example, in Bird, R. B.; Armstrong, R. C.; Hassager, O. Dynamics of Polymeric Liquids; John Wiley & Sons: New York, 1987; Vol. 1.

[0008]   Another aspect of the present disclosure relates to a method to determine the predisposition of a polymer to form a network or gel in a composition such as a lubricating oil which comprises (a) obtaining a composition of a polymer in a diluent, (b) determining at least one of (i) the storage modulus G' and loss modulus G" of the composition by subjecting the composition to sinusoidal (oscillating) stress or strain of certain amplitude and frequency, (ii) the phase lag (angle) of the response strain or stress δ, or (iii) the tangent (tan) δ, and assessing at least one of the G', G", δ, or tan(5) determined, thereby determining the predisposition of the polymer to form a network or gel, wherein δ is the phase lag angle for the composition to respond to the sinusoidal stress or strain.

[0009]   Still other objects and advantages of the present disclosure will become readily apparent by those skilled in the art from the following detailed description, wherein it is shown and described only the preferred embodiments. As will be realized, the disclosure is capable of other and different embodiments, and its several details are capable of modifications in various obvious respects, without departing from the disclosure. Accordingly, the description is to be regarded as illustrative in nature and not as restrictive.

BRIEF DESCRIPTION OF FIGURES

[0010]   **Figure 1** is a plot showing viscosity versus shear stress measurements carried out according to the present disclosure.

[0011]   **Figure 2** is a plot showing shear stress versus shear rate measurements carried out according to the present disclosure.

[0012]   **Figure 3** is a plot of a response strain or stress curve versus time (output) to an applied sinusoidal stress or strain of certain amplitude and frequency (input) as measured by oscillatory rheology carried out according to the present disclosure.

[0013]   **Figures 4** and **5** are plots of storage modulus G' and loss modulus G" versus temperature carried out according to the present disclosure.

[0014]   **Figure 6** is a plot of delta δ versus temperature measurements carried out according to the present disclosure. Tan(5) values listed in the figure are at -15°C.

[0015]   **Figure 7** is another plot showing shear stress versus shear rate measurements carried out according to the present disclosure.

PREFERRED EMBODIMENTS OF THE INVENTION

[0016]   The present disclosure provides improved rheological method(s) to characterize polymer interactions leading to gel formation in diluents, oils, and in particular lubricating oils using Steady State Flow Rheology or Oscillatory Rheology. The rheological methods according to the present disclosure can be used to design polymer having optimized properties as Viscosity Index Improvers in lubricating oils.

[0017]   The methods of the present disclosure are especially useful in evaluating copolymers of alpha-olefms, such as ethylene-propylene copolymers, and compositions thereof. For example, the methods of the disclosure can be used to evaluate polymer compositions comprising two types of ethylene copolymer. The polymer composition can have a first ethylene copolymer having relatively lower ethylene content (compared to the second ethylene copolymer) and which is a copolymer of ethylene, an alpha-olefm comonomer, and optionally an internal olefin and optionally a polyene, such as a diene. The polymer composition can have a second ethylene copolymer having relatively higher

ethylene-content copolymer (compared to the first ethylene copolymer) and which is a copolymer of ethylene, an alpha-olefm and optionally a polyene such as a diene. In one instance, the polymer composition can comprise a first ethylene copolymer, preferably at least 30 wt.%, 35 wt.%, 40 wt.%, 45 wt.%, 50 wt.%, or 5 1 wt.% of a first ethylene copolymer based on the weight of the polymeric composition, and a second ethylene copolymer, preferably 70 wt.%, 65 wt.%, 60 wt.%, 55 wt.%, 50 wt.%, or 49 wt.% or less of a second ethylene copolymer based on the weight of the polymer composition. In some embodiments, the polymer compositions being evaluated comprise from about 51% to about 60%, about 70%, or about 80% the first ethylene copolymer, and from about 49 % to about 20%, about 30%, or about 40% of the second ethylene copolymer, by weight of the polymer composition. Additional exemplary polymer compositions can be found in, for example, International Applications WO 10/126720, WO 10/126721, and WO10/129151, incorporated herein by reference in their entirety.

[0018]   The diluent or oil according to the instant disclosure may be derived from natural lubricating oils, synthetic lubricating oils or mixtures thereof. Suitable base oil includes base stocks obtained by isomerization of synthetic wax and slack wax, as well as hydrocrackate base stocks produced by hydrocracking (rather than solvent extracting) the aromatic and polar components of the crude. Suitable base oils include those in all API categories I, II, III, IV and V as defined in API Publication 1509, Appendix E, 15th Edition, April 2002. Saturates levels and viscosity indices for Group I, II and III oils are listed in Table 1. Group IV oils are polyalphaolefms (PAO). Group V oils include all other oils not included in Group I, II, III, or IV.

TABLE 1
Saturates, Sulfur and Viscosity Index of Group I, II, III, IV and V Base Stocks

Group	Saturates (As determined by ASTM D2007) Sulfur (As determined by ASTM D2270)	Viscosity Index (As determined by ASTM D4294, ASTM D4297 or ASTM D3120)
I	Less than 90 % saturates and/or Greater than to 0.03 % sulfur	Greater than or equal to 80 and less than 120
II	Greater than or equal to 90 % saturates and less than or equal to 0.03 % sulfur	Greater than or equal to 80 and less than 120
III	Greater than or equal to 90 % saturates and less than or equal to 0.03% sulfur	Greater than or equal to 120
IV	All Polyalphaolefins (PAOs)	
V	All others not included in Groups I, II, III, or IV	

[0019]   Natural lubricating oils may include animal oils, vegetable oils (e.g., rapeseed oils, castor oils and lard oil), petroleum oils, mineral oils, and oils derived from coal or shale.

[0020]   Synthetic oils may include hydrocarbon oils and halo-substituted hydrocarbon oils such as polymerized and inter-polymerized olefins, alkylbenzenes, polyphenyls, alkylated diphenyl ethers, alkylated diphenyl sulfides, as well as their derivatives, analogues and homologues thereof, and the like. Synthetic lubricating oils also include alkylene oxide polymers, interpolymers, copolymers and derivatives thereof wherein the terminal hydroxyl groups have been modified by esterification, etherification, etc. Another suitable class of synthetic lubricating oils comprises the esters of dicarboxylic acids with a variety of alcohols. Esters useful as synthetic oils also include those made from about C_5 to about C_{12} monocarboxylic acids and polyols and polyol ethers. Tri-alkyl phosphate ester oils such as those exemplified by tri-n-butyl phosphate and tri-iso-butyl phosphate are also suitable for use as oils.

[0021]   Silicon-based oils (such as the polyalkyl-, polyaryl-, polyalkoxy-, or polyaryloxy-siloxane oils and silicate oils) comprise another useful class of synthetic lubricating oils. Other synthetic lubricating oils include liquid esters of phosphorus-containing acids, polymeric tetrahydrofurans, polyalphaolefms, and the like.

[0022]   The oil may be derived from unrefined, refined, rerefined oils, or mixtures thereof. Unrefined oils are obtained directly from a natural source or synthetic source (e.g., coal, shale, or tar sand bitumen) without further purification or treatment.

[0023]   Examples of unrefined oils include a shale oil obtained directly from a retorting operation, a petroleum oil obtained directly from distillation, or an ester oil obtained directly from an esterification process, each of which may then be used without further treatment. Refined oils are similar to the unrefined oils except that refined oils have been treated in one or more purification steps to improve one or more properties. Suitable purification techniques include distillation, hydrocracking, hydrotreating, dewaxing, solvent extraction, acid or base extraction, filtration, and percolation, all of which are known to those skilled in the art. Rerefined oils are obtained by treating used oils in processes similar to those used to obtain the refined oils. These rerefined oils are also known as reclaimed or reprocessed oils and often are additionally processed by techniques for removal of spent additives and oil breakdown products.

[0024]   Oil derived from the hydroisomerization of wax may also be used, either alone or in combination with the aforesaid natural and/or synthetic oil.

[0025]   Such wax isomerate oil is produced by the hydroisomerization of natural or synthetic waxes or mixtures thereof over a hydroisomerization catalyst.

[0026]   The typical alpha olefin used as a comonomer with ethylene are from C_3 to about C_{20} alpha-olefms such as propylene, 1-butene, l-pentene,l-hexene, 1-octene of styrene. Propylene is preferred comonomer. The polymer backbone is the ethylene copolymer or terpolymer of C_3 to about C_{20} alpha-olefms. The terpolymer variations may contain about 0.1 to 10 mole percent of conjugated diene or triene. The polymerization reaction used to form the ethylene-alpha-olefm copolymer backbone is generally carried in presence of Ziegler-Natta or metallocene catalyst system.

[0027]   A visual gel test used to test for gellation is described below. This test involves preparing a solution of the polymer to be tested, and placing about a 10 ml sample of the solution into 40ml glass vial with screw cap. A typical vial is available from VWR Corporation as catalog number (VWR cat #: C236-0040). The sample is then heated in an 80°C oven for about 1 hour to remove any thermal history. The vial is stored at 10°C+ 5°C for 4-6hr in a Low Temperature Incubator. A typical incubator is available from VWR corporation as catalog number 35960-057. The vial is then stored at -15°C +/- 0.5°C overnight in a chest freezer. A typical chest freezer is Revco Model UTL 750-3-A30. A thermocouple is placed into a reference vial, identical to the sample but containing only the solvent or base oil to monitor the actual sample temperature. After 16 hours remove the vial from the freezer, do not remove the cap and immediately tilt the vial 80-90 degrees to an almost horizontal position. If condensation forms on the outside of the vial quickly wipe the vial with a paper towel. The test is carried out for multiple cycles. The samples are rated twice a week up to 8 weeks with final ratings as follows:

[0028]   No Gel - free flowing liquid

[0029]   Very Light Gel - minor surface texture

[0030]   Light Gel - rough surface

[0031]   Medium Gel - visible lumps

[0032]   Heavy Gel - large visible lumps

[0033]   The following visual grading can be used to rate the sample visually.

TABLE 2

GRADE	DESCRIPTION	DETAILED COMMENTS
0	No gel	Free flowing fluid with mirror surface
1	Light gel	Slight non-homogeneity, surface roughness
2	Medium gel	Large non-homogeneity, slight pulling away from vial
3	Heavy gel	Pulls away from vial, large visible lumps
4	Solid	Solid gel

[0034]   The following oil compositions were used in testing according to the present disclosure.

[0035]   The Vll/poly-alpha-olefm (PAO) solutions contain 2.4 wt% polymer in 4 cSt PAO lubricating oil to measure the interactions. No wax interference was observed during testing.

[0036]   10W-50 formulations in Group I/III/PAO base oils were used. The polymer interaction was measured in the final oils. High polymer content, 10W-50, lubricating oils were used to amplify the rheological response of the VII interactions.

[0037]   Experimental polymers for evaluation are shown in Table 3. Samples designated VII-A, VII-B, VII-C and VII-D are ethylene-propylene copolymers with their respective ethylene contents provided below.

TABLE 3

	VII-A	VII-B	VII-C	VII-D
% Ethylene (wt%)	64	64	64	62
SSI, % (ASTM D6298)	24.0	24.0	27 (est.)	24.4

[0038]   PAO solutions containing the test polymers and the resulting properties of the oils are shown in Table 4.

TABLE 4

	Oil 1	Oil 2	Oil 3	Oil 4
VII	A	B	C	D
Concentration, wt%	2.4	2.4	2.4	2.4
Kinematic Viscosity (KV) at 100°C, cSt	16.6	16.8	17.4	15.3
Gel-cycle ratings	Heavy	No	Medium	No

[0039]   10W-50 lubricating oils containing the test polymers and the resulting properties of the oils are shown in Table 5.

TABLE 5

	Oil 5	Oil 6	Oil 7
DI Package	13.0	13.0	13
Base Oils (Group I, III, IV), wt%	70.7	70.7	70.7
PPD, wt%	0.3	0.3	0.3
VII-type	VII-A	VII-B	VII-D
VII, wt%	16	16	16
Kinematic Viscosity at 100°C, cSt	18.05	18.06	17.90
Cold Cranking Simulator Viscosity@-25°C, cP	6627	6706	7417
MRV@-30°C, cP	30603	48237	44518
Scanning Brookfield, Gelation Index	8.6	12.2	8.0

[0040]   The present disclosure makes it possible to significantly reduce the testing time. The present disclosure provides for highly sensitive torque and displacement measurements and provides torque measurement resolution as low as 10^{-2} μN -m and displacement resolution of 25 nrad. The techniques provide for precise temperature (peltier plate) and shear rate (about 10 decades) control. An advantage of the present disclosure is the ability to use a small quantity of a sample (~5 ml). The methods of the present disclosure are suitable for various geometries/fixtures for a wide variety of compositions, especially lubricating oils

[0041]   According to the present disclosure, yield stress is determined. Yield stress is typically measured at 0°C and -15°C, by steady state flow method by varying stress from about 100 Pa to about 10^{-5} Pa. Generally, the stress/shear rate curve fits the Herschel-Bulkley equation.

[0042]   In particular, a steady state uni-directional rotation is used at the specified temperature. The shear rate or shear stress is varied and the shear stress or shear rate is measured (e.g. see Figure 2) and the viscosity is calculated (e.g. see Figure 1). A sample profile of 60 mm, 2°2'01" steel cone geometry is typically employed with a gap of 54μιη

between the plates. The testing is carried out by equilibrating the device at 40 °C, cooling to 0 °C (at ~ 20 °C/min), ramping the stress from 100 Pa to 2×10^{-3} Pa, cooling to -15 °C (at ~20 °C/min), and ramping the stress from 100 Pa to 2×10^{-3} Pa.

[0043]   With respect to flow measurements of VII/PAO solutions; VII OCPs of the same overall ethylene content have different responses in steady state flow rheology (e.g. see Figure 1). The method of the present disclosure can be used to characterize the polymer-polymer interactions in lubricating oil.

[0044]   Yield stress is calculated using the Herschel-Bulkley equation.

$$\tau = \tau_0 + k\left(\gamma\right)^n$$
$$where, \tau = Shear\ Stress$$
$$\tau_0 = Yield\ Stress$$
$$k = consistency$$
$$\gamma = shear\ rate$$
$$and\quad n = power\ law\ exponent$$

[0045]   Not all high ethylene OCPs are same. The calculated yield stress are 3-4 orders of magnitude different depending on the polymer design even at same ethylene content (e.g. see Figure 2). The above described gel-cycle test can be carried out to develop a standard. As shown in the table below generally, the yield stress calculated by Herschel-Bulkley model to fit shear stress-shear rate response of VII/PAO solutions correlates with the gel-cycle test rating of its corresponding 10W-50 lubricating oil. The table can be used as a standard to compare the results from a yield stress test to determine whether a particular polymer is likely or not to form a gel in lubricating oil.

TABLE 6

Gel-cycle Method Ratings	Yield Stress (Pa)
Heavy Gel	0.8 – 4
Medium Gel	0.05 – 0.8
Light Gel	0.02 - 0.05
No Gel	Below 0.01 Pa

[0046]   It is noted that polymer interactions are an order of magnitude lower than the interactions present in lubricating oil system (base oil/VII/PPD/DI) (For example, MRV measures yield stress only above 35 Pa).

[0047]   The storage modulus G' and loss modulus G" of the composition to be tested are determined by oscillatory rheology. Sinusoidal stress or strain of certain amplitude and frequency is applied and the corresponding sinusoidal strain or stress response is measured to calculate δ as follows (e.g., see Figure 3),

$$\sigma = \sigma_0 \sin(\omega i)$$
$$\varepsilon = \varepsilon_0 \sin(\omega t + \delta)$$

where,

σ = applied stress

σ_0 = applied stress amplitude

ε = measured strain

ε_0 = strain amplitude

ω = frequency

t = time

δ = phase lag

[0048]   The temperature, strain or stress amplitude, and frequency can be varied. The storage modulus and loss modulus are measured. See Figure 3.

$$G' = \frac{Stress}{Strain} \, x\cos(\pounds) \qquad G'' = \frac{Stress}{Strain} \, x\sin(d)$$

[0049]   A sample profile of 60 mm, 2°2'01" steel cone geometry is used with a gap of 54μιη between the plates. The testing is carried out by equilibrating the device at 40 °C. The temperature is ramped from 40°C to -19°C at an oscillatory stress of 0.2 Pa and 1 rad/s frequency. The testing is carried out by equilibrating the device at -19°C. The

temperature is ramped from 40°C to -19°C at an oscillatory stress of 0.2 Pa and 1 rad/s frequency.

[0050]   The oscillatory rheology measures various rheological parameters, such as storage modulus, G', loss modulus, G'', δ or tan(5), gel-point (G'=G''), parameters that can characterize polymer-polymer interactions in lubricating oil.

[0051]   Oscillatory measurements of VII/PAO solutions: Gel-Point and delta (δ). Oil rated as heavy gel in the gel-cycle test also exhibits a gel-point (G'≥G'', δ≤45 °) in the oscillatory rheology method. Additional parameters such as delta, δ, at given temperature (e.g., at -15°C) or tan(5) characterize polymer-polymer interactions. (e.g. see Figures 4 and 7).

[0052]   Oscillatory Measurements of VII/PAO Solutions: Oscillatory rheology can be used to select VII molecules with desired structure-performance in lubricating oils. (see Figure 6).

[0053]   The crossover point of G' and G'' is the gel point that indicated heavy gelation. However, the information concerning the crossover point of G' and G'' is not necessarily sufficient to determine whether in a particular system, polymer interaction not rising to the level of heavy gelation is likely to occur. According to the present disclosure, it has been found that δ or tan(5), measured by the oscillatory rheology, further quantifies VII interactions. For instance, it has been determined that a tan(5) greater than 2.0 indicates the formation of networks at a lower level than the heavy gelation identified by the crossover point of G' and G''. See figure 6. Thus, the δ or tan(5) can be used to select VII which do not exhibit gelation at low temperatures in lubricating oils.

[0054]   Figure 7 illustrates that the magnitude of yield stress in high VII content 10W-50 lubricating oils is 10^{-2} times lower compared to 2.4wt% VII/PAO solutions.

[0055]   Exemplary embodiments of the invention include:

A.   A method to determine the predisposition of a polymer to form network or gel in a composition, comprising the steps of:

(a)   obtaining a composition of a polymer in a diluent,

(b)   measuring the shear stress of the composition as a function of shear rate
         or measuring the shear rate of the composition as a function of shear stress,

(c)   determining the yield stress using the Herschel-Bulkley equation:

$$\tau = \tau_0 + k\,(\gamma)^n$$
$$where, \tau = Shear\ Stress$$
$$\tau_0 = Yield\ Stress$$
$$k = consistenc\ y$$
$$\gamma = shear\ rate$$
$$and\quad n = power\ law\ exponent$$
, and

(d)   comparing the yield stress, thereby determining the predisposition of the
         polymer to form a network or gel.

B.   The method according to Embodiment A, wherein the diluent comprises a
        lubricating oil and the polymer is an alpha-olefm copolymer.

C.   The method according to any of Embodiments A and B, wherein the lubricating
        oil contains a Group I, II, III, IV or V base oil.

D.   A method to determine the predisposition of a polymer to form network or gel in
        a composition, comprising the steps of:

        (a)   obtaining a composition of a polymer in a diluent, and

        (b)   determining at least one of (i) the storage modulus G' and loss modulus
        G" of the composition by subjecting the composition to sinusoidal (oscillating)
        stress or strain of certain amplitude and frequency, (ii) the phase lag (angle) of the
        response strain or stress δ, or (iii) the tangent (tan) δ, and assessing at least one of
        the G', G", δ, or *tan(6)* determined, thereby determining the predisposition of the
        polymer to form a network or gel.

E.   The method according to Embodiment D, wherein the diluent comprises a
        lubricating oil and the polymer is an alpha-olefm copolymer.

F.   The method according to any of Embodiments E and E, wherein the lubricating oil contains a Group I, II, III, IV or V base oil.

G.   The method according to any of Embodiments A-F, wherein the polymer is an ethylene copolymer having an ethylene content of at least about 50 wt. %, by weight of the ethylene copolymer.

H.   The method according to any of Embodiments A-G, wherein the polymer is a polymer composition that comprises at least 30 wt.%, based on the weight of the polymer composition, of a first copolymer of ethylene and an alpha-olefin comonomer, and 70 wt.% or less, based on the weight of the polymer composition, of a second copolymer of ethylene and an alpha-olefin comonomer, wherein the first copolymer has a lower ethylene content than the second copolymer.

I.   The method according to any of Embodiments A-H, further comprising selecting the polymer for use in a lubricating oil composition.

J.   The method according to Embodiment I, further comprising forming a lubricating oil composition comprising the polymer.

K.   A lubricating oil composition comprising a polymer selected according to the method of Embodiment J.

M.   A method to determine the predisposition of a test polymer to form gel in a composition, comprising the steps of:
      (a)   forming a sample composition comprising a sample polymer and a diluent,
      (b)   determining the yield stress of the sample composition,
      (c)   determining the gellation level of the sample composition,
      (d)   obtaining a correlation between yield stress with the gellation level of the sample composition to obtain a standard,

(d)   obtaining a test polymer,

(e)   determining the yield stress of the test polymer,

(f)   applying the correlation obtained in step (d) to determine the

predisposition of the polymer to form a network or gel.

N.   The method of Embodiment N, further comprising the step of (g) selecting the

polymer for use in a lubricating oil composition, and forming a lubricating oil

composition comprising the polymer.

O.   The method of Embodiment G, wherein the ethylene copolymer is an

ethylene/propylene copolymer.

[0056]   The term "comprising" (and its grammatical variations) as used herein is used

in the inclusive sense of "having" or "including" and not in the exclusive sense of

"consisting only of." The terms "a" and "the" as used herein are understood to

encompass the plural as well as the singular.

[0057]   All publications, patents and patent applications cited in this specification are

herein incorporated by reference, and for any and all purpose, as if each individual

publication, patent or patent application were specifically and individually indicated to be

incorporated by reference. In the case of inconsistencies, the present disclosure will

prevail.

[0058]   The foregoing description of the disclosure illustrates and describes the

present disclosure. Additionally, the disclosure shows and describes only the preferred

embodiments but, as mentioned above, it is to be understood that the disclosure is capable

of use in various other combinations, modifications, and environments and is capable of

changes or modifications within the scope of the concept as expressed herein,

commensurate with the above teachings and/or the skill or knowledge of the relevant art.

[0059]   The embodiments described hereinabove are further intended to explain best

modes known of practicing it and to enable others skilled in the art to utilize the

disclosure in such, or other, embodiments and with the various modifications required by

the particular applications or uses. Accordingly, the description is not intended to limit it to the form disclosed herein. Also, it is intended that the appended claims be construed to include alternative embodiments.

CLAIMS

What is claimed is:

1.   A method to determine the predisposition of a polymer to form network or gel in
        a composition, comprising the steps of:

        (a)   obtaining a composition of a polymer in a diluent,

        (b)   measuring the shear stress of the composition as a function of shear rate
                 or measuring the shear rate of the composition as a function of shear stress,

        (c)   determining the yield stress using the Herschel-Bulkley equation:

$$\tau = \tau_0 + k\,(\gamma)^n$$
$$where, \tau = Shear\ Stress$$
$$\tau_0 = Yield\ Stress$$
$$k = consistenc\ y$$
$$\gamma = shear\ rate$$
$$and\ \ n = power\ law\ exponent$$
, and

        (d)   comparing the yield stress, thereby determining the predisposition of the
                 polymer to form a network or gel.

2.   The method according to claim 1, wherein the diluent comprises a lubricating oil
        and the polymer is an alpha-olefm copolymer.

3.   The method according to claim 2, wherein the lubricating oil contains a Group I,
        II, III, IV or V base oil.

4.   A method to determine the predisposition of a polymer to form network or gel in
        a composition, comprising the steps of:

        (a)   obtaining a composition of a polymer in a diluent, and

        (b)   determining at least one of (i) the storage modulus G' and loss modulus
        G" of the composition by subjecting the composition to sinusoidal (oscillating)
        stress or strain of certain amplitude and frequency, (ii) the phase lag (angle) of the
        response strain or stress δ, or (iii) the tangent (tan) δ, and

(c) assessing at least one of the G', G'', δ, or tan(5) determined, thereby determining the predisposition of the polymer to form a network or gel.

5.   The method according to claim 4, wherein the diluent comprises a lubricating oil and the polymer is an alpha-olefm copolymer.

6.   The method according to claim 4, wherein the lubricating oil contains a Group I, II, III, IV or V base oil.

7.   The method according to claim 1, wherein the polymer is an ethylene copolymer having an ethylene content of at least about 50 wt. %, by weight of the ethylene copolymer.

8.   The method according to claim 1, wherein the polymer is a polymer composition that comprises at least 30 wt.%, based on the weight of the polymer composition, of a first copolymer of ethylene and an alpha-olefm comonomer, and 70 wt.% or less, based on the weight of the polymer composition, of a second copolymer of ethylene and an alpha-olefm comonomer, wherein the first copolymer has a lower ethylene content than the second copolymer.

9.   The method of claim 1, further comprising selecting the polymer for use in a lubricating oil composition, and forming a lubricating oil composition comprising the polymer.

10.   The method of claim 4, further comprising selecting the polymer for use in a lubricating oil composition, and forming a lubricating oil composition comprising the polymer.

11.   A lubricating oil composition comprising a polymer selected according to the method of claim 9.

12.   A lubricating oil composition comprising a polymer selected according to the
        method of claim 10.

13.   The method of claim 1, wherein the comparing in step (d) comprises correlating
        the yield stress to a predetermined standard.

14.   A method to determine the predisposition of a test polymer to form gel in a
        composition, comprising the steps of:
        (a)   forming a sample composition comprising a sample polymer and a diluent,
        (b)   determining the yield stress of the sample composition,
        (c)   determining the gellation level of the sample composition,
        (d)   obtaining a correlation between yield stress with the gellation level of the
                sample composition to obtain a standard,
        (d)   obtaining a test polymer,
        (e)   determining the yield stress of the test polymer,
        (f)   applying the correlation obtained in step (d) to determine the
                predisposition of the polymer to form a network or gel.

15.   The method of claim 14, further comprising the step of (g) selecting the polymer
        for use in a lubricating oil composition, and forming a lubricating oil composition
        comprising the polymer.

16.   The method according to claim 7, wherein the ethylene copolymer is an
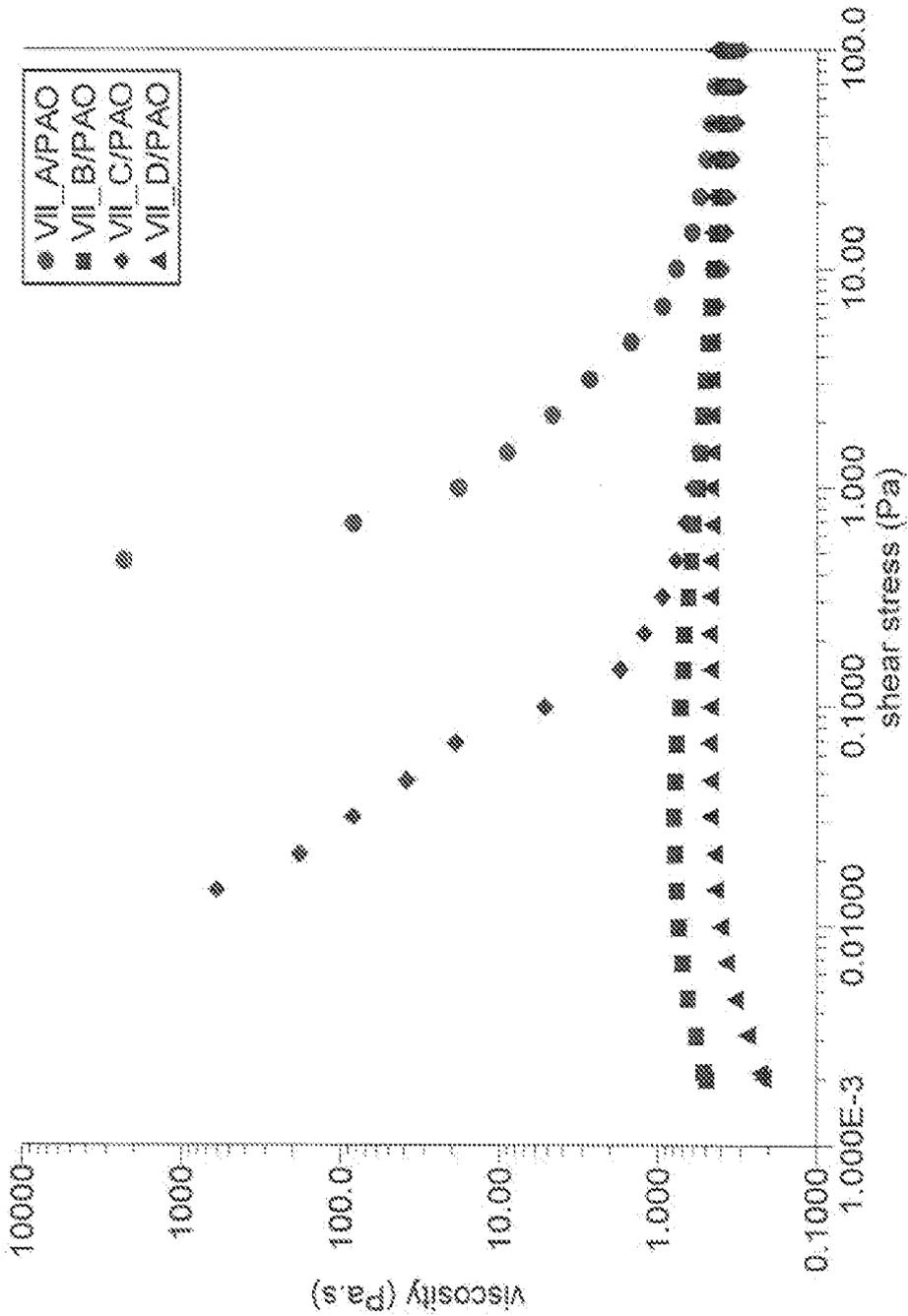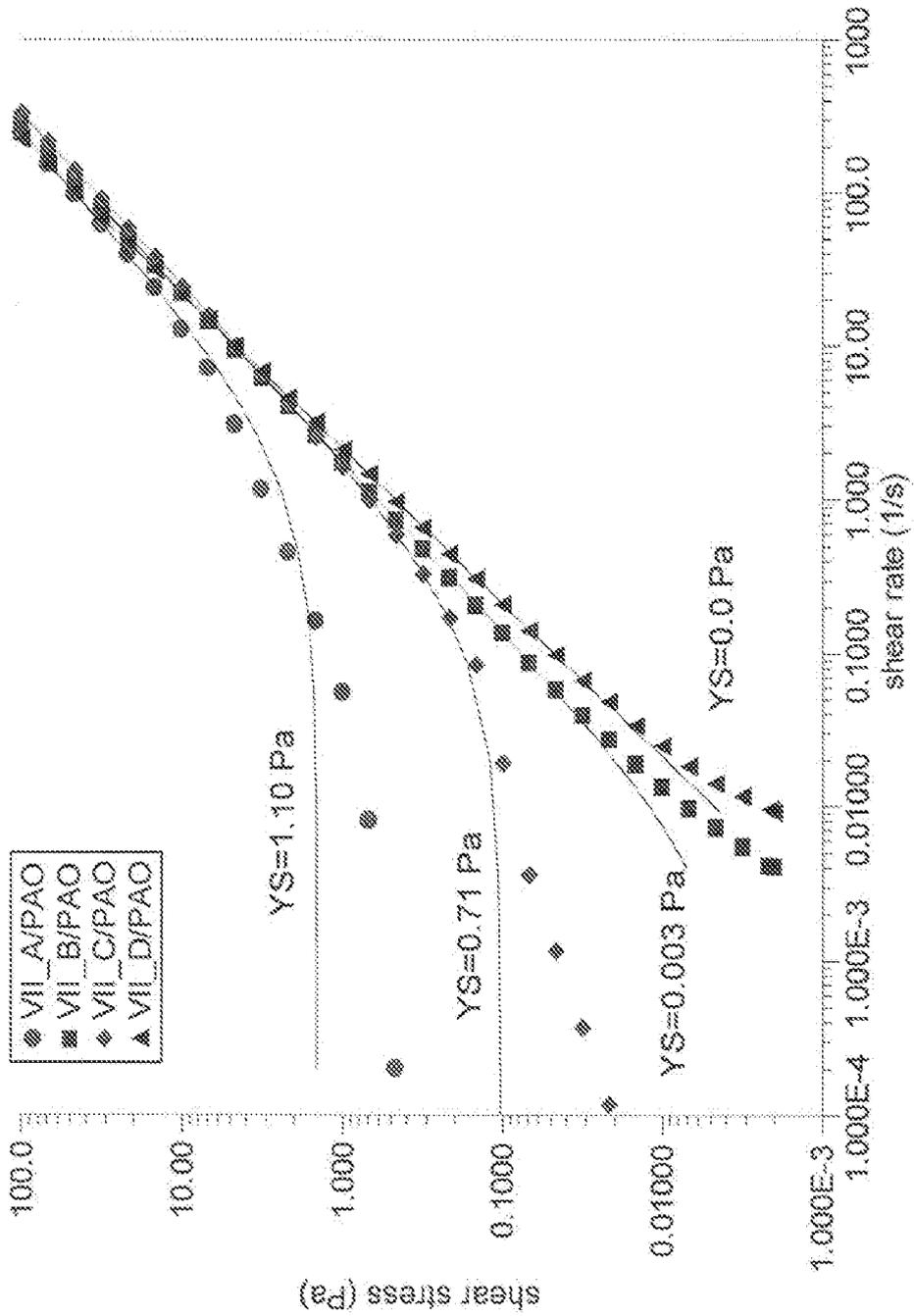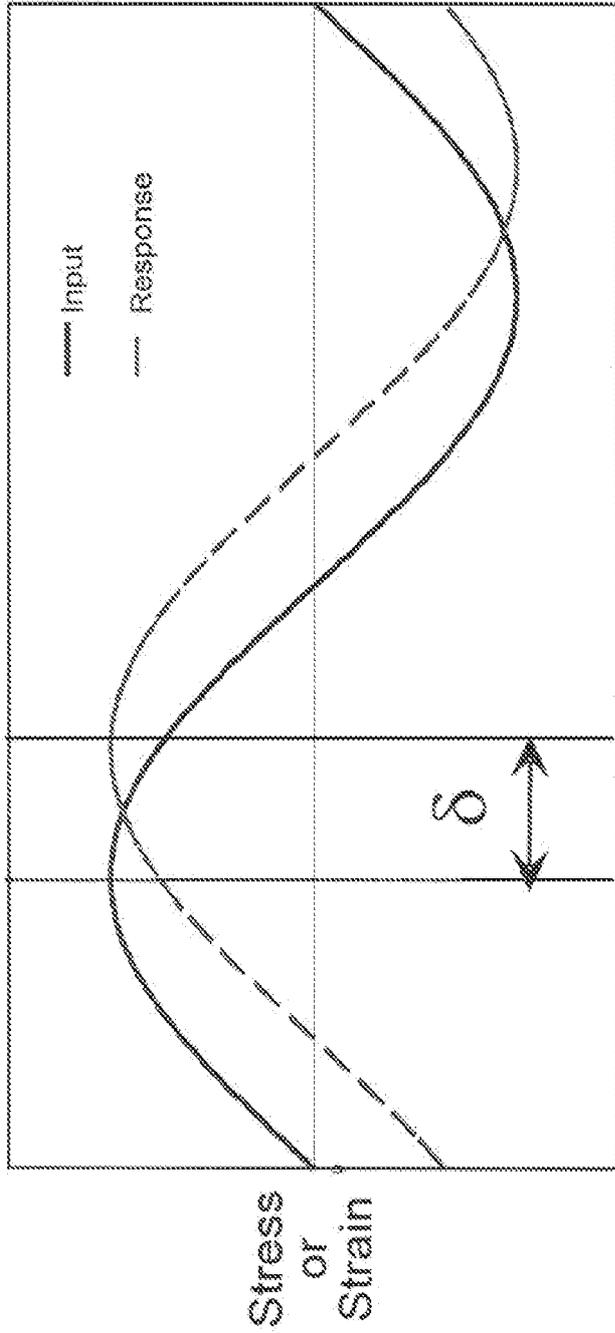   ethylene/propylene copolymer.

FIGURE 1

Figure 2

$$\sigma = \sigma_0 \sin(\omega t)$$
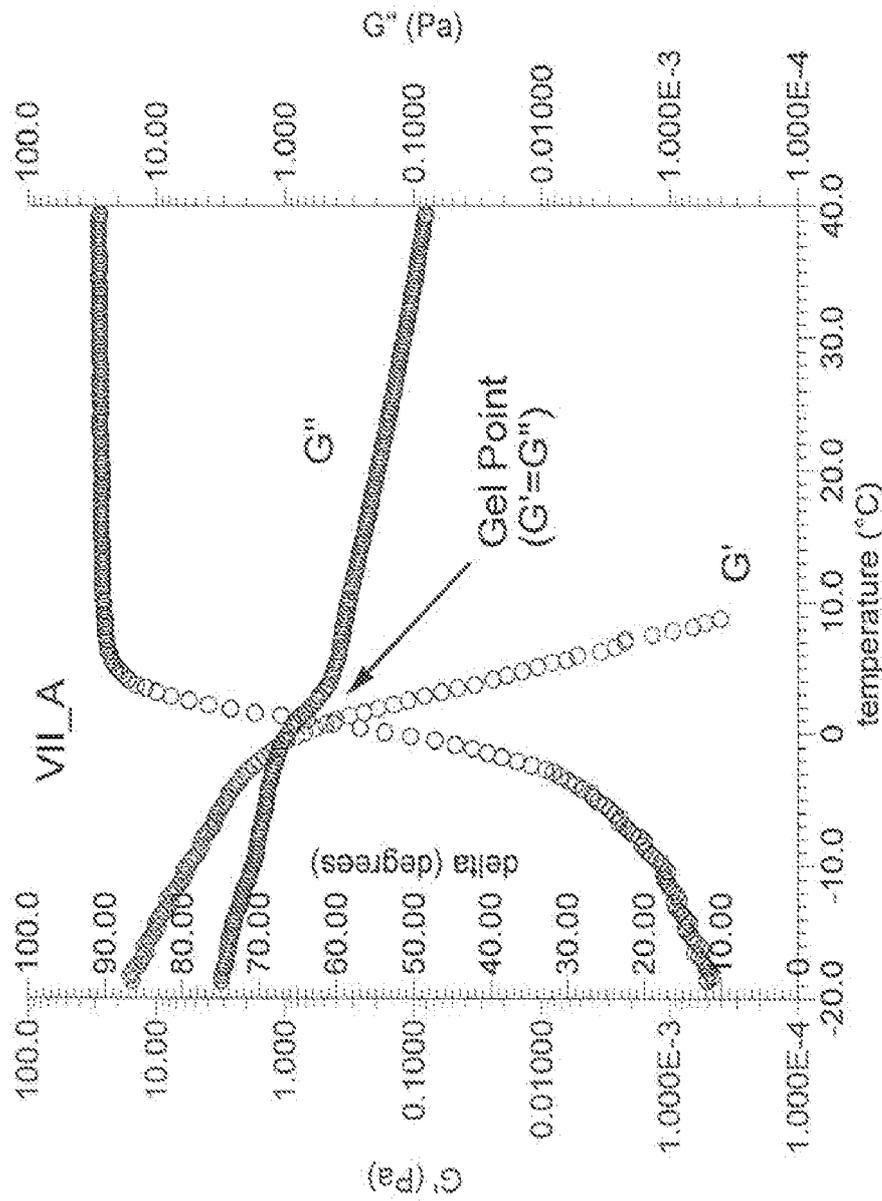$$\varepsilon = \varepsilon_0 \sin(\omega t + \delta)$$

Figure 3

Figure 4

Figure 5

Figure 6

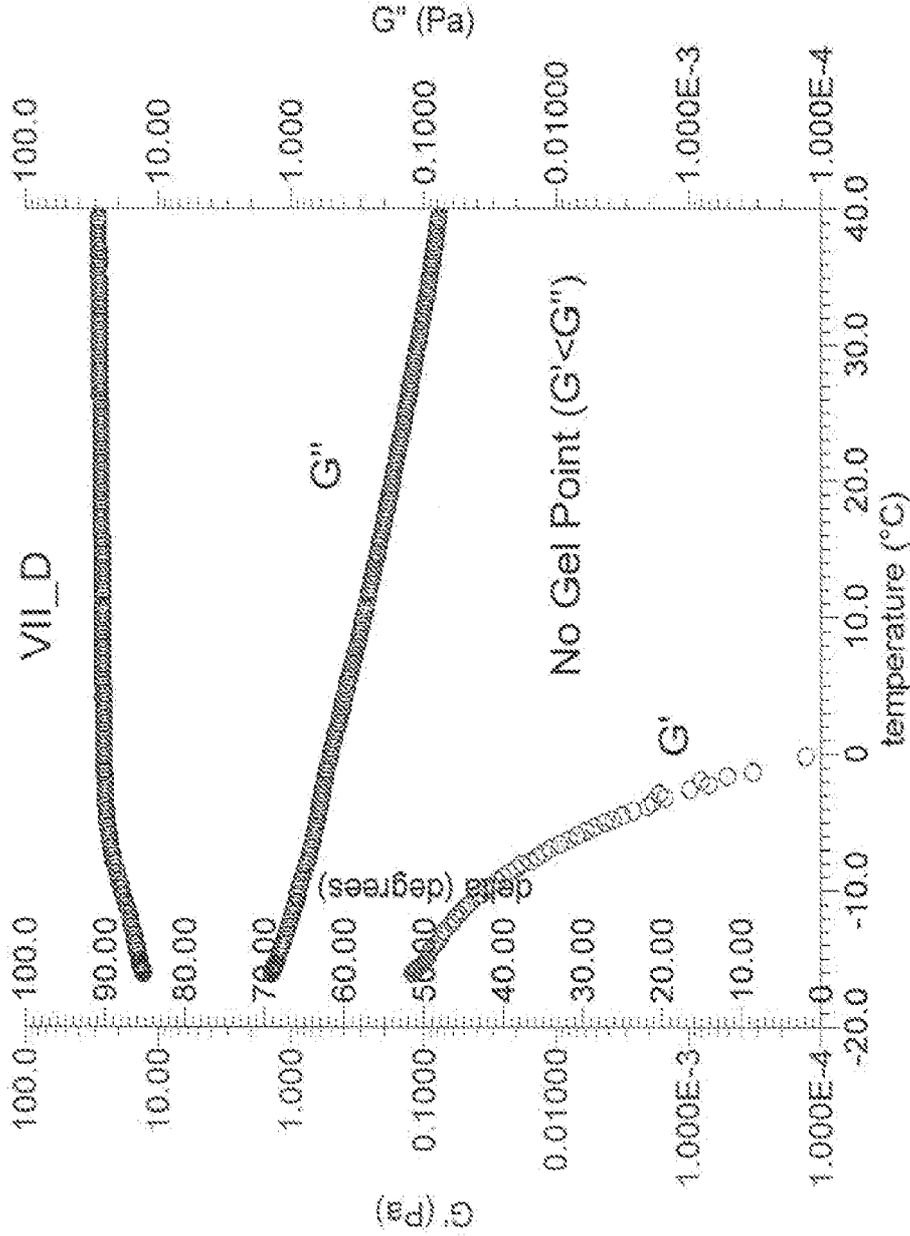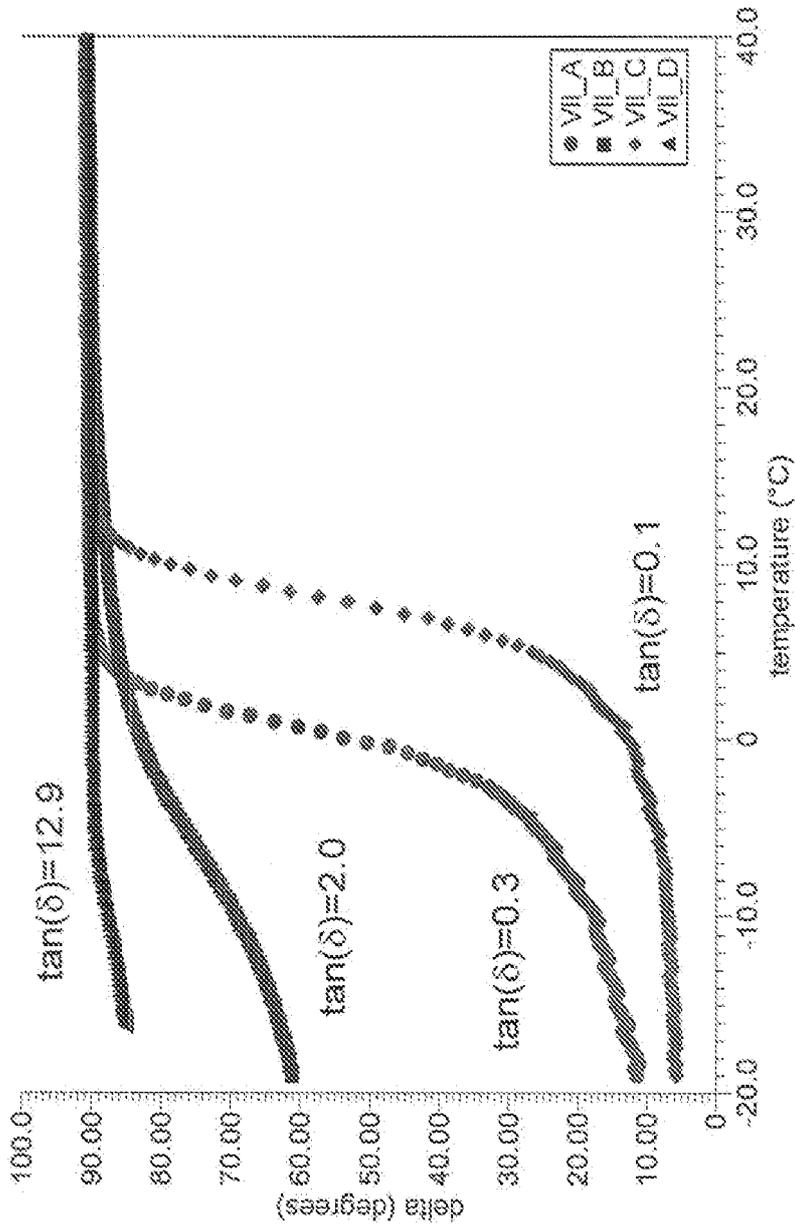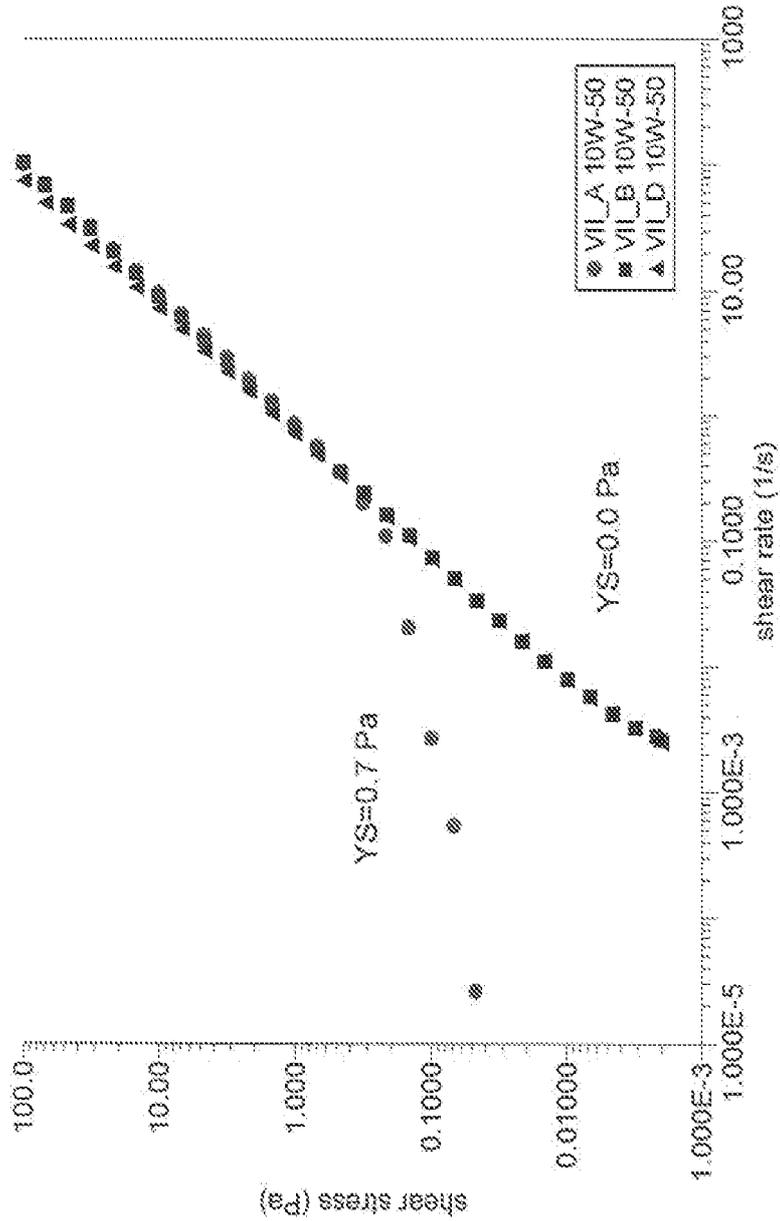Figure 7

INTERNATIONAL SEARCH REPORT

A. CLASSIFICATION OF SUBJECT MATTER
IPC(8) - C08F 210/16 (2012.01) **USPC - 508/591**
According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED
Minimum documentation searched (classification system followed by classification symbols) IPC(8) - C08F 210/16, 210/18; C10L 1/16; C10M 143/02 (2012.01) USPC - 508/312, 543, 591; 525/240; 526/348
Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched
Electronic data base consulted during the international search (name of data base and, where practicable, search terms used) Orbit.com, Google Patents, Google

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X --- Y	US 2010/0105597 A1 (HARRINGTON et al) 29 April 2010 (29.04.2010) entire document	1, 13 ----------------- 2-12, 14-16
Y	US 5,112,510 A (ROSSI) 12 May 1992 (12.05.1992) entire document	2, 3, 5-12, 15, 16
Y	US 2003/0050387 A1 (FUJISAWA) 13 March 2003 (13.03.2003) entire document	4-6, 10, 12
Y	US 2002/0028860 A1 (KERR et al) 07 March 2002 (07.03.2002) entire document	14, 15

☐ Further documents are listed in the continuation of Box C.   ☐

* Special categories of cited documents:	
"A" document defining the general state of the art which is not considered to be of particular relevance	"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
"E" earlier application or patent but published on or after the international filing date	"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)	
"0" document referring to an oral disclosure, use, exhibition or other means	"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
"P" document published prior to the international filing date but later than the priority date claimed	"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
18 October 2012	**1 3 NOV 2012**

Name and mailing address of the ISA/US	Authorized officer:
Mail Stop PCT, Attn: ISA/US, Commissioner for Patents P.O. Box 1450, Alexandria, Virginia 22313-1450 Facsimile No. 571-273-3201	Blaine R. Copenheaver PCT Helpdesk: 571-272-4300 PCT OSP: 571-272-7774