Hydrocolloid Rheology

There are two rheological properties of particular importance to hydrocolloid science. These are their gel and flow properties.
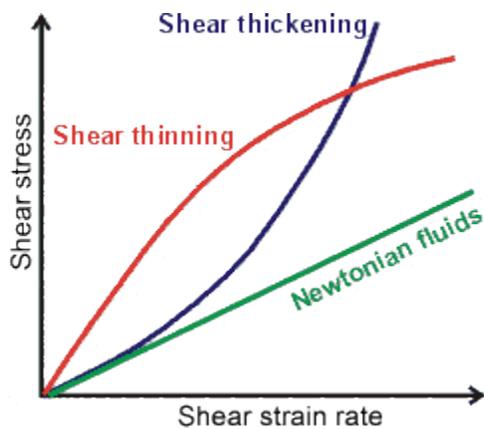
Viscosity

Viscosity is a property of fluids that indicates resistance to flow. When a force is applied to a volume of material then a displacement (deformation) occurs. If two plates (area, A), separated by fluid distance (separation height, H) apart, are moved (at velocity V by a force, F) relative to each other, Newton's law states that the **shear stress** (the force divided by area parallel to the force, F/A) is proportional to the **shear strain rate** (V/H). The proportionality constant is known as the (dynamic) **viscosity** (η).
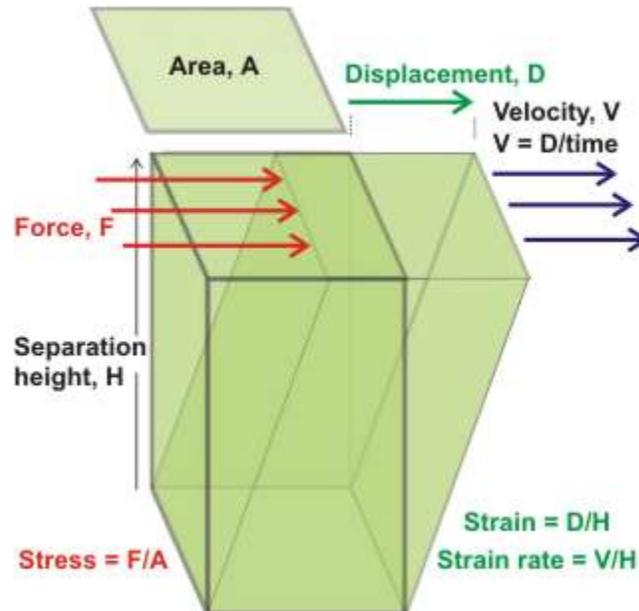
The effect (**shear strain**) is quantified by the displacement per unit height (D/H) and the rate of this effect (**strain rate**) is the velocity per unit height (V/H), where the height is the distance to a relatively unaffected position. The viscosity (η) is the tendency of the fluid to resist flow and is defined by:

$$\eta = \frac{shear\ stress}{strain\ rate} \quad (Pa\ s)$$

Increasing the concentration of a dissolved or dispersed substance generally gives rise to increasing viscosity (that is, thickening), as does increasing the molecular weight of a solute.

With Newtonian fluids (typically water and solutions containing only low molecular weight material) the viscosity is independent of shear strain rate and a plot of shear strain rate (for example, the rate of stirring) against shear stress (for example, force, per unit area stirred, required for stirring) is linear and passes through the origin.


$$\eta = \eta_{\infty} + \frac{\eta_0 - \eta_{\infty}}{(\tau\gamma)^m}$$
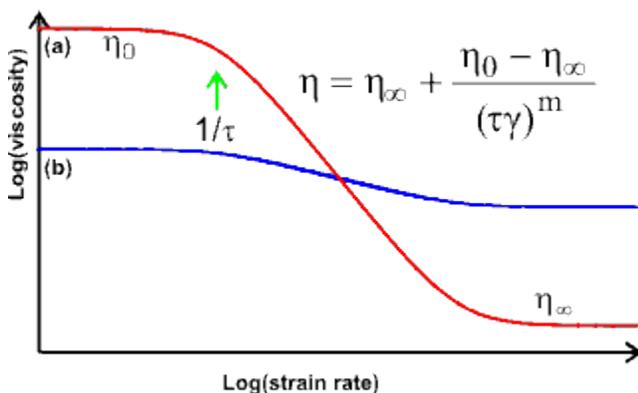
At moderate concentrations above a critical value (C*, [244]) hydrocolloid solutions exhibit non-Newtonian behavior where their viscosity depends on the shear strain rate, typically as opposite, where γ is the shear strain rate, η_0 and η_∞ are the viscosities at zero and infinite shear strain rate respectively and τ is a shear-dependent time constant that represents the reciprocal of the shear strain rate required to halve the viscosity.

The exponent (m) gives the degree of thinning (0 = no thinning, that is, Newtonian behavior; 1 = maximal thinning; < 0 = shear thickening) and determines the slope of the graph (that is, the slope is greater when m is greater). The equation is one of a number of empirical relationships that can be used. The viscosity depends on the cross-sectional area in the direction of flow. At low flow rates, molecules with preferred conformations that are long and thin have effectively large cross-sections due to them tumbling in solution but at high shear strain rate the molecules align with the flow, giving much smaller effective cross-sections and hence much lower viscosities (see red line (a) above). More compact molecules are not so much affected by their orientation relative to flow and hence their viscosity changes little with shear strain rate (see blue line (b) above representing a solute with the same molecular volume but more compact shape). The gradient of the central linear part of the above log-log curve is equal to minus the exponent (-m); 1-m is the behavior index (n) also given by the exponent in the Ostwald relationship: shear stress is proportional to the shear strain rate to the power n (that is, shear stress = $k\,\gamma^n$). A value for n of unity indicates Newtonian behavior, increasingly non-Newtonian behavior results in a lowering in this behavior index towards zero (for example, 0.25% xanthan solution has n = 0.4).

Viscoelasticity

Many hydrocolloids are capable of forming gels of various strength dependent on their structure and concentration plus environmental factors such as ionic strength, pH and temperature. The combined viscosity and gel behavior (viscoelasticity) can be examined by determining the effect that an oscillating force has on the movement of the material.
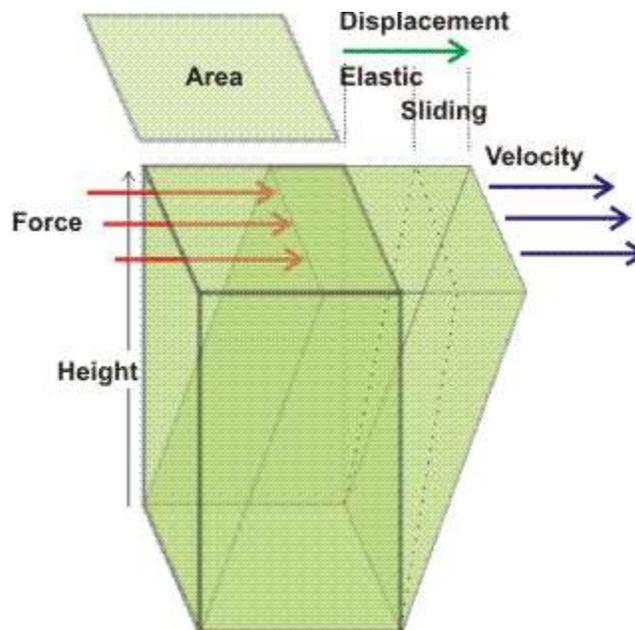
With viscoelastic hydrocolloids, some of the deformation caused by shear stress is elastic (for example, contortion of the chains into high energy conformations) and will return to zero when the force is removed. The remaining deformation (that is, the sliding displacement of the chains through the solvent) will not return to zero when the force is removed. Under a constant force the elastic displacement remains constant whereas the sliding displacement continues, so increasing.

If the force varies sinusoidally with time, then the viscous (sliding) energy is always positive and lost as heat whereas the changes in the elastic energy may be positive or negative and is recouped.
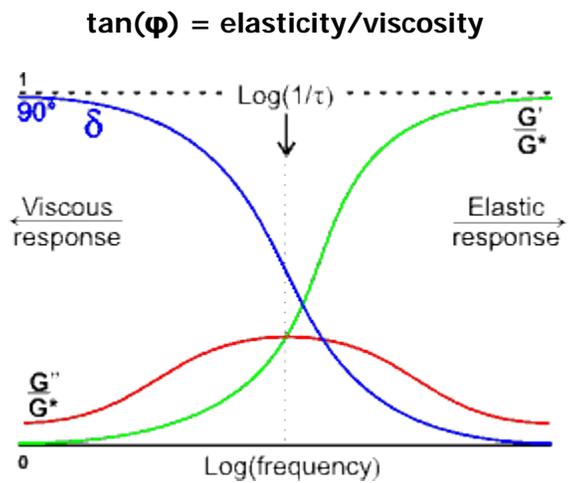
strain rate   shear stress

$\leftarrow \phi \rightarrow$

90   180   270   360
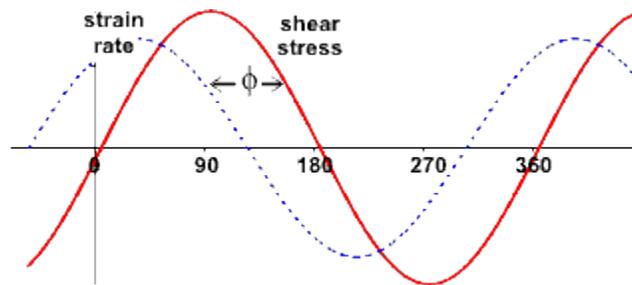
Under such conditions the shear strain rate lags behind the changes in the causative force by a phase angle ϕ. ϕ is zero for an ideally elastic gel (all energy stored in the material) and 90° for an ideally viscous liquid (all energy dissipated as heat).

Varying stress

shear stress

elastic stress

ϕ
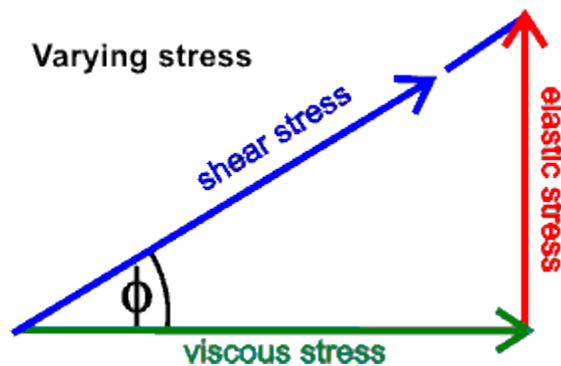
viscous stress

It is convenient to express the relationship between the shear stress, elastic stress and viscous stress (resulting from changing stress) in terms of a complex number ($\sqrt{-1} = i$) where the viscous stress is in-phase and the elastic stress is out-of-phase and oppositely-directed.[a]

shear stress = viscous stress - i x elastic stress
complex viscosity = viscosity - i x elasticity

tan(φ) = elasticity/viscosity

The shear modulus (resulting from changing strain) is the ratio of the shear stress to the shear strain. It follows from the complex relationship similar to the above that:

$$G^* = G' + iG''$$

where G^* is the complex shear modulus, G' is the in-phase storage modulus and G'' is the out-of-phase similarly-directed loss modulus; $G^* = \sqrt{(G'^2 + G''^2)}$. The frequency where these parameters cross over corresponds to a relaxation time (τ) specific for the material.
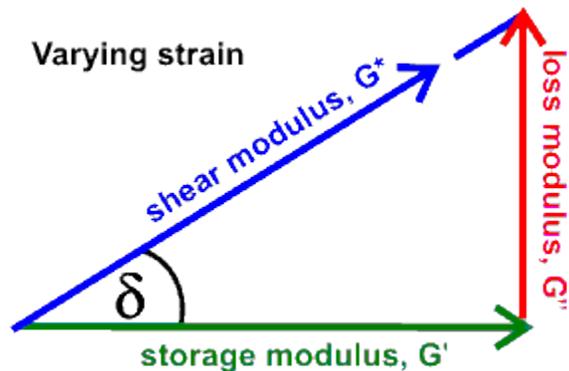

It follows that,

$$\tan(\delta) = G''/G'$$

where $\tan(\delta)$ quantifies the balance between energy loss and storage.
As $\tan(45°) = 1$, a value for $\tan(\delta)$ greater than unity indicates more "liquid" properties, whereas one lower than unity means more "solid" properties, regardless of the viscosity.

Structural effects

Linear and substantially linear polymers behave in a qualitatively predictable way with respect to the relationship of their viscosity to their structure and conformation. In dilute solutions this relationship depends effectively on the volume "swept out" (that is, the hydrodynamic volume) by the molecules as they tumble in the solution. At these low concentrations, where there is effectively no interaction between molecules and they are at their most extended, the viscosity may be little different from that of water; this small difference depending on the total spherical volume (itself dependent on concentration and radius of gyration of the solute) taken up by the freely rotating molecules. The relationship between viscosity with concentration is generally linear up to viscosity values of about twice that of water. This dependency means that more extended molecules increase the viscosity to greater extents at low concentrations than more compact molecules of similar molecular weight. Generally less-flexible links between sequential monomers in the polymeric chains give rise to more extended structures but the linkage spacing, direction and charge density are all important factors. The molecules most capable of an extended structure, due the maximal linkage spacing and direction are -(1→4)-diequatorially linked between pyranose residues whereas those least capable contain -(1→3)-diaxially linked pyranose residues. Where residues are negatively charged, the repulsion between similar charges increases molecular extension but this can be reduced at higher ionic strength or below the pK_a's of the anionic groups and this reduction is particularly noticeable for polymers with high molecular weight The lack of much change in viscosity of such molecules with ionic strength is indicative of an inflexible rod-type conformation. It should be noted that although attaching short sugar units as branch-points to linear polysaccharides does increase their rigidity into an extended structure, this is at the cost of greatly increased molecular weight. The extended nature of the molecules has an extreme effect on the molecular weight dependency of the viscosity as the hydrodynamic volumes (and hence viscosities) of compact (highly flexible but poorly hydrated) molecules increase approximately as the cube root of their molecular weight whereas those of more-extended well hydrated molecules (such as alginate and xanthan gum) increase approximately linearly with molecular weight. The relationship between the intrinsic viscosity [η] and the relative molecular mass (M_w) is given by $[\eta] = K M_w^a$, the Mark-Houwink equation where K and a are constants. Amylose, carboxymethylcellulose, arabinoxylans and guar all have exponents (a) of about 0.7. Knowledge of these constants allows the viscosity-averaged molecular weight to be calculated from viscosity data.

The viscosity increases with concentration until the shape of the volume occupied by these molecules becomes elongated under stress causing some overlap between molecules and a consequent reduction in the overall molecular volume with the resultant effect of reducing the amount that viscosity increases with concentration (under stress).
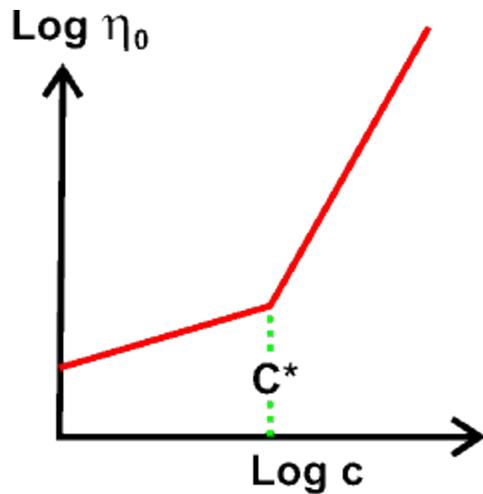
At higher concentrations (above a critical concentration C*) all the polymer molecules in the solution effectively overlap, interpenetrate and become entangled (that is, their total hydrodynamic volume appears greater than the solution volume) even without being stressed, so changing the solution behavior from mainly viscous to mainly elastic with the viscosity (η_0 at zero stress) being mainly governed by the mobility of the polymer molecules. C* will depend on the shear strain rate as, at high shear strain rate, the molecules take up a less voluminous shape. At higher concentrations the viscosity increases up to about the fifth power of the concentration and this can cause apparently synergic behavior of hydrocolloid mixtures, particularly if they cause phase separation with its inherent concentration increases.

At high shear strain rate (and sufficient concentration) molecules may become more ordered and elastic. Shear flow (and its related stress) causes molecules to become stretched and compressed (at right angle to stretch) resulting in isotropic solutions becoming anisotropic. After release from such conditions, the molecules relax back with time (the relaxation time). At low concentrations below the critical value (C*), the shear modulus of hydrocolloid solutions is mainly determined by the loss modulus at low frequencies (that is, G'' is relatively high for viscous materials).
As G'' depends on the frequency but G' depends on the square of the frequency, G' becomes more important at higher frequencies. At higher concentrations in viscous solutions G' is generally greater than G'' throughout a wide frequency range. This difference is very large for strong gels when the frequency has almost negligible effect (that is, G' is high for elastic materials). Such gels often form above another critical concentration specific to the hydrocolloid, where junction zones occur so stabilizing intermolecular associations.

Further rheological terminology

Dilatancy (**shear thickening**) shows an increase in viscosity with shear stress and strain due to structural enhancement. An example is uncooked corn starch paste where shear stress squeezes the water from between the starch granules allowing them to grind against each other. This property is often used in sauces where, for example, tomato sauce flow is prevented under small shear stress but then catastrophically fails, producing too great a flow, under greater stress (shaking). Another (and the strictly correct usage for the term) meaning for dilatancy concerns the increase in volume

of suspensions of irregular particles with shear due to the creation of small but empty cavities between the particles as they scrape past each other.

Dynamic viscosity is the commonly used form of viscosity, often abbreviated to just
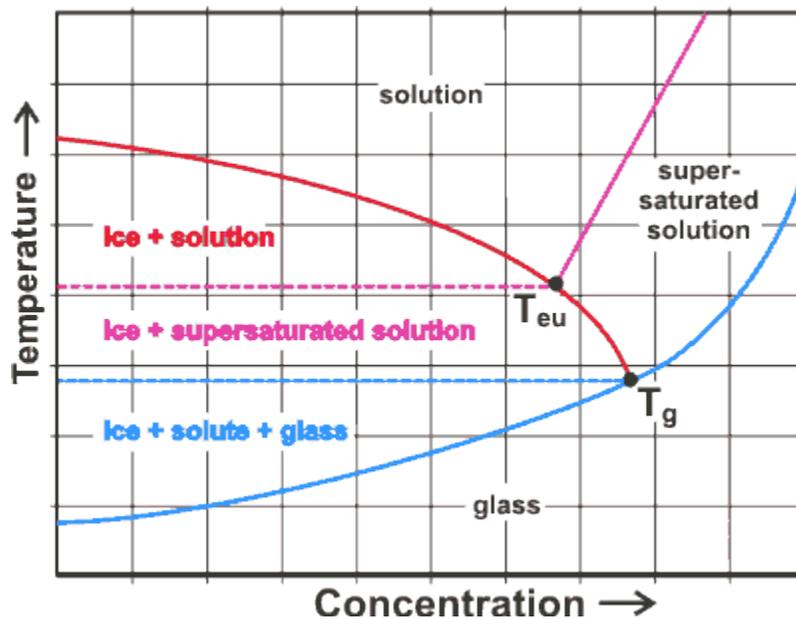
viscosity

$$\eta = \frac{\text{shear stress}}{\text{strain rate}} \quad (\text{Pa s})$$

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The units are either the SI units of pascal seconds (Pa s) or the <u>poise</u> (P).

Eutectic point is the lowest possible melting point (equilibrium freezing point) that a mixture of solutes may have. No other composition of the same materials will have a lower melting point. Thin films of fluid may remain below the eutectic point in microcrystalline ice due to surface effects [<u>1010</u>].

Fluidity is the reciprocal of the viscosity (= 1/η).

In the **glassy state** the viscosity is extremely high (> 10^{12}-10^{13} Pa s), conformational changes are severely inhibited and the material is metastably trapped in a solid but microscopically disordered state. The segmental motion of macromolecules occurs when the temperature increases through the glass transition temperature (see the blue line opposite; T_{eu} is the eutectic point and T_g is the **glass transition temperature** at the end point of freezing).

The **glass transition temperature** (Tg) is the temperature at which the molecular relaxation time reaches 100 s and the viscosity of the system becomes 10^{12} Pa s. It is a kinetic rather than a thermodynamic transition and different methods of cooling produce slightly different glass transition temperatures. Therefore, the value of T_g depends somewhat on the method of its determination; the glass transition (unlike true thermodynamic phase changes) occurring over a range of a few Kelvin. In the diagram, the supersaturated solution is unstable with respect to solution and crystalline solid. Further discussion of this topic may be found in a review of water and solids mobility in foods [720].

Intrinsic viscosity ([η]) is the limit of the reduced viscosity extrapolated to zero concentration. As with the reduced viscosity, it has units of reciprocal concentration, for example, mL g^{-1}.

Kinematic viscosity is the dynamic viscosity divided by the density of the liquid (= η/ρ). The units are either the SI units of meter squared per second ($m^2 s^{-1}$) or the stoke (St).

Poise (P) is a unit of dynamic viscosity (dyne s cm^{-2}). The SI unit of viscosity is Pa s (pascal second = N s m^{-2} = 10 poise).

Pseudoplastic materials instantaneously decrease in viscosity with increase in shear strain rate (for example, flow) and are therefore easier to pump and mix. They are **shear-thinning**. This is often a consequence of high molecular weight molecules being untangled and oriented by the flow. Generally this behavior increases with concentration.
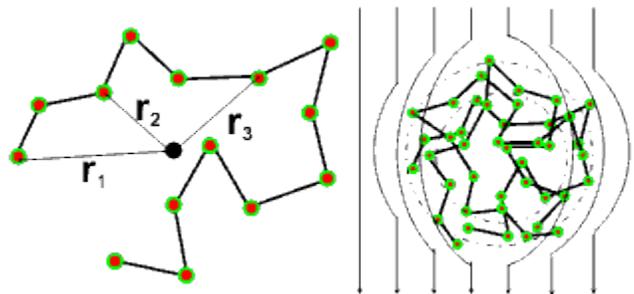
Radius of gyration (R_g) is defined as $R_g = \sqrt{\left(\frac{1}{n}\sum_i r_i^2\right)}$

where n is the number of entities in the chain and r_i is the radius of each from the center of mass

(also defined using the distance between all pairs of entities $R_g = \frac{1}{n}\sqrt{\left(\frac{1}{2}\sum_{ij} r_{ij}^2\right)}$).

Typically for a linear polysaccharide (M_w 10^6) this would be approximately 6 nm if spherically packed

($R_g = radius \times \sqrt{3/5}$), 940 nm if as an extended stiff rod ($R_g = length/\sqrt{12}$), and 17 nm (

$R_g = unit\_length \times \sqrt{units/6}$) if as a random coil. Its relationship to the effective radius the tumbling molecule represents to a flowing liquid (hydrodynamic radius, R_h) depends upon the flexibility and density of the structure; R_g/R_h generally being about 1.6 but lower for branched and globular structures and gels.

Reduced viscosity (η_{red}) is the specific viscosity divided by the concentration. It has units of reciprocal concentration, for example, mL g^{-1}. It is related to the <u>intrinsic viscosity</u> [η] by the Huggins-Kramer equation: $\eta_{red} = [\eta] + k_1[\eta]^2 c$, where c is the concentration.

Relative viscosity (η_{rel}) is the ratio of the <u>dynamic viscosity</u> of the solution to that of the pure solvent ($\eta_{rel} = \eta/\eta_0$ where η is the dynamic viscosity of the solution and η_0 is the dynamic viscosity of the solvent). As it is a ratio, it is dimensionless having no units. It is related to the <u>intrinsic viscosity</u> [η] by the Huggins-Kramer equation: $\ln(\eta_{rel})/c = [\eta] + k_2[\eta]^2 c$, where c is the concentration.

Shear stress is the force divided by area parallel to the force, F/A. The SI unit is the pascal, Pa.

Specific viscosity (η_{sp}) is one less than the <u>relative viscosity</u> ($\eta_{sp} = \eta_{rel} -1$; $\eta_{sp} = (\eta - \eta_0)/\eta_0$ where η is the dynamic viscosity of the solution and η_0 is the dynamic viscosity of the solvent). As with the <u>relative viscosity</u>, it has no units.

Stoke (St) is a unit of kinematic viscosity (cm^2 s^{-1}). The SI unit of kinematic viscosity is m^2 s^{-1} (= 10000 stoke).

Thermogelling materials gel above a temperature; usually reversible.

Thixotropic liquids exhibit a time-dependent response to shear strain rate over a longer period than that associated with changes in the shear strain rate. They may liquefy on being shaken and then solidify (or not) when this has stopped.

Source : <u>http://www1.lsbu.ac.uk/water/hyrhe.html</u>