Advances in Additive Manufacturing of Materials: Current status and emerging opportunities

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Fundamentals of Rheology

Lecture 31

In this lecture I will be covering some of the important concepts of rheology. Now these concepts are mostly relevant for extrusion printing of soft hydrogels. this particular lecture should be considered as an integral component of the description of the process science for 3D extrusion printing of soft hydrogels or soft biomaterials. if you look at the different materials and particularly different liquids, you start from our daily life like water, we use for various regular uses as well as the oil for cooking oil and so on. these are like some of the examples of the viscous liquids. Then if you go towards the soap which is detergents, egg white, these are not essentially viscous but if you look at that yellow substance within the egg, so this egg white that actually is not a viscous but viscoelastic material.

Then if you go to polymer melt, it also is viscoelastic material. viscoelastic essentially means it is a combination of viscous liquid and elastic solid. And what are the elastic solid we are talking about? Like ceramic is a classical example of the linear elastic material. Metal is also elastic and plastic.

So, when you deform this material initially the deformation is more elastic then goes to the plastic. Elasticity essentially described by the spring model. Like springs, you stretch it, the moment you release it, it comes back to the original position. Viscoelasticity essentially is described by the spring dashpot model. this is the dashpot here and this is the spring.

if you stretch it, so that spring and dashpot combination essentially describe the viscoelastic material and if you have a viscous liquids, then viscosity is nothing but stress by strain rate and from your basic mechanics, you remember that modulus is nothing but ratio of the stress versus strain. this is what has been mentioned again in this plot that this is that your elastic this slope of the linear part and this is the slope of the linear part of the stress versus shear rate which give you the n (eta) is the viscosity. Rheometer is the equipment which is been extensively used to measure or to determine the rheological properties of any viscous or viscoelastic fluids. Now detailed description, detailed functioning of the rheometer is outside the scope of this particular course. However, one must know that is something called parallel plate rheometer which has been extensively used by researchers to analyze the viscosity of the materials So, you have the displacement sensor and then you can also apply the torque to the materials and then you see the response of the materials under the application of torque.

how does the rheometer work? Essentially, again if you go back to the rheology, it is a stress with deformation relationship. If you distort a block of material by applying the shear stress, shear stress is F by A. F is the force that you are applying equal force into opposite directions on the two parallel planes that is force divided by the area on which that you are essentially applying the force. Shear strain, essentially delta x, delta x is the relative displacement of the top plane with respect to the bottom plane and y_0 is the distance between the two planes. Then there is shear rate, it is defined as the 1 by y_0, that is y_0 is the distance between two planes, dx t by dt, that is that how the relative displacement of the top plane changes as a function of time and that is how the shear rate has been mentioned.

shear strain we have defined in this slide and shear rate also we have defined in slide. n (eta) is the material function, the viscosity and this is the constitutive equation n (eta) is equal to stress divided by strain rate. viscosity is nothing but stress by strain rate there is Newtonian behavior and non-Newtonian behavior of fluids. in case of Newtonian behavior, viscosity is independent from shear rate and shear stress and viscosity only changes as a function of temperature T. In non-Newtonian behaviour, viscosity is shear dependent, that function of n (eta).

Viscosity is shear dependent and also viscosity is time dependent. time dependent behavior can be described by either thixotropic behavior like how viscosity decreases with time or rheotropic or rheopectic behavior how viscosity increases with time. That means one is that shear thickening behavior and one is shear thinning behavior. In shear thickening behavior also can be analyzed by plotting viscosity with shear and if it increases then it is called shear thickening and if the viscosity essentially decrease with shear, it is called shear thinning. in case of the 3D extrusion printing these two behavior one is the shear thinning and one is the thixotropic.

This combination of behavior is essentially ideal gel behavior for successful 3D extrusion printing of the viscoelastic gels. Newtonian fluids the viscosity is independent of the shear rate and shear stress that means if you plot the viscosity as a function of shear stress or shear rate like sigma by gamma dot then viscosity is constant. And if you plot stress versus shear rate that viscosity is sigma by gamma dot so this is a constant and this constant is essentially viscosity. I repeat viscosity is n (eta) is equal to sigma by gamma dot and then this has been already mentioned here in this particular slide. And then if you go to this shear thinning fluid, so as I said shear thinning fluid can be described either by decrease in the viscosity with increase in the strain rate.

And also if you look at the n (eta) versus sigma that also shows a decrease and what are the popular example like paint or coating these are like shear thinning behavior. What are the important specification of the rheometer like as I said before that in this particular schematic diagram that you keep the sample between the two parallel plate and this in the central region you give the torque and this is attached to the non-contact drag cup motor where displacement sensor is placed and you measure strain or rotation here. And in this kind of case what is the torque range that you are used, what is the angular resolution, what is the angular velocity range, frequency range and normal force that are being applied. now if you change the plate diameters. if it is a 20 millimeter diameter to 60 millimeter diameter as plate diameter increases shear stress is increases simply because sigma is equal to m into 2 by pi r cube.

as this gap between the 2 plates that decreases from 2 millimeter to 0.5 millimeter. H essentially decreases shear rate gamma dot is nothing but omega into R by H that also essentially increases this plate gaps. Effective shear rate essentially varies for a parallel plate. Here, gamma is dx by h.

So, dx increases further from the center and where h is essentially constant. For a given angle of deformation, there is a greater arc of deformation at the edge of the plate than at the center. Now in case of cone plate rheometer, so there are two types , one is a parallel plate and one is a cone plate The cone shape essentially produces the smaller gap compared to the parallel gap and height closer to inside so that the shear on the sample is constant and here in the shear is gamma is equal to dx by h so essentially this gamma is constant. Now if you look at the example that how rheological principles are being utilized to determine the characteristics of some of the gel or soft hydrogel which are used for 3D printing purpose. I will introduce the concept of hydrogel and then what is

3D extrusion printing later on when I will be giving the lecture on the process science of the 3D extrusion printing.

But at this point of time, what I am trying to show you, this is like gelatin-based hydrogel, 3% alginate, 5% gelatin, 3A 5G and here you can use some of the carbonaceous additive like cellulose nanoparticles and with different concentration or different amount like 1%, 2%. And if you look at that viscosity as a function of shear rate, so n (eta)as a function of shear rate, So, what you see here independent of the hydrogel composition shear rate decreases, viscosity decreases with shear rate. If viscosity decreases with shear rate that will clearly tell you that this is the shear thinning behavior. What you learnt before, there are two type of attributes which are important for 3D extrusion printing. One is the shear thinning behavior and one is thixotropic behavior.

In the thixotropic behavior, viscosity essentially decreases with time. In shear thinning behavior, viscosity essentially decreases with shear rate and if viscosity increases with shear rate, then it is known as shear thickening behavior. n (eta) is equal to K gamma dot to the power n minus 1 and n value if you see in all this hydrogel it is much less than 1, it is like either 0.5 and with addition of other elements this n value even decreases to 0.

14. So when n is less than 1 it is called pseudo plastic flow shear thinning behavior n is equal to 1 Newtonian fluid. Newtonian behavior as I have shown you before in case of Newtonian that there is it is constant irrespective of gamma dot or sigma and n (eta) is essentially does not show any change. Now, shear thickening fluid, it is just for your reference, it is of not that much use in 3D extrusion printing, viscosity essentially increases with sigma or gamma dot. here it is plotted either sigma or gamma dot. One of the example is a mud slurry.

it is viscosity, it decreases with time that has been mentioned to you before. This is like thixotropic behavior and different flow diagrams. Now, what you see here that this is like different type of flow diagram. Newtonian fluids, this is shear thickening fluids, pseudo plastic fluid and Bingham plastic fluid. In all these cases, shear thickening fluid basically yield stress also increases with shear rate that is gamma dot.

there are different type of test that one can do using the rheometer and most commonly used test are in adhesive evaluations like phase angle, delta or epsilon and also this is dynamic oscillatory test. You can add the sinusoidal stress to the sample at a certain frequency. and monitor the sample response in strain deformation and then shift between the input stress and output strain is the phase angle that we essentially measure. these are like again different type of dynamic testing just to measure the responses of the soft materials or soft gels like whether it is a purely elastic response that is delta is equal to 0 degree. This is delta 90 degree Newtonian fluid and this is phase angle is between 0 and 90 that is a delta is a viscoelastic response.

you can see there is a lag between stress versus strain. Whereas when delta is at 0 degree, lag and phase angle is 0. essentially stress and strain is almost in the phase. Delta 90 degree stress and strain is completely out of phase. Now what are the different viscoelastic parameters? This is one is modulus.

This is measure of the overall resistance to deformation of materials. G star is the stress versus strain. And there are 2 components of this overall modulus, one is called elastic or storage modulus, typically the real value that is the G prime and there is a viscous and loss modulus that is G double prime. G prime is essentially stress by strain into cos delta, G double prime is stress by strain into sin delta. If you take the ratio of the G double prime to G prime, you get the tan delta where delta is essentially phase angle as it is shown.

G star essentially square root of G prime square plus G double prime square. these are like very basic viscoelastic parameters normally we use. Now, if you plot for many of the viscoelastic solid, the G prime or G double prime as a function of temperature T. Then you will get this kind of characteristic behaviour. If you follow the blue one that is called G prime plot, so it goes through a decrease, sometimes steady state, then decrease.

then it goes to different region from glassy region to transition region to rubbery region to terminal region. If you look at the loss modulus again this dotted line if you follow then it shows not a very consistent trend initially it increases in the transition region then it goes from stiff to soft rubber and then finally it goes to viscoelastic liquid. viscoelastic liquid is essentially terminal region where there is little bit higher temperature, this temperature high means does not mean several 100 degree Celsius as you have seen in case of metals, but this is normally close to room temperature. or below room temperature in many cases where you will see that most of the 3D extrusion printing operates in those particular temperature window. Just to show you some real-life example, this is all about theory.

The real-life example, the rheological analysis of the alginate gelatin again, this is one of the examples that I have given you before. This is a temperature sweep. That means in the parallel spectrometer, you do temperature sweep. You will see that how G prime and G double prime changes with temperature. And qualitatively you will see in all these cases this G prime and G double prime essentially decreases with temperature.

And if you look at the storage modulus, this is G prime and this is G double prime. this is G prime, this is G double prime and loss factor, loss factor is tan delta and you know tan delta is nothing but G double prime by G prime as explained in one of the previous slides and this is the n (eta) plot, viscosity plot. all these four parameters how they change with temperature and you can very clearly see that G prime, G double prime and n (eta) all decreases with temperature but tan delta essentially beyond certain 32 degree Celsius or something it increases with temperature and tan delta is the loss factor. But these results are essentially validated with alginate gelatin nano cellulose based biomaterial inks. Then you can do the dynamic oscillation method like stress, strain or amplitude sweep, time sweep, frequency sweep or temperature sweep.

You can essentially see how strain, stress and amplitude sweep essentially used to find out linear viscoelastic response. LVR is essentially linear viscoelastic response. in this linear viscoelastic response essentially means the storage modulus is independent of strain. And if you look at this particular region, there is what is a nonlinear region that is a function of strain. here it is the strain amplitude that has been plotted.

and here you can plot either G prime or you can also put the stress if you see that how stress is increases and there is a constant slope and you can always find out that what is the critical strain of this particular case of the material response. As mentioned the linear viscoelastic response where essentially viscoelastic characteristics is independent of strain and in this particular case what we are showing that if you take polydimethylsiloxane, this PDMS at different frequency 0.1 hertz, 1 and 50 hertz. If you see that you know how 40% this is it is decreased by 5%, 60% that how the storage modulus is decreases and 80% that PDMS is 0.

1 hertz that how it is decreases. In all these cases you can see in the 25 millimeter parallel plates 1 hertz frequency and 30 degree Celsius how modulus increases with increasing frequency. We have done similar analysis for the shear stress sweep here you can see or amplitude sweep. in the amplitude sweep you can vary the shear strain and then you can see that how G prime or G double prime actually varies with shear strain and loss factor that is tan delta which is the ratio of the G double prime to G prime also this varies with temperature or with shear stress in this particular case. Now, how this LVR is dependent on the temperature? LVR is shortest when the sample is

in the most solid form and if you see that this is the solid case, this is the LVR region and this is the LVR region when it is liquid, this actually extends to a more wider region in terms of strain. In time sweep essentially that amplitude goes to let us say sinusoidal variation and material response is essentially monitored at a constant frequency, amplitude and temperature.

It determines the stability, thixotropy and curing studies in this particular linear viscoelastic response. One of the things that I have mentioned earlier in thixotropic behavior. Thixotropic behavior essentially G prime and G double prime should decrease with time to some extent and this also depends on the storage of this particular hydrogels. here you can see G prime and G double prime as a function of time up to 40 minutes. You can see with the prolonged prime confirms the storage stability and mechanical strength synthesis hydrogel over a certain period of time.

this thixotropic property is very important but that is more with respect of n (eta) versus time and here you are essentially plotting G prime, G double prime as a function of time just to show how this mechanical properties is maintained and retained in this kind of alginate gelatin based system. In frequency sweep, when there is a time dependent response is being shown, this material response is essentially being measured with increasing frequency and that is also monitored at a constant amplitude and temperature and similar but opposite trend what you have seen before can be observed here. that when you plot G prime or G double prime as a function of frequency and you can see that initially it increases in terminal region go to rubbery or plateau region then go to transition region finally reaches the glassy regions. When you see that G double prime that is the red dotted part it also shows similar kind of transition behavior finally it reaches the glassy region. frequency dependent rheological properties that alginate, gelatin, hydrogel and here again storage modulus like G prime or loss modulus G double prime.

This is the plot on the frequency sweep and this is the tan delta which is nothing but G double prime by G prime as has been defined before. storage modulus is higher than the loss modulus that is very important results and which confirms this is the viscoelastic in nature. G prime is greater than G double prime over large frequency domain And over a large frequency domain this kind of results essentially signifies that this is a viscoelastic gel that we have measured. This has been mentioned before. Now, step dynamic method that you know that if the strain is plotted against time within LVR there is a very regular oscillations.

Outside LVR there is a large oscillation and again it comes back to the LVR. it is a stepwise method like it goes through small oscillation to large oscillation to within oscillation. Now if you plot G prime as a function of time, then it shows from high to low and structure is recovered. This is good for measuring high viscosity samples. In our alginate gelatin, nanocellulose part hydro gel, it also shows this kind of behavior when n(eta) is plotted as a function of time.

This clearly shows this is a thixotropic behavior because n(eta)essentially decreases with time. And there is a regime that what you have shown here this low regime where modulus also is low storage modulus this G prime is nothing but storage modulus that what you learnt from the earlier slides and you can see this viscosity n(eta) also decreases as G prime also decreases and that it certainly increases and this structure is recovered. This is the region where structure recovery region and this again essentially indicates this material has thixotropic behavior. overall what we learnt in this fundamentals of discussion on the fundamentals of rheology that we need to do frequency sweep. we need to do temperature sweep to measure the viscosity, measure the storage modulus, loss modulus, loss factor and also characterize the behavior of the soft hydrogel materials and for the extrusion 3D printing as I am going to explain to you later on.

This is the shear thinning behavior of the viscous hydrogel. that is most important. therefore you have to establish that viscosity indeed decreases with shear rate. Viscosity indeed decreases with time that is essentially thixotropic behaviour and the hydrogen structure can be recovered when you do this time sweep for a longer period of time. There are other concepts that you have learnt also, linear viscoelastic regime.

You have also seen that how Newtonian fluid, non-Newtonian fluid and viscous fluid they behave and one of the equations that you, one of the empirical relationship that you have learnt, n(eta) is equal to k gamma dot to the power n minus 1 and n is the shear thinning exponent and this value is always less than 1. And, we have shown in that basically soft hydrogel formulation that you can modify the hydrogel composition in order to reduce the n value. I am sure that this kind of fundamentals will be very relevant in discussing the process science for the 3D extrusion printing. Thank you.