

The Abbott Instant Guide to Rheology Or What I wish I'd been able to read when I was trying to understand rheology

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Introduction

What is it about rheology that makes it so hard for us all to understand? We all know that we should understand it and use it every day. Yet somehow it seems to be easier just to measure a few viscosities at a few shear rates and hope that we don't need anything more sophisticated.

Besides, a fancy rheometer is an expensive bit of kit; can we really justify having a few of them around in the lab just so we can do some fancy experiments?

This document is what I would have liked to read whilst I was struggling to understand books, articles, web-sites on rheology. If you find it useful, great. If you know it already, even better. If I've not explained myself properly or have missed things that are important to you, well at least I tried.

Starting with confusion

I can never forgive whoever it was who decided to give two different (but related) concepts names that start with the same three letters, sound similar and, even worse, in common speech mean the same thing. I'm talking about "stress" and "strain". The whole of rheology depends on these two concepts, yet we get off to a bad start not able to remember which is which. To say that my life is under "stress" or under "strain" is to say approximately the same thing. Yet for rheology stress and strain are completely different. Things would be much easier if we could give them distinctive names, but we can't change decades of rheology so we have to overcome the confusion.

Strain is an extension, a dimensionless ratio of Increase_Of_Length/Length. If I pull on something with a strong force and it gets 1% longer then we can say that Strain = 1%. Because we're often pulling on viscous materials, it's really important to know what strain we're producing.

Stress is a force per unit area. So when I apply a stress to something then its dimensions will change. It might, for example, get 1% longer so my stress has caused a strain of 1%. Now, if I wrote "my strain has caused a stress of 1%" it sounds more or less the same and you can imagine a strain as being a force and a stress could be an extension, so it's very, very easy to get confused. Somehow we need to get used to the fact that stresses cause strains, and not the other way round.

To make things worse, in rheology we show Strain as γ and Stress as τ . Why? I just don't know. So when we say that a shear modulus = Stress/Strain we say $G = \tau / \gamma$. And when we want to talk about viscosity η we say that $\eta = \tau / \dot{\gamma}$ where $\dot{\gamma}$ is the strain rate. How are we supposed to remember what all these things mean? To add more confusion, some people use μ instead of η as the symbol for viscosity – as a chemist I use η but engineers tend to use μ .

Another confusion comes from units. Shear is in Force/Area which means Newtons/Area which means N/m^2 . For viscosity we're usually comfortable using "centiPoise" (cP) because water is a familiar 1cP, olive oil ~ 100cP, glycerine~1000cP, honey ~ 10,000cP. However, in calculations we need viscosities in Pa.s, where 1Pascal = $1N/m^2$ so one Pa.s is $1N.s/m^2$ which isn't the most obvious of units. The fact that $1000cP=1Pa.s$ means that converting between them is easy (so glycerine has a viscosity~1Pa.s). But there's further confusion. A cP is $1/100^{th}$ of a Poise. And Poise and Pascal.s both begin with P so it's easy to mix up them up (yes, I've done it myself and so have many other people). So if you are told that something has a viscosity of 1Poise it's easy to get confused into thinking that it's 1Pa.s, and you would be out by a factor of 10 because $1Pa.s=10Poise$.

Finally, rheologists tend to talk of "strain rate" but in the real world we tend to talk about the "shear rate". It turns out that our sort of strain is "shear strain" so really we should always be talking about the "shear strain rate" which some people shorten to "strain rate" and others shorten to "shear rate" or even to "shear".

No wonder we find rheology confusing!

Clearing up confusion

When I don't properly understand something I find it really helpful to write an Excel spreadsheet (or, if it's too complicated, a computer program) so that I can "play" with all the inputs to see what happens to the outputs. So as part of this Guide I've provided a spreadsheet that has allowed me to make sure that I know what I'm talking about and which gives me a nice source of diagrams for the Guide and which allows you to play too, so you can make sure you understand it your way.

I can't change the words "strain" and "stress", I can't avoid using η , τ and γ in equations, I can't make 1Pa.s a more convenient unit, but I can make sure that for each equation you can go to the spreadsheet to make sure you understand what's going on.

And fairly often I will put a reminder after the word stress (applied force) and strain (elongation) so you don't have to remember which is which. If these get a bit repetitious then congratulate yourself – it means that you have no trouble remembering which is which.

So when you read this Guide, make sure you have the spreadsheet open at the same time; life will quickly become less confusing. Guaranteed!

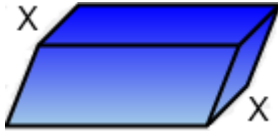
Viscosity

We know what it is, but we have to remind ourselves formally what it means.

I have a rectangle of liquid of height Y and surface area A:



The bottom surface is fixed. I push the top surface with a force F which produces a stress τ ($=F/A$) and it moves a distance X in time t.



The strain, γ , is X/Y . This makes sense: the larger X or the smaller Y , the bigger the % increase so the larger the strain.

Remember that we moved a distance X in time t and $\text{Velocity} = \text{Distance}/\text{Time}$, so $V = X/t$. The *strain rate*, γ' is $X/t/Y$ or V/Y with units of “per second”, $1/s$. Why “per second”? Velocity is m/s , Y is m so $m/s/m = 1/s$.

What we find, for simple liquids, is what we'd expect intuitively: the harder we push, the bigger X and V . But exactly how hard we have to push to go a distance X in time t depends on two things:

- The resistance of the liquid
- Y

It's easy to see why the resistance is important. But why is Y important? Well, imagine that the liquid has a very large height, Y . The stationary part of the liquid is a long way away, so its influence on the liquid at the top is small, so a large X (or V) is easily achieved with a small push. Now imagine that it's a very thin layer of liquid. You're trying to have a fast-moving layer of liquid very close to a slow-moving (in fact, stationary) bit of liquid and that's hard to do (we'll explain why soon).

Putting this all together we can say that $\tau = \eta \cdot X/t/Y$ (or $\eta \cdot V/Y$) where η is a constant. But we know that $X/t/Y$ is the rate at which the strain, γ , changes, i.e. γ' . So finally we see that $\tau = \eta \cdot \gamma'$ which is the classic equation of viscosity because the constant, η , is the viscosity.

Let's spell out that equation: The higher the stress, τ , the larger the strain rate, γ' , i.e. the larger the change of strain with time. The constant of proportionality is the viscosity η .

Or to put it in terms that interest us, $\eta = \tau/\gamma'$, which says that viscosity is $\text{stress}/\text{strain_rate}$. So a high viscosity liquid needs a high stress for a given strain rate or gives a low strain rate for a given stress. This all makes intuitive sense.

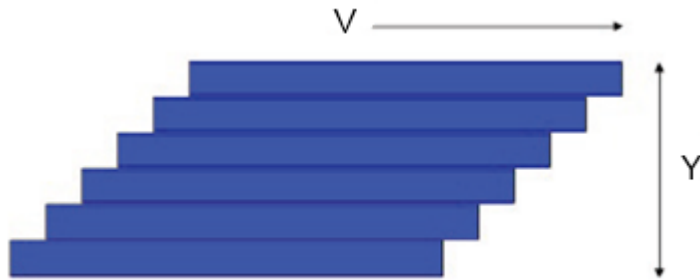
As a sanity check we note that τ is in N/m^2 , γ' is $1/s$, so η has the units $N/m^2/(1/s) = N \cdot s/m^2$ which is what we showed earlier.

On The Basics worksheet in the spreadsheet you can play with all the variables to see how they come together.

We all know that the assumed constancy of η applies to many simple liquids such as water or glycerine and this is called Newtonian viscosity because the equation was derived by Newton. We will discuss non-Newtonian viscosity later.

But first, what *is* viscosity. The definition tells us how to measure it, but where does viscosity come from?

The classic analogy is with a pack of cards.



As you slide the top card with velocity V all those cards have to slide over each other, with friction between them. The faster V or the smaller Y , the more friction loss there is between cards so the harder you have to push, so $\tau \sim V/Y$. And different packs of cards have different friction forces between them (let's call it η) so $\tau = \eta \cdot V/Y$. But what does this have to do with real viscosity?

A real fluid flows in layers, called streamlines. Each streamline is like one of the cards in the diagram. Imagine you are a molecule in the 2nd layer from the top. You are moving with a velocity slightly lower than V . But by chance you stray upwards and find yourself in the top layer. Suddenly those faster molecules bump into you and you slow them down. Or if you strayed into the 3rd layer you would bump into slower-moving molecules and tend to speed them up. Viscosity arises because of this random motion between streams. Think of the impact of "lane jumpers" on crowded freeways. Nice flows of traffic are messed up every time someone changes lanes. Incidentally, lane jumpers are a nuisance to everyone, including themselves. They think they are travelling faster but in fact they slow down everyone, including themselves.

And when the molecules are polymers you can see that half a chain in the top layer gets tangled with the faster moving polymer molecules whilst the other half of the chain is tangled with the slower moving molecules so there is a much bigger mix-up between the two layers, in other words, a higher viscosity. This isn't just a nice analogy. It's what really happens. And it now makes it easy to understand where non-Newtonian viscosity effects comes from.

Shear rate dependency

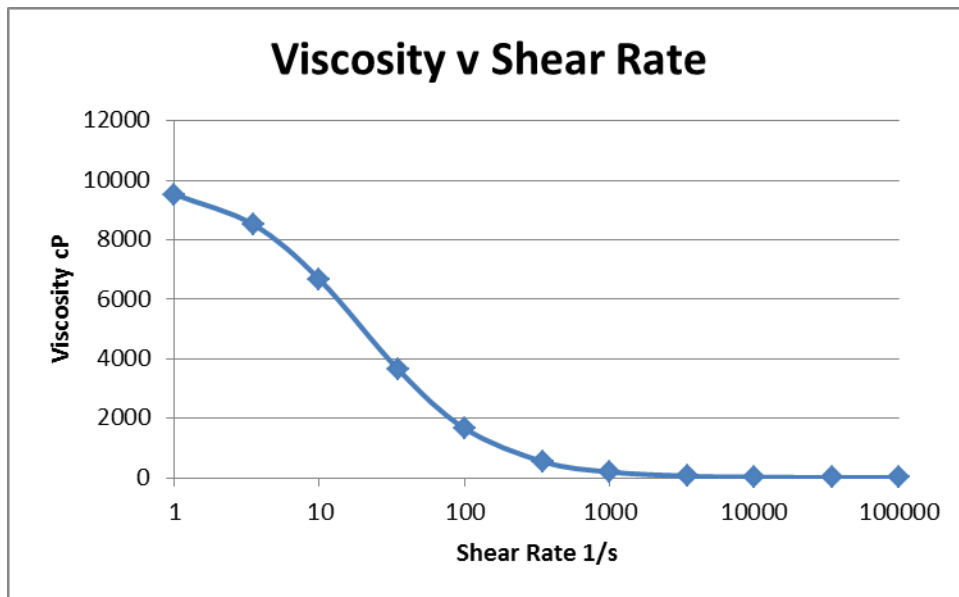
Note that I've completely changed language from "strain rate" to "shear rate" because that's the language we use in this industry.

There's nothing really surprising about viscosities changing with shear rate. Imagine our polymer chain caught between two of the streamline layers. As the shear rate increases the velocity difference between layers gets higher so the fast half of the chain is pulled more forward and the slow half is dragged back more so that the polymer becomes more and more aligned with the streamlines. But if it's more aligned, it has less chance to straddle the two streamlines. In other words, the polymer provides less of a drag, so the viscosity decreases.

Although the simple explanation tells you why the viscosity decreases with shear rate, it doesn't tell you how much it decreases. There aren't really any simple explanations so we have to make do with formulae. I use the Cross formula which you can find in the Shear Effects worksheet on the spreadsheet:

$$\text{Viscosity} = V_{\text{inf}} + (V_0 - V_{\text{inf}}) / (1 + (\text{Alpha} \cdot \text{Shear})^n)$$

and a typical example of the results of the formula are shown:



What does the formula mean? At any given shear rate, the actual viscosity depends on V_0 , which is the viscosity at (very) low shear, V_{inf} , the viscosity at infinite (well, very high) shear rate and the two parameters Alpha and n which control the overall shape of the curve between V_0 and V_{inf} . Because you have the spreadsheet you can go to the Shear Rate worksheet and play with the parameters. In the spreadsheet you have the same data plotted within logarithmic shear (as above) or linear shear. Each form is useful in different circumstances.

For those who like fancy names, the above formulation is termed **pseudoplastic**. If the viscosity increased with shear (e.g. corn starch which allows you to walk on a swimming pool full of the stuff) then it's called **dilatant**. Although I'm only discussing shear thinning in this Guide, the Cross model lets you model dilatant effects too. Feel free to play with the parameters in the spreadsheet any way you want.

Some of you might have said that the above graph was an example of thixotropy. Sorry, you're wrong in an important way as I will explain in a moment.

Who cares about shear thinning?

We all should! In what follows I use a cosmetics example. You can (and should!) easily think of examples in your own area of rheology.

Sitting in a pot it might be really nice that you have a thick, rich, (i.e. viscous) cream. But when you rub it onto your skin you want it to offer little resistance to rubbing, so you want low viscosity. Or if it's coming out of a tube you don't want too much resistance, but you don't want it to squirt out too quickly. So to design your cream you need to know the shear rates for each of the important moments that your customer will encounter it and then make sure you have the right viscosity at that shear rate.

In the pot, the shear rate is 0, so the viscosity is V_0 , which is nice and easy to understand. Though hold on a second. What V_0 do you need for your cosmetic? If the consumer opens a pot and sees a runny liquid they might not be too impressed. Yet if it's so viscous that it doesn't level out between uses, they might not be too impressed either. Getting V_0 right is important, though at these low shear rates (and therefore low stresses) there are other issues we'll discuss soon.

There are other key moments in your customer's experience. Shear rate is Velocity/Gap, so coming out of a tube with a hole 0.5cm diameter at 5cm/s the shear rate is $5/0.5=10/s$. Rubbing 100nm of cream on the skin at 1m/s is $1/0.0001=10^4/s$, which is very high shear.

You may also need to know the shear rate during manufacture. For potting out, the rate might be $\sim 10/s$. In a "high shear mixer" rates are typically $10^2-10^3/s$ and in large-scale manufacture I suspect that rates are at the lower end of the scale.

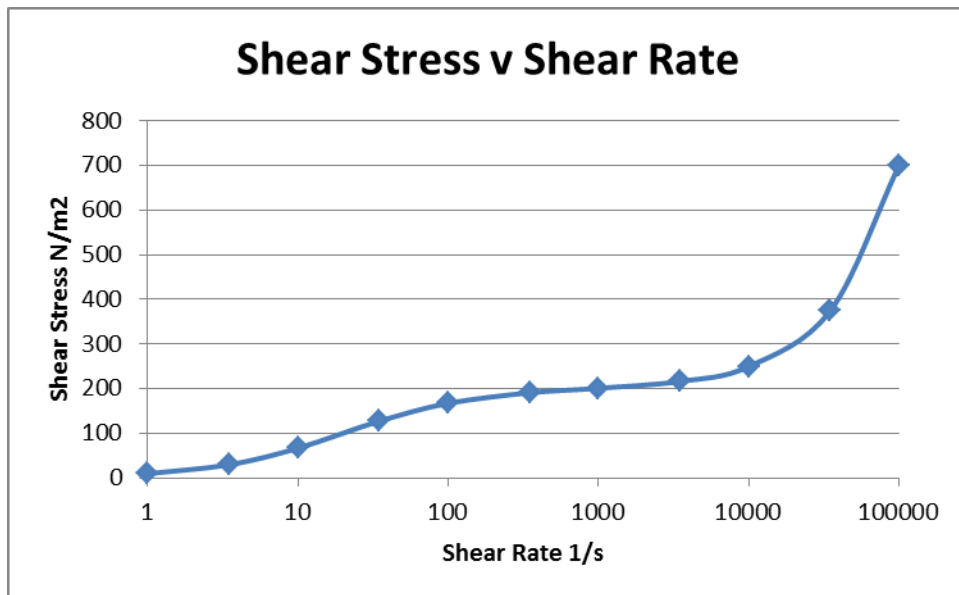
The spreadsheet lets you create a list of the key steps and calculates the viscosity for you. Here are the values I chose to enter for the above scenarios for the viscosity curve shown in the above graph.

Where	Shear/s	Viscosity cP
In the pot	1	9524
Potting out	10	6668
Out of the tube	10	6668
Mixing	100	1671
High shear mixing	1000	201
Rubbing	10000	25

So to fully grasp what your formulation will do during manufacture and use, you really need a full viscosity v shear rate curve. You *can* get these from (fancy) viscometers. But there is lots more you need to know that you can only get from a rheometer. So make sure your boss understands that you can't do your job without a rheometer. A decent rheometer can crank out viscosity/shear curves and automatically provide you with the parameters for a Cross model fit which you can then put into the spreadsheet for study against your own needs.

Other ways to plot the same thing

Most of us like to see Viscosity v Shear Rate plots. But rheologists and rheometers are much happier doing Stress v Shear Rate plots because that's what their machines actually measure. I find these plots completely unhelpful because I'm only interested in the viscosity. The plot of Stress v Shear is exactly the same data, because from stress and shear rate you get viscosity and from viscosity and shear rate you get stress. The spreadsheet calculates the plot for you so you can see what a rheologist sees. But it took me a long time to convince myself that this plot of exactly the same data didn't contain some spreadsheet error that made it look so odd.



If you set $V_0=V_{inf}$ in the spreadsheet and look at the Stress v Shear plot it will still look odd on the log-scale, but on the linear scale you'll get a graph that makes sense to you. Try it for yourself!

Time dependence

Many viscometers come with special helical devices that move through your material when the measurement is being made. This is their attempt to make sure that the measurement is always on "fresh" material because they know that for many systems the viscosity, at a fixed shear rate, decreases with time. In a typical rheometer using, say, a cone and plate device, it's simply assumed that there is a good chance that viscosity varies with time, so the viscosity is calculated from the very first revolution and any decrease (or increase) with time is plotted. Incidentally, a rheometer usually requires much smaller samples for testing, so you don't have to make so much of each formulation if you have to do a lot of tests.

Systems which lower their viscosity over time at a constant shear are called **thixotropic**. For those who like fancy words, those that thicken over time are called **rheopectic**. As it happens, if something is thixotropic it's highly likely that it is also pseudoplastic (shear thinning, as discussed above). But there are many systems that are pseudoplastic that are not thixotropic.

For a formulator it is very important for you to know whether you have a system that is just pseudoplastic or if it's also thixotropic.

Why does it matter? Again, let's use a familiar cosmetics example.

Suppose I'm a consumer and take some cream out of a pot. By swishing it with my finger I've applied some shear. If I decide to take another bit I might find that the second bit comes out "differently". Consumers in general don't like surprises. They want their cosmetic to behave predictably. Thixotropy means that it's not predictable.

However, if you know what you are doing, you can use thixotropy to your advantage. If you want the customer to experience an initially "rich" thick cream and then want them to magically make it thinner ready for application, then you need thixotropy.

But be careful. Not only do thixotropic systems thin on shearing, they also thicken when you stop shearing. The speed at which the viscosity recovers may be totally different from the

speed at which it was lost. A stir for 1s might halve the viscosity and it then might take 60s to recover. So if you get into the game of thixotropy you really need to know your numbers.

Measuring thixotropy with a viscometer is possible but not pleasant. So, as I keep insisting, just get yourself a rheometer and program it to do a “thixotropy” sweep and it will get you all the information you need: rate and size of viscosity decrease at each shear rate and time, plus recovery times from different reductions in viscosity. I’ve not attempted to model the complexity in the spreadsheet, but you can imagine it for yourself. A rheometer will typically plot stress v time at a given shear rate and you will see it decrease for a thixotropic material. Fortunately the shape of the curve is the same as viscosity v time so in this case you can intuitively work out the viscosity data even if you get stress data.

Is your liquid a solid?

That seems a strange question. But many applications require the answer to be “yes”. For example, many cosmetic gels are “solid” under the right conditions.

One characteristic of a solid is that if you apply a stress (a force) to it then you get a strain (a movement), just like a viscous liquid, but when you let go of the stress, the strain undoes itself and the solid springs back to its original shape. For a liquid, the strain is irreversible.

For some viscous liquids it turns out that for a very small stress the strain recovers when the stress is removed. At these small stresses, therefore, the liquid behaves as a solid. The stress at which the solid becomes a liquid, i.e. when the strain becomes irreversible is called the **Yield Stress**.

Typical yield stresses for formulations are small so you need delicate equipment to measure it. But once again, a typical rheometer will do it with no problem.

Cosmetics provide a good example of why knowing yield stress is important. Again it should be possible to think of similar arguments in your own domain.

The feel of a cosmetic with a (comparatively) high yield stress will be different from one with a (comparatively) low yield stress. In many cases a high yield stress is undesirable because the consumer sometimes finds that the cream flows and sometimes doesn’t, i.e. your formulation is unpredictable, which is generally undesirable. But if you know what you are doing then a high yield stress can give the impression of an expensive formulation. Remember, that most of us think that a viscous shampoo is much better than a runny one, even though the viscosity comes from additives that do nothing for your hair and make it rather harder to get it out of the tube (especially, I find, in hotel bathrooms). There is no logic to thinking that a “strong” cosmetic (or a viscous shampoo) is “richer” than the alternatives, but if that’s what customers want, you’d better learn how to provide it.

At the very least, you should be measuring the yield stresses of your most serious competitor products to see if they are using this trick to impress their customers or if, conversely, to see if one of your competitors is upsetting their customers with an unreliable feel because the yield stress confuses them.

A high yield stress can be guaranteed to annoy customers in one particular case. Suppose you have a nice pot of your cream with a pump action dispenser. The customer loves your cream and soon gets through the pot and will be eager to buy some more. But they find that stuff around the edge of the pot doesn’t flow to the inlet to the pump. This means that they feel cheated – you’ve sold them cream they cannot use. So if your product is going to be sold in a pump dispenser, make sure there is no yield stress. This absence of yield stress means that the cream has always had a chance to flow and sit under the pump inlet ready

for the next squirt, down to the final drop. If that flow is slow, the customer doesn't mind. They just want their "rich" cream to be available next time they come to pump it.

The importance of Deborah

In Judges 5:5 the prophetess Deborah made a profound rheological observation. She noted that "The mountains flowed before the Lord". In other words, if you wait long enough, even a mountain is viscous and will flow. Her insight has been immortalised in the Deborah number which is the ratio of the response time of the system to the time of observation. For a mountain being stared at for one hour the Deborah number might be 1billion hours/1 hour or $1E09$. For water it might be 1nsec/1sec or $1E-09$. In other words, in a timescale of 1 hour, a mountain behaves not like a viscous material but like an elastic solid because its Deborah number is $\gg 1$. And for water, in 1sec it behaves like a viscous liquid and not at all like a solid because its Deborah number $\ll 1$.

The point of introducing Deborah is that the yield stress discussion in the previous section is meaningless. If I measure the yield stress of a mountain over a 10 billion year timescale (don't try this at home) it will appear to be a pure liquid. If I measure the yield stress of water on the picosecond timescale it will probably look like a rock solid. Indeed, pure water has a modulus approximately the same as steel when measured on very short timescales.

In other words, to understand your formulation you need to know how it behaves over the sorts of timescales that are relevant to its use. In cosmetics if you are making a super-fast acting cream, then you must test your yield stress at short timescales. If you want a long, slow-acting cream you need to measure things over a longer timescale.

Whilst we are on the subject of ancient writings, "rheology" comes from the ancient saying (variously attributed to Heraclitus or Simplicius): Πάντα ῥεῖ, "panta rhei" or "everything flows". When rheology was invented by Charles Bingham he didn't have a snappy name for the subject and got the idea from a classic professor of using this quote and creating a science of flow-ology or rheology. His colleague Markus Reiner was familiar with the Bible and came up with the Deborah quote and the Deborah number as a counterbalance to Heraclitus. Reiner also comments that letters intended for his Department of Rheology often arrive addressed to the Department of Theology.

These discussions bring us to the scariest pair in rheology, G' and G'' and their terrifying offspring, $\tan \delta$.

Oscillations, phases, elastic and plastic.

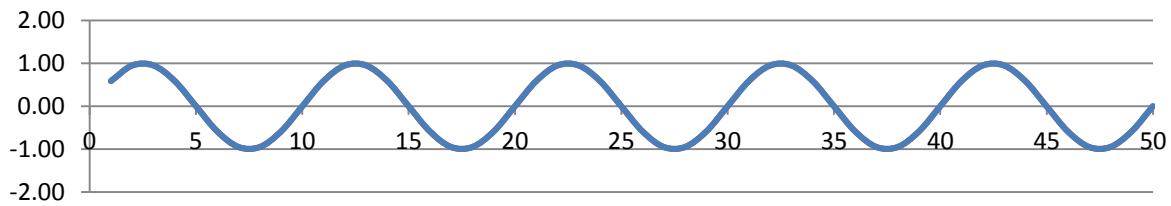
Because this is the scariest part of the whole of rheology, the Oscillations worksheet in the spreadsheet does all the calculations for you and you can play around with the values to see how it all hangs together. It's really not that hard!

We typically imagine our shear to be applied in a straight line in a continuous manner. But there's no reason why we can't apply it via an oscillating motion. Imagine, for a moment, that you apply an oscillating force (stress) to an elastic solid and, at the same time measured the deformation (strain). As you increased the stress the strain would increase at exactly the same time and as you decreased the stress to zero then reversed it, the strain would return to zero then go negative. Doing this would be a rather complicated way to show that Stress/Strain is a constant which is good old Hooke's law of a spring and that constant is called the modulus, G

$$G = \text{Stress/Strain}$$

The graph showing the Strain response along with the Stress stimulus is in two colours, but as they exactly overlap, you just see one line:

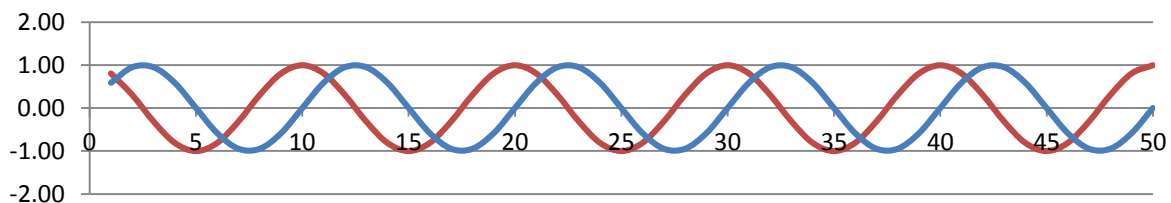
In Phase (0° $G''=0$)



In this case the G we are calculating is called G' .

Now try doing the same experiment with a pure viscous liquid (in other words, with a small Deborah number). As you increase the stress, the bit of liquid next to your stress-inducing device is keeping up with you, but the rest of the liquid is rather lagging behind. When you come to reverse the stress, your top bit of liquid follows you precisely, but the stuff below carries on in the original direction before realising that you've changed direction and it takes some time to reverse direction. In other words, the response lags behind the stimulus by 90° :

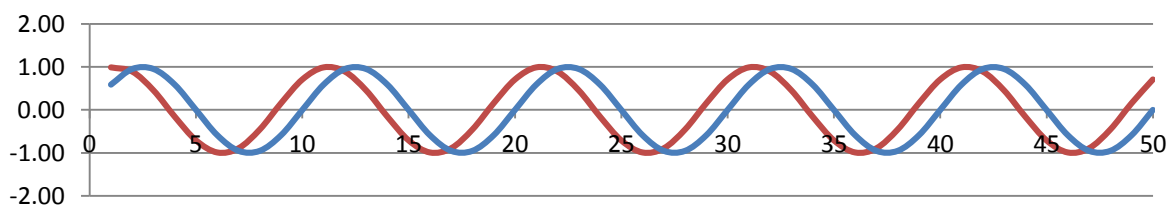
Out of phase (90° $G'=0$)



You can still calculate a $G = \text{Stress}/\text{Strain}$, but only if you take the values separated by 90° , in which case the calculated G is called G'' . Incidentally, if you look at some on-line rheology guides they show the out of phase plot with a 180° lag (peaks overlapping troughs) when they are talking about a 90° lag. This confused me greatly when I was preparing the spreadsheet because such plots have been prepared by rheometer companies and I at first assumed that they were right and I was wrong.

If you have something that is somewhere between an elastic solid and a viscous liquid you have some other behaviour:

Equal G' , G'' (45° $G'=G''$)



In this example it happens that the modulus is made from two components, G' and G'' which happen to be identical.

What we mean by "phase" is whether the peaks and troughs are together (phase= 0°), whether they are completely opposite (peaks coincide with troughs, phase= 180°), where the peaks of one coincide with the zero crossing of the other (phase= 90°) or anywhere between.

The phase angle is called δ . Although as humans we think of angles in terms of degrees, all the calculations have to be done in terms of radians. So the calculation with a phase angle of 90° is performed with $\delta=1.571$ which is $\pi/2$.

We now know that G' is the classic modulus for an elastic solid, the “bulk” modulus, the “Young’s modulus” or, as it’s called in rheology, the **storage modulus** because the stress energy is stored as you increase the stress then recovered when you release the stress.

G'' is a sort of “virtual” modulus (the two moduli make up an imaginary number based on the square root of -1) and is called the **loss modulus** because the energy from the stress is completely lost (well, it appears as heat) and not recovered.

For most materials there is a bit of both present. The ratio, G''/G' happens to be equal to $\tan \delta$. A small $\tan \delta$ means that G'' is small, so your material is nearly perfectly elastic. A large $\tan \delta$ tells you that G' is small, so your material is nearly perfectly viscous. And values in between tell you that you have a mixture of both.

Once you start to see plots of G' and G'' you quickly learn to spot where G' is higher so the material is elastic and where G'' is higher and the material is plastic. Plastic? Yes, another way to talk about viscous deformation is a plastic deformation. We tend to use “viscous” because we are generally interested in viscous systems. For polymer scientists it is assumed that the polymer is generally elastic, so if it starts to show viscous behaviour they call it “plastic” behaviour. It’s funny that the common word “plastic” is exactly the wrong word. A polyethylene bucket behaves mostly like an elastic. If it were really a plastic bucket it would not be much use for carrying heavy loads because it would deform irreversibly under the weight.

Who cares?

Again, you should care. Well, actually, you probably know if your formulation is a pure solid or a nicely viscous liquid so why would you want to do all these oscillation measurements?

The answer is Deborah. In all the graphs above I never said what the frequency was. If your rheometer runs the experiment at a nice, slow frequency then many formulations will behave as pure viscous liquids. But if you crank up the frequency, you might find that you’ve changed the Deborah number and your formulation is starting to behave with quite a lot of elasticity.

Because a rheometer doesn’t get tired of doing boring measurements, it’s very easy for you to ask it to measure G' , G'' and $\tan \delta$ at a big range of frequencies. In fact it’s standard to run a “frequency sweep” to get these data. If over the timescales that matter to you your G' (elastic) remains small and your G'' (viscous) remains large then you know your material won’t cause you or your user (e.g. manufacturing) any surprises. But if there is some big change right in the middle of the timescales that concern you, then you either really need to know about it before it confuses you in formulation, manufacture or end-use.

And there’s more. If you run the experiment with an amplitude sweep (starting with small stress amplitude and getting larger) you might find that it’s elastic at low amplitude and viscous at higher amplitudes. At the low amplitudes the small stress might mean that you have not exceeded the yield stress.

And of course even at constant frequency and amplitude over time you might see changes in G'' because the viscosity is getting lower due to thixotropy.

So really, if you set up your rheometer to do G' , G'' sweeps you can get all the information about all the effects that are of interest to us. The trick is to not be frightened by the

terminology and look for whether you are primarily in G'' territory or G' territory and how they change with time, frequency, amplitude.

We haven't even mentioned temperature. But clearly you need to worry about how your formula behaves in the pot at, say, 20°C and during application at, say, 35°C. Often there won't be much difference, but if there is you've got a potential problem. So when you set up your rheometer run, make sure it does the measurements at two temperatures, not just one. Those machines don't mind working for a living. You just need to know which buttons to press to get you the most information for the least work on your part.

Time-Temperature Equivalence

It doesn't take a genius to know that something which is elastic at low temperatures will be plastic (viscous) at high temperatures when it melts or goes above its T_g or some phase transition relevant to your application.

And you now know that measuring a viscous material quickly can show it to be a solid, and vice versa.

One of the amazing general laws of physics is "time-temperature equivalence". In many cases you can mathematically shift temperature-dependent behaviour into an equivalent plot in the time-dependent domain, or vice versa. For example, if you have a set of data (e.g. adhesion versus speed) taken at different temperatures, their curves are totally separate. But if you mathematically shift them to a common temperature (e.g. T_g) the lines all overlap into a continuum, but over a very different time range than the original. This mathematical shift is called the WLF equation (after Williams, Landel and Ferry):

$$\log(a_T) = \frac{-C_1(T - T_r)}{[C_2 + (T - T_r)]}$$

As it is rather hard for most of use to visualise the effect of the WLF equation, the TempTime spreadsheet does it for you. Once you start looking for Time-Temperature Equivalence you will find it everywhere.

Viscoelasticity

When we have significant values for both G' and G'' (or tan δ is an intermediate value) we have viscoelasticity. In general, viscoelastic materials are a real pain. They don't pour nicely, they get all stringy when you pull them apart and they can often have a "yuk" factor. Their behaviour (relative sizes of G' and G'') change with frequency and time so you need many more parameters to describe them. You start having to use Maxwell models and think about dashpots. My recommendation is to not go there if you can avoid it. Experienced formulators show their experience by doing "stringy" tests between their fingers. Who needs a rheometer when you have a pair of experienced fingers? But such tests don't compare to real numbers. If you have a set of formulae that are "stringy" to various extents, it should be possible to use, say, DOE techniques to know how to reduce the stringiness. But if the test results depend on someone saying "This one is a bit stringier than that one" you're in trouble. A rheometer will give you numbers and insights (e.g. frequency effects) that a stringy test just can't give.

A rheometer in QC?

The fancier you make your product, maybe the fancier the price you can charge your customers. But you have to pay a price too. If you are relying on thixotropic and/or yield stress and/or viscoelastic effects for performance then you either need a superlative grasp of your formulation to make sure it gives the same parameters whatever Production do to it, or you have to have an expensive rheometer in QC plus some highly trained staff who know

how to interpret the output. Imagine, it's 03:00 in the middle of the night shift and G' is 20% below the target value and $\tan \delta$ is out by 13%. What does QC tell Production? In other words, how do Production fix a formulation with the wrong yield stress or the wrong thixotropic parameters or the wrong viscoelastic behaviour?

And that's it

I know, there's plenty more to rheology than this. But with just a few rather simple ideas such as shear thinning (pseudoplastic), time thinning (thixotropic), yield stress, Deborah number and G' and G'' to tell you where you are in the elastic to viscous continuum, you have more than enough to really get to grips with optimizing your formula. I can't tell you which additive to add in which % to get you the right balance of G' and G'' . But I am confident that if you routinely formulate with a rheometer and get all these numbers all the time (even if you don't need all of them all the time), your ability to spot interesting phenomena (or spot possible problems) and create that perfect formulation will be greatly enhanced. That's guaranteed!

Good luck with your formulations!