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The Rheological Audit of the Process

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ABSTRACT

In the design of new materials for specific purposes, many of the physical or chemical characteristics can be determined by suitable deformation of the prototype. The skill lies in selecting the right mode of deformation. A number of examples of this will be given. Once a process has been determined, there is quite often a need to optimise performance, or solve a problem in the line. What is required is a rheological audit of the process, and this will be looked at in some detail.

INTRODUCTION

The branch of rheology concerned with quantitative measurements, using a suitable apparatus, of rheological properties is called rheometry. The rheological properties of a Newtonian fluid are fully characterized, at a given temperature and pressure, by one parameter only - the shear viscosity. In such a case a single measurement is sufficient, at least in principle, to determine this parameter. In the case of a generalized Newtonian fluid (a purely viscous non-Newtonian fluid exhibiting no memory effects) a flow curve, i.e. the functional dependence of shear stress on shear rate, has to be obtained. It is desirable that the flow curve be determined in as broad a range of shear rates as possible, including the range of very low shear rates (this may allow the determination of zero-shear-rate viscosity or the estimation of the value of yield stress). The measurements should ideally include the range of shear rates occurring in the practical problem of interest, which was probably the reason for carrying out the rheological measurements in the first instance. It should also be kept in mind that the same fluid at different ranges of shear rate may exhibit different rheological properties or even belong to a different rheological category of fluids.

The situation becomes even more complicated in the case of fluids exhibiting memory effects. For a thixotropic fluid, measurements over periods of time have to be carried out. The rheological characterization of a viscoelastic fluid requires the determination of the functional dependence on shear rate not only of shear stress but also of the first and possibly even the second normal stress difference.

It follows from the above considerations that rheological measurements have to be carried out using an absolute, multipoint instrument. Such instruments, in contrast to comparative viscometers and single point absolute viscometers, are called rheometers. In this case there should be an exact solution of the differential equations of motion and continuity describing the case of flow occurring in the instrument. If the solution is only an approximate one, the error introduced by the approximation should be less than the acceptable error of the measurement. Because of this condition we usually carry out rheological measurements for particularly simple cases of flow where a non-zero

velocity component occurs only in a single direction. Such flows are called viscometric flows.

However, we must always be aware that the various flow regimes in our process of interest are likely to be somewhat more complex. One way of overcoming this problem is to divide the process into different stages, and hope that each stage can be suitably modelled by a viscometric flow. The art lies in the division of the process, and the science in the modelling and the subsequent experimentation.

The mode of deformation to which a process fluid is subjected varies as the fluid passes through the processing operation. The fluid may even change chemically or in its physical state. The result is that in any one process a number of rheological techniques will have to be used to define the fluid's rheological state at any particular time.

In recent years it has become very clear that shear flow measurements alone are not sufficient to characterise the deformation behaviour of a fluid. In many industrially important processes, such as fibre spinning, blow moulding of bottles and film, vacuum forming and flow through porous beds, it has been recognised that extensional (elongational) rather than shear deformation is the dominant mode of deformation. There are three main forms of extensional flow, uniaxial, biaxial and planar. These give rise to extensional viscosities, η_E, η_b, η_p. The influence of the extensional properties of materials will now be illustrated using a well known process (coating). Though all three forms of extensional flow are likely, we will confine ourselves to uniaxial extensional flow.

EXTENSIONAL DEFORMATION IN THE COATING PROCESS

Coating is a process in which a liquid is applied continuously to a moving sheet in order to produce a uniform application of the fluid onto and/or within the sheet. The *web* is the sheet to be coated, e.g. paper, cellulosic films (photography), plastic films (magnetic surface coating for recording tape), textile fibres and fabrics (as finishes), metal foils (plastic coating for food uses etc). Note the difference between calendering (very high viscosity fluid) and coating (low viscosity fluid). In the first instance we will look at roller coating and the influence of a strain hardening fluid.

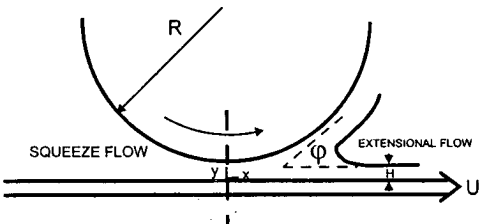

Figure 1. Roller Coating - geometry & flow deformation

Before the nip (Fig.1), the dominating deformation is a squeeze flow. As the fluid passes through the nip, a certain proportion will adhere to the web, whilst the remainder remains attached to the roller. Consider the extension between a fixed point on the moving web and a fixed point on the rotating roller. It is possible to determine the rate of extension as a function of x (in the direction of the web). One needs to know the linear velocity of the web (U mm s^{-1}), the rate of rotation of the roller (N rps), the radius of the roller (R mm), and the gap between the roller and the web (G mm). Many applications will have $U = 2\pi RN$, but it is not essential.

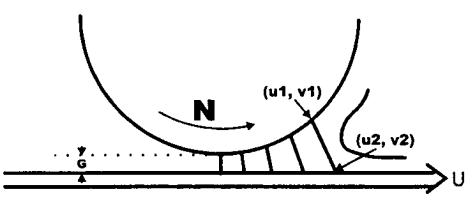

Figure 2. Roller Coating - parameters to determine extension rate

Two factors influence the rate of elongation (Fig.2).

- The surface point on the roller is accelerating away from the web ($dv_1/dt > 0$), and
- The component of the velocity of the point on the roller is less than that on the web ($u_1 < u_2 = U$).

We will see that the extensional strain (ε) is therefore not steady but increases up to a limiting value depending upon the web velocity. Strain rate ($\dot{e}$) meanwhile goes through a maximum (Fig.3).

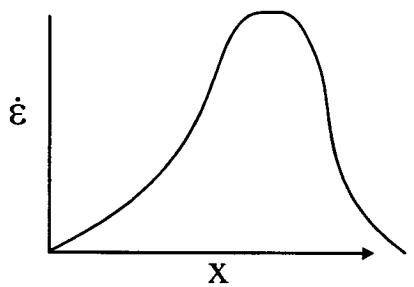

Figure 3. strain rate as a function of x

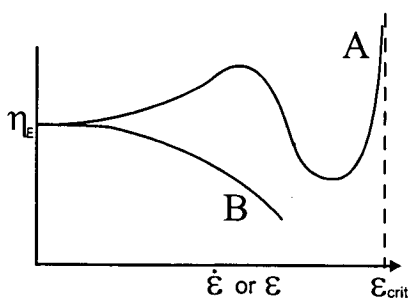

Figure 4. extensional viscosity as function of strain or strain rate

Now consider flow curves expected of both strain hardening (A) and strain thinning (B) fluids (Fig.4). These trace out the loci of points corresponding to varying rates of strain ($\dot{e}$) or total strain (ε) as the fluid moves in the x direction. In case A, as $\dot{e}$ increases, the viscosity is progressively: Newtonian → strain hardening → strain thinning → strongly strain hardening to a limiting value (elasticity dominated). The extensional stress (σ_E) will follow the same pattern.

If ε_{crit} is exceeded, cohesive fracture will occur. If ε_{crit} is <u>not</u> exceeded, the fluid's spinnability will cause it to form a sheet film Fig.5). This in turn can create a minimum pressure (-p) on the fluid and 'cavitation' will result.

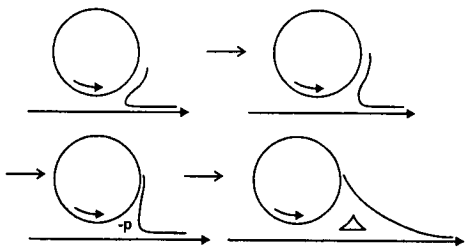

Figure 5. Development of a flow instability with a strain hardening fluid

This instability will then grow until a separate film is formed (Fig.6).

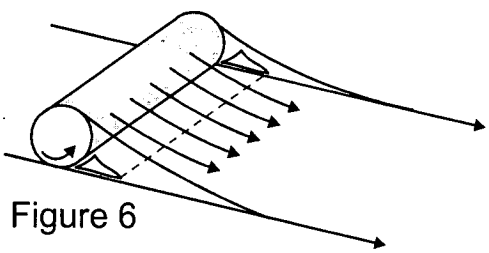

Figure 6

Because of the high orientation in the x direction, the film will be weak in the z direction and random perturbations could well cause the film to degrade into a series of filaments (Fig.7).

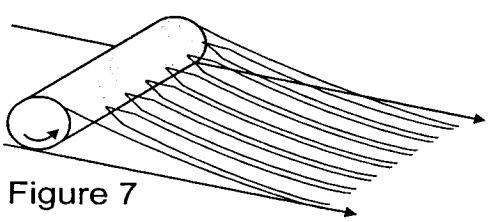

Figure 7

At high rates of deformation the film (or filaments) will fail cohesively, possibly with the creation of 'ink fly', i.e. small particles or ligaments of fluids discharged by recoil from the main bulk of fluid.

In Case B we have a strain thinning fluid. Since the maximum rate of strain will be on the exposed surface, the extensional viscosity will be a minimum at this point, and stable, uniform coating conditions will apply. As strain rate progressively falls the viscosity profile in the x direction will be the same as the curve shown as Case B. Very early thinning of the fluid will cause the surface to *move back* towards the nip until it reaches a position at which the lower strain rate produces a viscosity to balance the capillary failure at the fluid surface.

In the case of a cutain coater, the determination of the strain rate is somewhat simpler. [$\approx$ (V_1 - V_0) / L]. However, the following points need to be considered

- If die swell occurs, this can influence results.
- Rate of relaxation from shear.
- Rate of relaxation from elongation.
- Rate of hardening on the web.
- Flow instabilities.

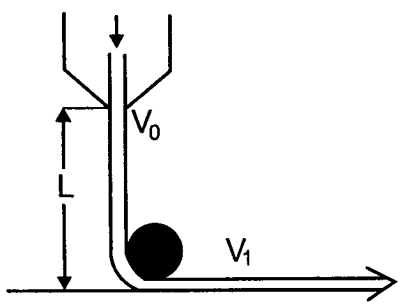

Figure 8. Schematic of the Curtain Coater

RHEOLOGICAL ASSESSMENT OF A PROCESS

As a case study we will take the roller printing process.

The problem was to assess the various flow processes encountered by the printing ink as it goes through a typical (e.g. a Deritend) printing press. The purpose of this exercise was to determine the important rheological parameters which should be measured in order to predict the performance of a particular ink.

Flow properties of inks

Inks are typical examples of suspensions in which pigment particles are suspended in a medium which itself can be of low or high viscosity. In order to stabilize the ink a number of additional ingredients are generally present, such as polymers, 'drying' agents, cross linking additives etc. Frequently the pigment is coated with a stabilizer to aid dispersion and prevent flocculation. All of these additives have a profound effect on the flow properties of the ink.

It is expected that a typical ink will show show some if not all of the following rheological behaviour:

- *Shear thinning*; viscosity falls as flow (shear) rate increases. The effect can be attributed to the change in structure of flocculated particles and is recoverable at rest.
- *Thixotropy*; viscosity, at a constant shear rate, falls with time, recovering when shear is stopped.
- *Yield value*; since the pigment particles can form a structure within the suspension, when a small stress is applied to the fluid, flow may not take place until the stress is large enough to cause breakdown of this structure. This is the yield value.
- *Relaxation time*; depending on what additives are present, the suspension may take a measurable time for the stress to relax when shearing is suddenly stopped. This is quantified by the relaxation time.
- *Deborah number*; this is the ratio of the relaxation time to a characteristic time of deformation. When Deborah number is

high, a fluid will exhibit solid-like characteristics, when it is low the fluid will be liquid-like. Note that the consequence of this concept is that whether or not a particular material will behave like a solid or a liquid depends only on the rate of deformation to which it is subjected. This could be of importance in the printing process.

- *Elasticity*; generally suspensions will not be elastic unless polymeric additives are present.
- *Extensional viscosity*; this resistance to tensile deformation has been little considered although some attempts have been made to measure it in inks. It is certainly of great importance in the printing process as will be shown later in this section.

Dividing the flow process into stages

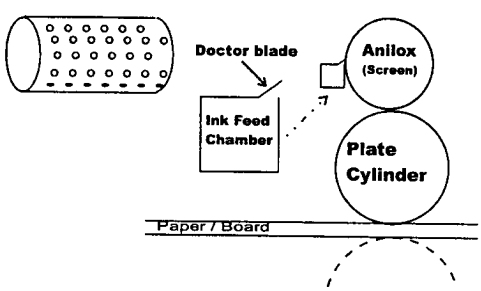

Figure 9. A representation of the printing process

At the ink feed chamber (Fig.9), the ink will not flow (because it has a yield stress) until the anilox (screen) roller begins to move. The edge of the roller between the doctor blades and the back edge of the chamber form a pseudo-parallel plate system. When the anilox roller is rotating, a small shear rate is induced in this system. For example, with the anilox roller rotating with a surface velocity of 2.79 m s^{-1}, and the width of feed chamber from roller to back edge $\approx$ 80 mm, then the shear rate at the roller $\approx 2790/80 \approx 35\ s^{-1}$. The ink then flows into the cells on the anilox roller. The doctor blade at the top serves as a wiper to clean the surface of the anilox roller. Here the gap is very small, say of the order of 0.5 mm. Therefore, the shear rate at the blade $\approx 2790/0.5 \approx 5600\ s^{-1}$. Hence, the ink on the surface of the roller will be very mobile and will flow into the cells. The stresses developed in the ink during this shear flow will now relax, and the structure will start to reform.

At the nip between the anilox roller and the plate cylinder, most of the ink flows out of the cell. This is due to surface energy differences between the two cylinders. The pressure exerted by the anilox on the plate cylinder increases the surface area available for this transfer, as well as making this area flat. The ink flows as a plug (so it does not smear) because of the yield stress and the fact that the Deborah number will be high as a result of the high speed of deformation. On the plate cylinder, the ink does not flow because of the yield stress, and so remains as separate drops.

At the nip between the plate cylinder and the paper/board, the flow is extremely complex. Because the velocities of the two are, in theory, equal, little or no shear deformation is present. Extensional deformation will dominate. In fact it is squeezing flow (planar extension) in this region. For example, with an ink layer of approximately 7μm travelling on the surface of the plate cylinder, of diameter 533 mm, then the angle through which the cylinder turns during the time the ink first contacts the paper and the minimum gap (of say 1 μm) is given by $\cos\varphi = 265.501/265.507$, i.e. $\varphi \approx 6.7$ mrad. The surface velocity of the plate cylinder is also 2.79 $m.s^{-1}$, so the time taken for the distance between this cylinder and the paper to reduce from 7 to 1 μm is given by $t = 0.2655 \times \varphi/2.79 \approx 640$ μs. The Hencky strain developed is given by

$2 \cdot \ln(\text{initial gap/final gap})$, i.e. $\varepsilon = 2 \cdot \ln(7/1) = 3.9$, thus giving an average strain rate of 6100 s^{-1}. This strain can be reduced by the paper compressing, thereby increasing the final gap.

At the same time as the squeezing flow is taking place, there is a flow of solvent into the paper, causing an instantaneous concentration (and hence viscosity) gradient through the ink in this region, which is highest at the edge of the paper. This should stabilise the phenomenon. Once through the narrowest part of the nip, the planar extension turns through 90°, the ink being extended between the board and the plate cylinder. There are two possible situations in this region, dependent upon the state of the ink layer as it approaches the nip.

Firstly, consider the case in which the droplets on the cylinder have coalesced under the influence of the squeezing flow. The three-dimensional wedge of ink is stretched at the forward edge, and eventually will fail, with a stress dislocation moving back into the wedge. If the conditions are such that the fluid flows forward at the same speed as the dislocation is moving backward, then a state of unstable equilibrium is achieved. Since there is a concentration gradient, this sheet is likely to fail closer to the plate cylinder, leaving about 10% of the ink to complete the full circle. The remainder of the sheet will remain on the paper/board.

In the second case, the droplets remain separate in the nip, and probably resemble coins (three dimensional flat discs) as they move through the nip. On exit, one side of the 'coin' is attached to the board, whilst the other remains attached to the cylinder. These filaments are then stretched, and eventually will fail in a cohesive, solid-like, fracture or by capillary (liquid-like) failure. Again, since there is a concentration gradient, the point of failure is likely to be nearer to the cylinder. Since the curvature of the cylinder is relatively small over the distances involved, the cylinder and board can be considered to be moving apart like parallel plates. The strain rates in this situation can be determined from first principles, as will be shown. As was seen with the roller coating example, there is a maximum in the strain rate. Hence, as long as the fluid between board and roller remains intact, we can say:

- as fluid moves out of the nip, the strain rate passes rapidly through a maximum;
- as the minimum gap set is increased, this maximum in strain rate is decreased;
- the position of the maximum depends upon the velocity of the roller.

AN AUDIT OF THE FLOW PROCESSES

Table 1 shows a breakdown of the flow processes dominating various parts of the printing process. Reading from left to right, the flow processes have been detailed, the major deformation mode is described together with its timescale, and the appropriate rheological test indicated. For example, the ink is initially held in a reservoir where the fluid is largely at rest, being subjected to a low rate of shear. The timescale is relatively large and the behaviour of the ink can be characterized by creep experiments, and by shear flow using a controlled stress rheometer. Finally the rheological parameters obtainable are summarized.

Each successive flow process has been analysed in the same way and the relevant rheological tests indicated. Note that the techniques described are not necessarily the only ones applicable but are those most likely to be available in a rheology laboratory. Other techniques may be particularly applicable to the study of ink behaviour in certain areas of the process. For example, high frequency oscillatory measurement should give useful data on the ink behaviour on the anilox roller and on the plate cylinder.

Table 1 - the process in stages				
Stage	Deformation	Time Scale	Rheological Tests	Parameter Obtained
Reservoir	Rest	large	creep, rotational shear flow	yield stress or zero shear rate viscosity; structure at rest
Flow into cells	low rate shear flow	~ 20ms	creep, rotational shear flow	yield stress; low shear rate viscosity as a function of shear rate
Wiping	high rate shear flow	~ 180μs	capillary shear flow	high shear rate viscosity as a function of shear rate
Ink on Anilox roller	relaxation from shear flow	~ 60ms	creep, oscillatory shear flow	yield stress; relaxation time; elastic modulus; loss modulus; structure at rest
Transfer to Plate Cylinder	plug flow	~ 5ms	creep	yield stress or zero shear rate viscosity
Ink on Plate Cylinder	rest	~ 300ms	creep	yield stress or zero shear rate viscosity; structure at rest
Nip before paper and plate cylinder	planar extension (squeeze)	~ 600μs	squeeze film	biaxial extensional viscosity
Nip after paper and plate cylinder	uniaxial extension	~ 800μs	extensional flow	uniaxial extensional viscosity

RHEOLOGICAL AUDITS IN GENERAL

Table 2 indicates the range of measurements necessary to characterize a polymer melt in a number of common plastics processing operations. The essence of rheological assessment is that each of the deformation regimes is successively analysed in terms of the flow regimes encountered by the fluid and their time scales. The effect of this strain history on the succeeding deformation process must then be considered. While this list is not intended to be comprehensive it will be noted that it includes some methods not normally considered in polymer processing, notably Spraying, Mixing and Printing. Nevertheless, these processes involve polymeric materials and their fabrication. Allied to the deformation processes are a number of other physical phenomena that can be of critical importance, for example, melting, solidification and phase change. It is, however, the rheological processes that are of primary concern. In any particular fabrication process the fluid will be subjected to several different deformation regimes. More examples will be given in the lecture.

Table 2. Manufacturing processes and rheological measurements
(Dark areas - essential data; light areas - desirable data)

Flow Parameters	Processing type						
	Extrusion	Injection Moulding	Bottle & Film Blowing	Vacuum Forming	Fibre Spinning	Printing	Coating, Spraying & Mixing
Shear viscosity (γ and σ)							
Flow curve							
N_1							
Die swell							
Dynamic viscosity η'							
Storage modulus G′							
Loss modulus G″							
Extensional viscosity η_e							
Relaxation time, τ							
Thixotropy							
Viscosity / temperature relationships							