Using Rheometry to Predict Liquid Adhesive "Processability".

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A controlled stress rheometer with normal force measurement capability was used to screen a series of liquid pressure sensitive adhesives. The samples were processed in a roll coating application with a pattern bar producing controlled bands of the final coating. Some samples coated well, but others produced surface irregularities such as ribbing or beading and were considered to have failed. Conventional viscometry could not predict which samples were likely to perform well and which were likely to fail. The use of rheometry proved more successful and by calculating certain dimensionless groups, the samples could be ranked in order of suitability. Surface tension information proved to be less relevant than overall viscoelastic data as provided by measurement of normal stress in the fluid under steady simple shear.

Introduction
A series of 9 pressure sensitive adhesives were submitted for study using rheological measurements in order to rank them in order of ease of processability. The samples - all liquids – are processed using roll coating apparatus, and a pattern is applied to the liquid film via a pattern bar, whose thickness is selectable. Poor coating is judged to exist when air bubbles or ribbing can be visually detected on the film. In addition to the samples, information regarding their viscosity [measured by a Brookfield LV device] and surface energy at a single temperature was provided. This latter piece of information is important because the surface tension force in the liquid film is the driving force to create a smooth finish and erase any irregularities in the liquid film caused by the processing. Such irregularities can easily occur in pressure sensitive adhesives due to their polymeric nature. Polymer solutions or melts are elastic liquids above a certain critical concentration or temperature [respectively] when the molecules are sufficiently crowded and/or mobile as to exhibit entanglement coupling. This interaction causes the solution to exhibit some solid-like properties and thus the materials are essentially viscoelastic [show both solid like and liquid like behavior].

Typically such materials have a viscosity which is not constant, but rather decreases at the high shear rates [velocity gradients] typically encountered during processing. Furthermore they can exhibit tension thickening in elongational flow, such that fibers or threads may be drawn from the bulk, leading to "stringing". Finally, at medium to high shear rates or processing velocities they can demonstrate normal forces [perpendicular to the direction of flow] that cause the surface film to distort. A familiar example of an elastic fluid demonstrating normal forces is cake batter that is seen to climb up the drive

shafts of an electric mixer rather than drawing a vortex like a Newtonian fluid would. This non-Newtonianism is referred to as the "**Weissenberg Effect**" [see below]. It is caused by the circular streamlines contracting and drawing inward to the axis of rotation instead of being pushed outward as in say, water. The latter phenomenon [Coriolis Effect] is found in tornadoes, whirlpools etc.

Weissenberg Effect – "Rheological Phenomena in Focus" D.V. Boger & K. Walters
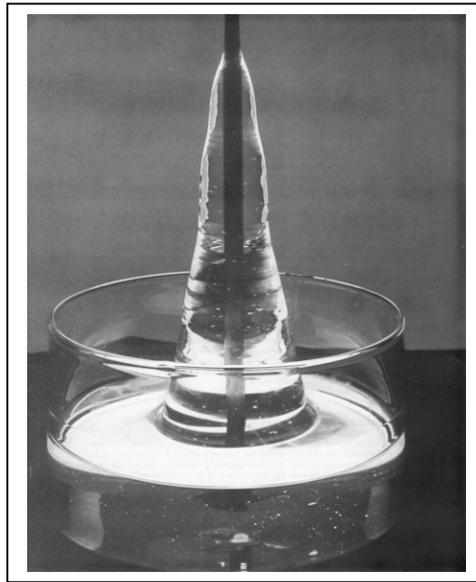
It is clearly desirable to be able to predict a candidate fluid's propensity for being sheared at typical processing conditions, so that any problems are avoided in scale up to final use. Viscosity information can show the presence of non-Newtonianism as far as shear thinning is concerned, but no elastic data is generated. The elasticity of a fluid is what is key in predicting the surface distortions due to normal forces, and can be measured only on a rheometer. A rheometer is typically a rotational device that imposes a shear field on the test fluid and can derive viscoelastic information. Often this is done using a dynamic mode of operation where the fluid is driven by a sinusoidal input signal [stress or strain] and the output which is also sinusoidal [strain or stress respectively] is measured. The input and output amplitudes and the raw phase difference are the basic parameters from which elasticity and dynamic viscosity are derived. This technique is simple but is limited to small strains where the fluid is considered to be behaving in a linear fashion [stress is proportional to strain]. This situation in no way reflects real processing conditions that are decidedly non-linear.

The second method uses a transducer to detect the normal forces generated during a flow experiment and the presence and magnitude of these forces is used to compare the amount of elasticity from fluid to fluid. When the normal stress is calculated from the transducer output and the geometry characteristics [surface area] then it may be compared with the shear stress to give a dimensionless group called the Weissenberg number [(normal stress/shear stress)/2]. This group represents the balance between the elastic

[solid like] and viscous [liquid like] effects in the sample. A high Weissenberg number is likely to be indicative of a tendency to form surface distortions at high shear. A second dimensionless group known as the capillary number is also important in the roller coating process. This group is derived from the ratio of the viscous forces to the surface forces [u.η / σ] or velocity times viscosity divided by surface tension. Thus the magnitude of the group reflects the dominance of forces promoting surface irregularities over forces trying to remove these irregularities.

Samples

Table 1

Sample	Solvent	Viscosity cps	Surface Energy dyn/cm
[1]	heptane	780	20.3
[2]	water	400	72.8
[3]	water	300	72.8
[4]	heptane	1640	20.3
[5]	heptane	1775	20.3
[6]	heptane	9000	20.3
[7]	heptane	14500	20.3
[8]	hexane	8400	17.91
[9]	hexane	7800	17.91

The samples were clear liquids except for [2] & [3] which were opaque white liquids. Samples [8] & [9] were particularly prone to "stringing" , indicating a high extensional viscosity. All samples showed a tendency to dry out in the rheometer, so a solvent trap geometry and cover was used with the appropriate solvent where possible. N.B. Heptane was not available, so hexane was used.

Apparatus

The rheometer used was a TA Instruments AR1000N controlled stress rheometer with normal force measurement capability. This device has a dynamic operating range of ~ 1,000,000 : 1 [highest torque : lowest torque] and can perform dynamic [oscillatory] tests as well as creep tests [step stress] and conventional and equilibrium flow. It is depicted below in figure 1.
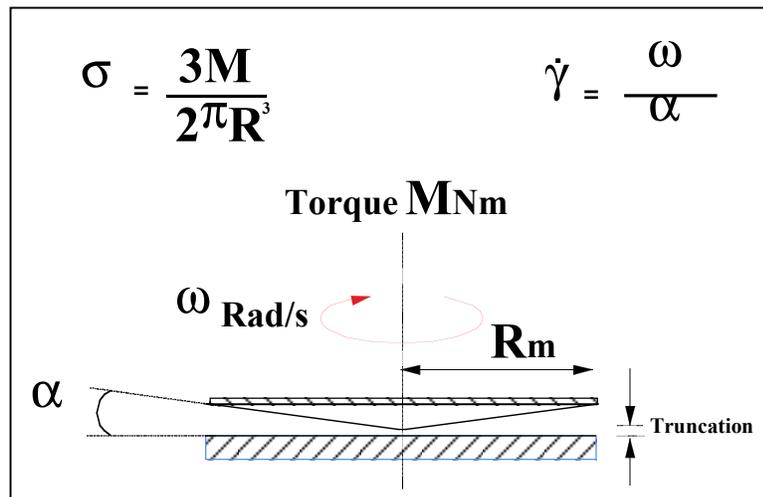
Figure 1
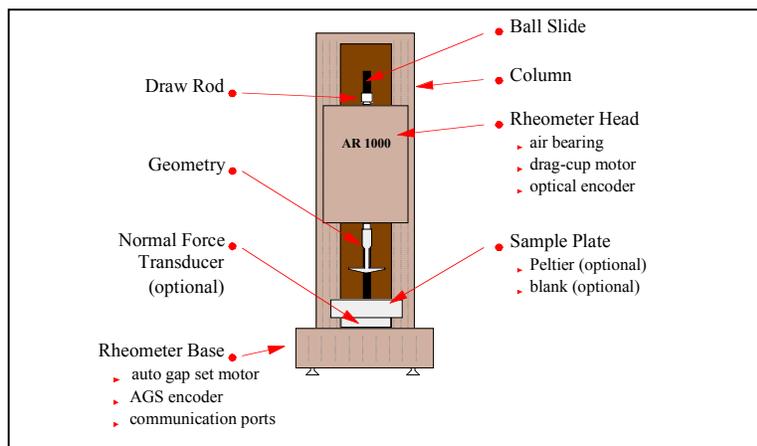
The features of the instrument can clearly be seen including the attached conical geometry, this makes up a cone and plate system when the Peltier temperature control plate is used.

A cone and plate geometry is ideal for making normal force measurements since the shear rate [velocity gradient] is constant across the entire geometry surface. Thus the transducer output of force can be converted to stress by the geometry factor stored in the software automatically.

Figure 2 shows the cone and plate geometry and the geometric factors used in converting torque and displacement into stress and strain.In the figure below the stress factor [sigma] and the shear rate factor [gamma dot] are defined based on the torque [M], the radius[R], the angular velocity [omega] and the cone angle [alpha]. The cone is not shown as a solvent trap configuration, but figure 3 below includes the cone and its cover.

Figure 2

$$\sigma = \frac{3M}{2\pi R^3} \qquad \dot{\gamma} = \frac{\omega}{\alpha}$$

Torque **M**Nm

ω Rad/s

Rm

α

Truncation

The solvent trap system is normally able to minimize drying such that an hour or more's work can be performed without artifacts due to drying of the solutions.
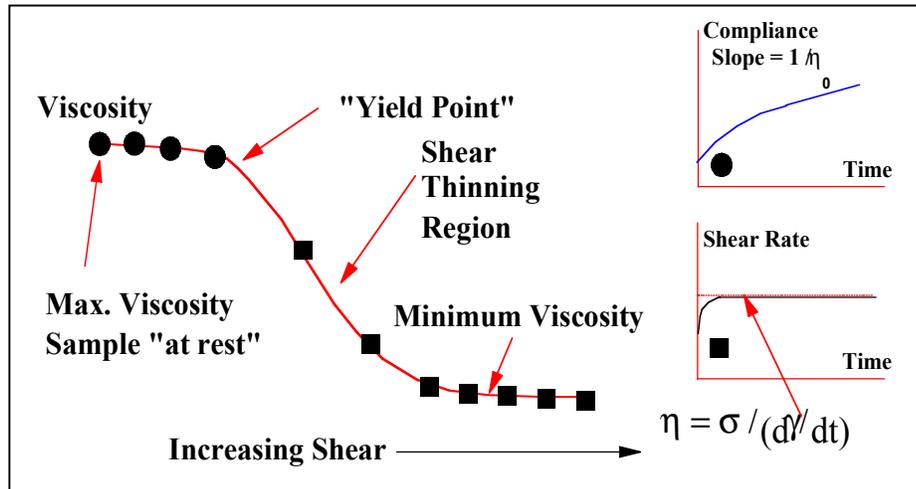
Figure 3
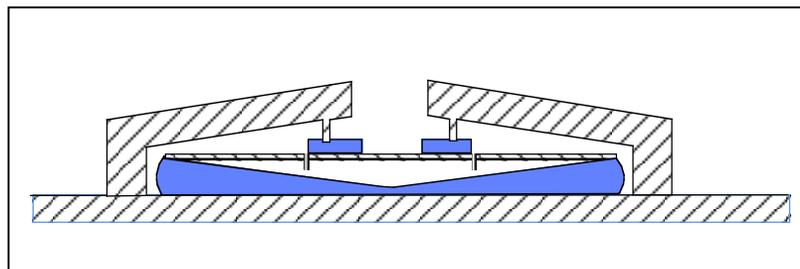
Methods

All the samples were tested using a steel 4cm 2 °cone and plate geometry with acrylic solvent trap cover. Flow tests were performed at 25°C . The flow tests performed were all equilibrium flow measurements. That is each data point was derived from a creep test [step stress test] and the viscosity at that stress calculated from the steady state slope of the strain or shear rate response [see figure 4].
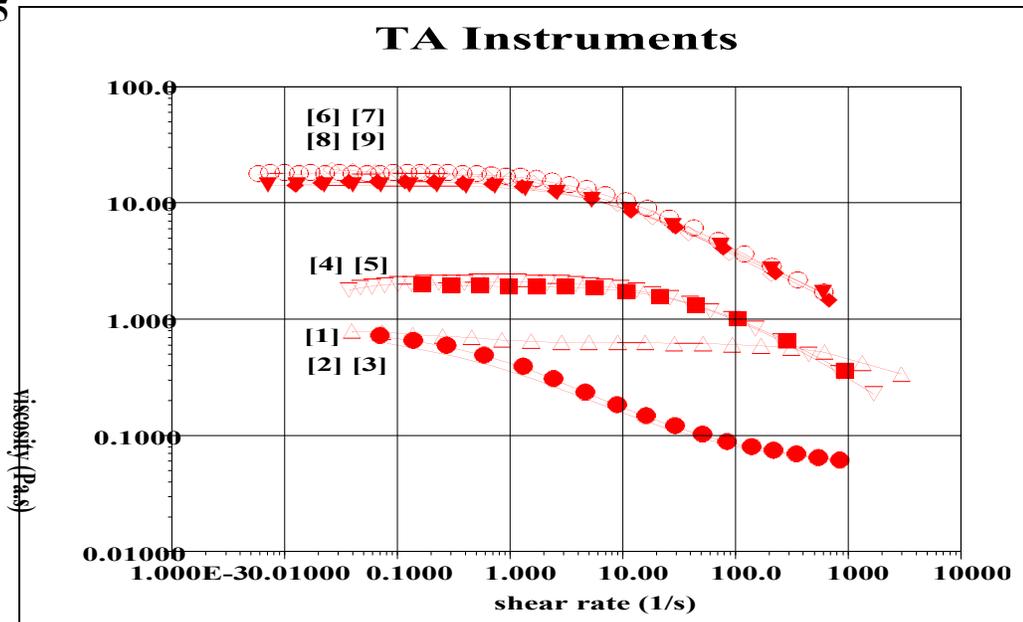
Figure 4

Results

Figure 5 shows the results of the flow tests performed at 25°C. The samples can clearly be ranked in terms of their viscosity as a function of shear rate. The two aqueous samples are of a lower viscosity than the seven organic solvent-based systems.

Figure 5

The rheometer also discriminates successfully between samples [2] & [3], ranking them such that [2]>[3], just as predicted by the Brookfield measurements. The Brookfield measurement is however a single point measurement, and does not predict the shear thinning seen clearly by the rheometer. In this case the viscosity traces are seen to be parallel, so there is no potential confusion caused by the viscosity ranking reversing itself at certain shear rate thresholds. When this occurs it is difficult to use single point viscosity determinations at all. By interpolation, it can be seen that the shear rate equivalent of the Brookfield measurement must lie ~ 2-4 s^{-1} although unless a cone and plate or concentric cylinder geometry is used the apparent shear rates are not constant throughout the sample and equate to a mean value through the bulk.

Next comes[1] which is fairly Newtonian until moderately high shear rates where it becomes shear thinning. The plateau viscosity value is close to but lower than the 708 cps predicted by the Brookfield viscometer, again raising the issue of whether a special geometry such as a rotating disk or T bar spindle was used.

Above [1] come samples [4] & [5], with the samples placed in the same ranking as the Brookfield predicted – [5]>[4]. These samples begin to shear thin about an order of magnitude earlier than [1] did. Finally samples [6] – [9] are all packed together with little difference between them. All four samples begin to show shear thinning at ~ 5 s^{-1}

From the viscosity data alone it would seem that the four samples with the highest viscosity might well be the ones that process poorly, but the results from actual testing under coating conditions ranked the samples as seen in the table below.

Table 2

Sample	Pass/Fail	Comments
[1]	n/a	no data
[2]	fail?	no data
[3]	fail?	no data
[4]	Pass	fail at high speed
[5]	Pass	fail at high speed
[6]	Pass	Slight Ribbing
[7]	Pass	Orange peel
[8]	Fail	All conditions.
[9]	Fail	All conditions.

The data above is difficult to reconcile with the groupings based on viscosity alone and so it is likely that some other parameter such as surface tension [surface energy] or elasticity [normal stress] might discriminate more effectively.

If the surface tension is assumed to be important then it is useful to calculate the Capillary Number [Ca] as follows: Ca = (viscosity * velocity)/ surface tension.The flow data can be converted to capillary number data and plotted as a function of velocity derived from the shear rate data. The software for the AR 1000N allows for the data to be plotted in these various formats, and the calculated results are shown in figure 6.

Figure 6

Capillary Number = Viscous Force/ Surface Tension Force [η .u σ]
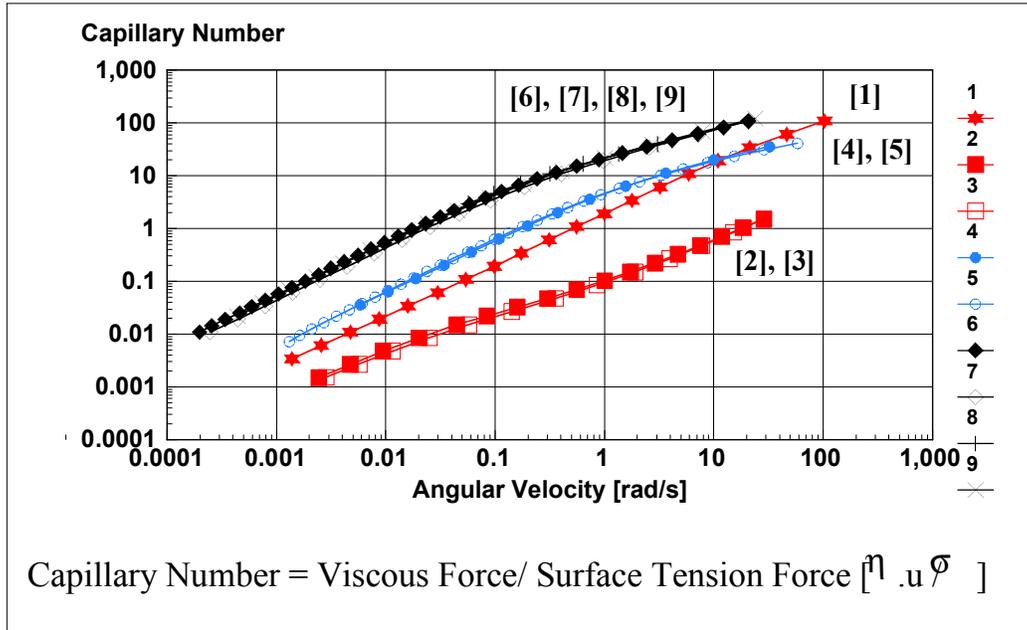
The data splits the samples into the same arrangement as the viscosity data, which is not surprising since the calculation involves simply dividing the viscous force by a constant [surface tension]. It is clear then that the "processability" of a sample cannot be predicted in this way.
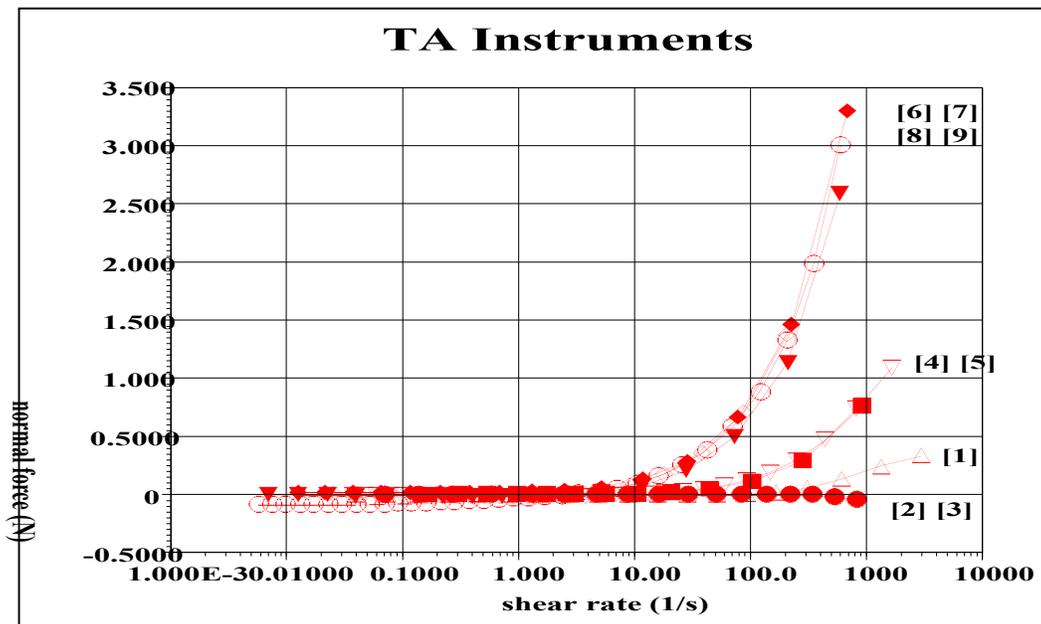
Figure 7

Figure 7 shows the same flow curves as in figure 5 but this time the normal force data is plotted instead of the viscosity. The data show essentially the same ranking as the viscosity plots, but the two aqueous materials generate no normal forces. This may be due to the fact that the polymer is dispersed rather than dissolved in a similar way to a latex, which precludes the same type of entanglement coupling. The presence of data around zero prevents the use of a log scale for more detailed examination. If the two aqueous samples are no longer considered, then figure 8 is generated.
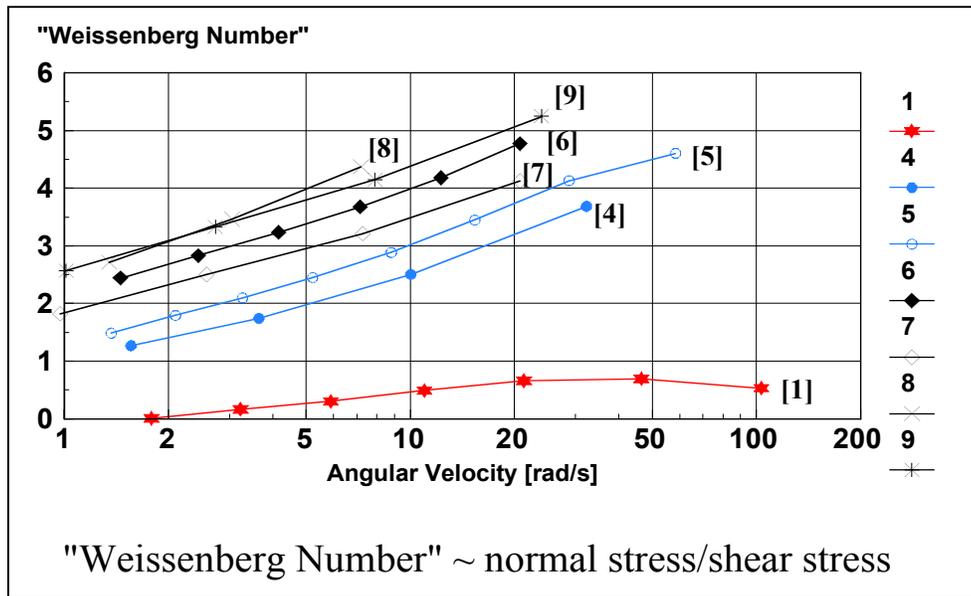
Figure 8
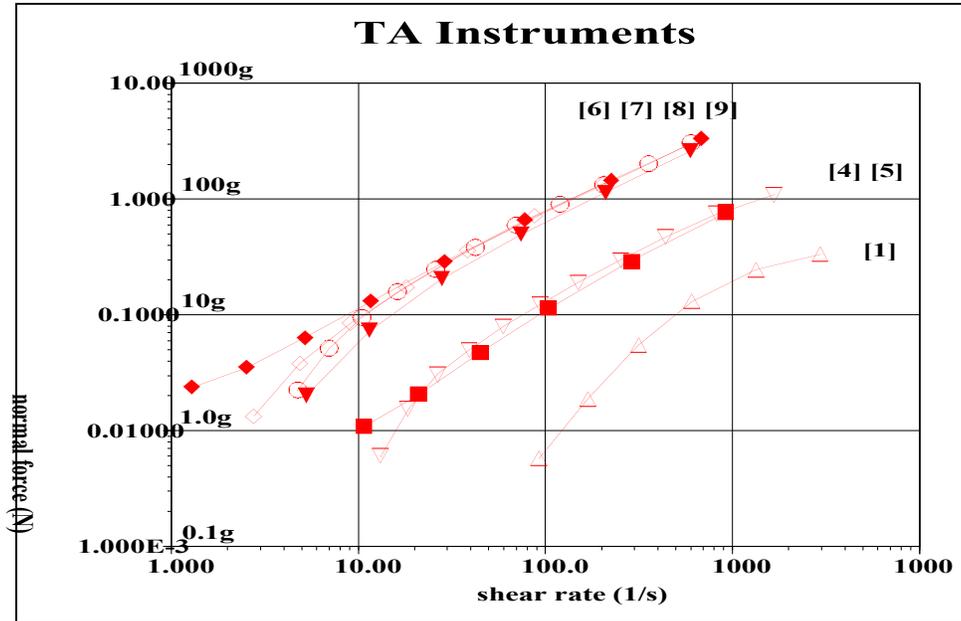
The samples clearly fall in the same pattern as predicted by the viscosity data, and there is still no way of weeding out [6], [7], [8] & [9] from one another.

For a more sensitive discriminator of elasticity versus viscosity, the ratio of the normal stress generated by a fluid to the shear stress in the flow field can be used, since it equates to the dimensionless group called the Weissenberg number [We]. – (personal communication from Prof. G Mc.Kinley MIT). When this ratio is calculated the data in figure 9 are generated.

Figure 9

"Weissenberg Number" ~ normal stress/shear stress

As can be seen in figure 9 the samples are now separated into distinct plots and the samples that consistently fail in the processing tests, i.e. [8]& [9] have the highest Weissenberg numbers at a given rotational velocity. This means that at a given processing speed, these samples will be more likely than the others to generate normal forces that can result in surface irregularities. Since samples [6],[7],[8]&[9] have similar Capillary numbers, then the normal forces generated by [8] & [9] will make them especially prone to perform badly.

Conclusions

It is difficult to predict which of these adhesive samples is likely to perform badly on the basis of factors such as viscosity or surface tension alone. Rheometry can help by providing insight into elastic behavior that viscometry can not. This is often especially important in complex non-linear flows such as in the processing of liquids in roller coaters etc.

The viscosity data from the AR1000N agreed well with the Brookfield data. The rheometer showed a much closer overlap of viscosity between samples [6] – [9], although this was at shear rates too low for the Brookfield to probe. Without clearer insight into the geometry and test method used by the Brookfield LV it is difficult to comment as to why the discrepancy exists. It is certain however, that a cone and plate geometry is the preferred way to get absolute viscosity data for simple viscous liquids.

Using the normal stress data from the AR1000N, it was possible to calculate a dimensionless group like the Weissenberg Number that discriminated between samples with closely related viscosities and Normal Force behavior that did not process equally well [6],[7] & [8],[9]. Samples [8] & [9] exhibited only slightly lower surface tension than [6] & [7], yet they consistently failed to perform in comparison. Samples with high Weissenberg numbers appear to process less effectively than samples with low

Weissenberg numbers. This technique would seem to show promise as a means of rapidly screening candidate adhesives, but does not apply to aqueous systems where surface tension is more likely to dominate over entanglement phenomena.

<u>References</u>

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Handbook of Chemistry & Physics [Dimensionless Groups F 326 – 343] CRC