Assessment of Rheological Properties of Materials used in Printing of Solder Paste

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SUMMARY

The printing process is the most critical step in surface mount assembly, with over half of production defects being attributed to it. To control a printing process the correct process parameters must be set and monitored to ensure quality, and to correct for any deterioration. Fully automated printing machines can, to some extent, correct process parameters, but the wide range of degradation modes makes a complete control system difficult. Rheological properties are the key factor in designing new solder pastes. This project will focus on rheological properties that are vital for print grade solder paste materials. By optimising the rheological properties to widen the process window, demands on the machine setting are reduced.
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1. INTRODUCTION

Rheology is the science of the deformation and flow of matter. Measurement of rheological properties of solder paste in SMT is part of a suite of tools used for robust statistical process control. Managing the flow of materials and applying the correct forces is critical to printing quality. Predominantly it is how these materials behave under shear that is most important. Rheological methods establish the relationship between shear stress of solder paste and shear strain rate.

If stress is removed after deformation has occurred, the strain may or may not return to zero. If the strain does not eventually return to zero, flow has occurred. If flow occurs, even for a vanishingly small shear stress, the material is said to be liquid, otherwise it is solid. No recovery occurs with some materials, and they are said to be inelastic. For some liquids, partial recovery occurs, and such are termed elastic liquids (for example many adhesives are elastic liquids). If we also consider the time taken for recovery. For material where the response is not immediate, but quite slow, as with some polymers or leather, the materials is visco-elastic.

Mathematical models have been developed to analyse the rheology data from experiments and predications, to closely approximate actual behaviour. However, the models assume that solder paste is isotropic and homogenous. A review of various aspects of rheology, relevant to solder paste are now considered.

1.1 Components of solder paste

To understand rheology measurements of solder paste composition of solder paste is discussed as a system made of 5 parts:

- **binder (resin)** – this part is responsible for tackiness, providing there is no significant loss of solvent, which reduces tackiness. During reflow resin reacts with metal oxide layer in a reduction reaction and removes (cleans) soldering contacts helping solder to wet.
- **solvents** – used to hold binder in solution. They can absorb water, which makes the binder less efficient. Loss of solvent (evaporation) is responsible for shortening solder paste stencil life (drying)
- **thickeners** – thixotropic materials responsible for gel structure (elastic rather than viscous) of solder paste. Paste needs some recovery time from stressed state (time-dependant, non-Newtonian), and this recovery can be characterized as a time change of difference between G’ and G” (elastic and viscous modulus). Dispersing solder particles in a gel is safe way to eliminate sedimentation. This is the attributed to yield stress (famous as ketchup on a shirt shake).
- **activators** – improve activity of binders in reduction of surface metal oxide layer of a pad/termination. Their contribution in rheology of solder paste system is minimal.
**Solder particles** – SnPb of lead-free alloy particles of spherical shape in various diameter ranges starting from 5 to 40 µm. To assess the solder particles size and shape a conventional SEM. Particles can be inspected directly after dissolving from flux and gelling agent. Metal content can be checked by weighing printed deposits before and after reflow, providing flux residues are removed after reflow with iso-propyl-alcohol (IPA).

Adding a gelling agent (thixotropic part) into the flux causes an increase in viscosity at very low strain rate, compared to simple flux formulations with no solder particles present. A controlled strain rate rheometer (rather than stress controlled) is required to measure this property.

Solder paste is mixed in two stages. In the first stage the medium (vehicle) is mixed from activators, gelling agent (rheology part), resin and solvent. This phase of mixing is critically important in final product quality. The second mixing phase is mixing of solder particles with medium into final solder paste (cream). The quality of input compounds should be checked before mixing to cut down production defects. Development of bubbles in the gel-flux mixture before the solder particles are mixed in can cause difficulties and should be monitored (mixed at elevated temperature). Bubbles of air or trapped gasses in cartridges for enclosed print heads can deteriorate print quality (skipping, insufficient paste).

### 1.2 Simple Rheological Models

The first model to be described represents a solid, and the other models are all applied for materials that can fully or partly flow. Flowing materials, are therefore inelastic and have time-independent flow curves, as shown in Figure 1.

a) The Hooke model

This model is defined by the relationship:

\[
\frac{\sigma}{\gamma} = \text{constant} = G'
\]

(1)

generally known as Hooke’s law. G’ is the shear modulus.
**Table 1 Some mathematical models used in rheology**

<table>
<thead>
<tr>
<th>Figure 1</th>
<th>Name of the model</th>
<th>Materials</th>
<th>Rheology behaviour</th>
</tr>
</thead>
<tbody>
<tr>
<td>(a)</td>
<td>The Hooke model</td>
<td>many solid such as metals</td>
<td>does not flow, not viscoelastic</td>
</tr>
<tr>
<td>(b)</td>
<td>The Newtonian fluid model</td>
<td>low molecular weight liquids, water, water solutions, oils, dilute polymer solutions, organic liquids, silicones, liquid metals</td>
<td>does flow, inelastic, time independent flow curves</td>
</tr>
<tr>
<td>(c)</td>
<td>The Bingham model</td>
<td>concentrated suspensions and emulsions for example paint, printed inks, clay slurries, plastic emulsions, colloidal systems</td>
<td>does flow, inelastic, time-independent flow curves, plastic viscosity with yield stress</td>
</tr>
<tr>
<td>(d, e)</td>
<td>The Power law fluid model (The Ostwald model)</td>
<td>polymer solution, melts and solvent based coatings</td>
<td>does flow, inelastic, time-independent flow curves, shear thinning or shear thickening</td>
</tr>
<tr>
<td>(f)</td>
<td>Others as combination previous models: Hershel-Bulkley, Vocadlo models</td>
<td>many industrial fluids</td>
<td>does flow, inelastic, time-independent flow curves, has a yield stress</td>
</tr>
</tbody>
</table>

**Figure 1 Flow curves and Viscosity curves for models inelastic materials**

Shear Stress $\sigma$

Strain Rate $\gamma$ [rad/s]

Viscosity $\eta$

Strain Rate $\gamma$ [rad/s]
b) The Newtonian fluid model, Figure 1 (b)
For fluids, the viscosity $\eta$ [Pa.s] (dynamic viscosity), defined by equation 2 and for Newtonian fluids is constant.

$$\gamma = \frac{\sigma}{\eta} \quad (2)$$

The $\gamma$ is strain rate at which a material is sheared. The reciprocal of viscosity, $\phi = 1/\eta$, is called the fluidity. In some applications the parameter, kinematic viscosity $\nu = \eta/\rho$ is used, where $\rho$ is the density of the fluid.

c) The Bingham model, Figure 1 (c)
The Bingham model represents a solid but is used only when flow occurs. It is postulated that the material behaves as an elastic solid for stresses less than yield stress $\sigma_Y$ (yield point) and that, for greater stresses,

$$\gamma = \frac{\sigma - \sigma_Y}{U} \quad (3)$$

The Flow curve is linear, Figure 1(c), with an intercept $\sigma_Y$ on the stress axis. $U$ is called plastic viscosity and is equal to slope of the flow curve. The viscosity, Figure 1 (c), becomes infinite as $\gamma \rightarrow 0$ and approaches the value $U$ as $\gamma \rightarrow \infty$. The elastic deformation before flow begins is almost invariably ignored because the corresponding strain is small in comparison with the strain due to flow. Behaviour in elastic region is usually not well defined.

d) The Power Low fluid model (Ostwald model), Figure 1(d, e)
The equation for the model may be written

$$\gamma = k_p \sigma^N \quad (4)$$

Where $k_p$ is material constant. A power law model with $N > 1$, the viscosity decreases as the shear rate increases, Figure 1(d), the fluid is said to show shear thinning. This phenomenon is time-independent, opposite of thixotropy or rheomalaxis, which are time-dependent effects.
The power law model has been used for shear thickening materials, i.e. materials that increase in viscosity as the rate of shear increases. In this case, $N < 1$, Figure 1(e).

e) Others inelastic flow models:
Above the yield stress, the flow curve is no longer straight, because the Bingham and power law models can be regarded as special cases, the models represent the behaviour of a large number of materials, defined by equation 5 and 6, where $K_H$ and $K_V$ are material constants.

Herschel-Bulkley model, Figure 1(f)

$$\gamma^* = \left( \frac{\sigma - \sigma_Y}{k_H} \right)^N \quad (5)$$
Voadiao model, Figure 1(f)

\[ \gamma = \frac{\sigma^N - \sigma^N_y}{k_y} \]  

(6)

f) Visco-elastic liquid models:
These are materials having viscous and elastic properties, and the term is usually restricted to solids. There are two important special cases of the use of models to represent the behaviour of elastic liquids in simple shear. If the liquid is subject only to small strains, as for example in oscillatory or creep tests the strain rate, the stress and time derivatives of stress may be related by a linear equation.

1.3 Time Effects During Flow

When a shear stress is applied suddenly to a fluid, the initial strain rate may not be maintained apart from any inertial effects for two distinct reasons. One is, that part of the mechanical energy supplied to the material may be stored as elastic energy. As the maximum stored energy for a particular stress is reached the rate of supply of energy falls to that necessary to maintain flow, so that the strain rate falls. Reducing the stress to zero and observing elastic recovery may establish the existence of the stored energy.

The second effect for a change of strain rate is that the structure of the material changes in some way. Perhaps weak bonds between suspended particles are broken, irregularly shaped particles or long chain molecules become aligned, or particles collide and form aggregates. No elastic recovery is observed, when the stress is removed. The strain rate usually increases, but may decrease, with time. Sometimes a limiting value of strain rate is reached, but often the change in strain rate continues for the whole of a test of reasonable duration. The change in material property may be permanent: an irreversible loss of viscosity is termed **rheomalaxis** or rheodestruction. Often the change of viscosity is temporary, the material being restored to its original condition by resting for a sufficient time free from stress. A reversible time-dependent increase in viscosity is termed **thixotropy**, and reversible time-dependent decrease of viscosity is called **negative thixotropy**. Figure 2 shows some ways in which the strain rate varies with time when a constant stress is applied, removed, and then reapplied to materials showing time-dependent behaviour. Thixotropic and viscoelastic behaviours are quite distinct, but viscoelasticity could apparently be confused with negative thixotropy if the recovery on removal of stress was not observed.
1.4 Wall effect (slippage)

Wall effect occurs when fluid adjacent to a metal surface (spindle) does not move with the velocity of that surface. A velocity difference could occur though slippage if, for example liquid vehicle separates form particle suspension. A test using the standard, parallel plates in a flow type experiment can be performed to ascertain where slippage occur. A steadily increasing stress is applied ranging from the materials yield stress to 500 to 1000 Pa above that value, depending on the material being tested and

Figure 2 Variation of Strain rate with time for various liquids. The stress has either a constant value $\sigma_0$ or is zero. (a) Elastic liquid; (b) Thixotropic liquid; (c) Liquid showing negative thixotropy; (d) Liquid showing thixotropy with rheomalaxis
the plate geometries. Any slippage is determined where there is a double peak on the viscosity curve (shear stress vs. instantaneous viscosity), example is shown in Figure 3 (blue curve). The difference when compared to the curve measured using sand blasted plates of the same geometry also indicates that there has been some slippage.

Sintered and sand blasted parallel plates (20 mm in diameter) are better for avoiding wall slippage on the other hand a gap in between the plates is not defined so well.

![Slippage Test Graph](image)

**Figure 3 Slippage test**

2. **Rheometry Tests Applied on Solder Pastes**

Solder paste is an isotropic visco-elastic fluid with time dependent behaviour. From a rheological point of view it is a highly loaded solid dispersion in a medium viscosity continuous creamy phase. The relatively large metal particles are supported against phase separation by the viscous suspending phase. The choice of the solder paste for a particular application depends on several properties, including deposition ability, holding capability of components during pick and place process, soldering performance and the reliability of the solder joint. The rheology of solder paste is an important consideration since the flow and deformation behaviour directly affects the print quality. The flow and deformation correlate with the number of **print defects**, and post print behaviour of the solder paste, such as **tack value** and **slump resistance**. Hence,
the correlation of solder paste rheology with its performance prior to reflow is extremely important for the selection, as well as formulation, of solder paste.

Solder paste (cream) is non-newtonian suspension of solid particles in liquid vehicle with thixotropic properties. The thixotropic consistency is important, as this is indicative of whether slumping or smearing will occur. The viscosity of solder paste depends on the metal particle content (88-91% by weight), size and shape of solder particles and on the compounds that are added to make the paste thixotropic. The viscosity requirements depend upon the method of application of the paste such as dispensing, screen or stencil printing.

Viscosity is temperature and humidity dependant and at higher temperatures it can decreases significantly. Thixotropic compounds added to solder pastes are similar to bee’s wax, and their viscosity can decrease dramatically at above 30°C. The application of solder paste should be not carried out at the temperatures above 27 °C. Consideration should be given to the pad design and reflow temperature profile with attention to pre-heat, to allow for controlled evaporation of solvents and rheology modifiers. Paste viscosity can increase substantially during storage and it should therefore be stored in a temperature-controlled environment.

2.1 Rheometer Requirements for Determining Solder Paste Properties

Requirements for solder paste rheometry for use in the electronic industry are as follows:
   a) Small sample volumes
   b) Easy to clean measuring system
   c) Uniform share rate for good reproduction

Most rheometers are based on rotation systems. The great majority of rotational instruments use geometries with common axis and a ‘parallel plates’ geometry. This has the advantage of measuring small samples of solder paste without crushing solder particles in the plate gap.

There are two ways that the rotation can be applied and the couple, or force torque, measured: the first is used in a controlled stress rheometer, Figure 4. The control stress rheometer consist of a constant torque motor which works by a drag cup system and an angular position sensor which detects the movement. The rheometry instrument is connected to a computer and software automatically converts the applied value of torque to a shear stress. The reading from the position sensor is converted to a strain and by monitoring the change of strain as a function of time the shear strain rate can be obtained.
The second design, is called a controlled strain rate rheometer, see Figure 5. The instrument comprises of a motor with constant angular velocity turn drive system with the same geometries as the control stress rheometer. Twist from the sample is transferred to the torsion bar and torque detection system, which measures the resistance torque caused by sample.
2.2 Selected Rheological Tests for Solder Paste Investigation

Deformation is measured in the non-destructive region of elastic or visco-elastic deformation. In the controlled stress rheometer instrument, stress can be applied and released at will, and the actual behaviour of the sample can be measured directly. Typically an induction motor drive is mounted on a minimum friction low inertia air bearing, and includes a high resolution optical encoder. Three major categories of tests are conducted with the use of this rheometer: oscillation or dynamic testing, creep or step change tests, and flow tests.

Flow Test
Describes the relationship between the stress and shear rate of the sample. In this test a range of stresses are applied in either a continuous (ramp) or stepped manner. The flow test is intuitively destructive of the sample’s structure and typical only provides viscosity data, although it may be combined with oscillation to generate visco-elastic data. The yield stress (yield point) is the point between the elastic and viscous regime and is the most commonly taken parameter from the flow curve.

Oscillation Test or Dynamic Testing
The oscillation technique is a non-destructive test, which simultaneously measures both the viscous and the elastic behaviour of a sample. The stress is applied in a sinusoidal manner, see Figure 6 and hence the sample is simply “wobbled”.

\[ \sigma = \sigma_0 \cos \omega t \]  

(7)

The stress oscillation produces a strain:

\[ \gamma = \gamma_0 \cos(\omega t - \delta) \]  

(8)

where \( \sigma_0 \) and \( \gamma_0 \) are magnitudes of harmonic waves

The phase lag \( \delta \) between stress wave and strain wave, and the amplitude ratio \( \gamma_0 / \sigma_0 \) depends on the material and its previous state. The oscillation test is used to characterize visco-elastic behaviour and can also be used to determine structural changes occurring in the sample. The elastic component in the oscillatory test is given by rheological function \( G'(\sigma) \), Equation 9, which is called the storage modulus (elastic modulus).

\[ G' = \frac{\sigma_0 \cos \delta}{\gamma_0} \]  

(9)

This \( G' \) represents the mechanical energy stored and recovered. It is a measure of how well structured a material is. If the sample is predominantly elastic or highly structured, the storage modulus will be large. Increasing \( G' \) over time is indicative of building structure and conversely, decreasing \( G' \) is indicative of structure being destroyed.
The viscous component is given by rheological function $G''(\sigma)$, defined by Equation 10, the **loss modulus** (viscous modulus), and is the measure of the mechanical energy that is dissipated as heat.

\[
G'' = \frac{\sigma_0 \sin \delta}{\gamma_0}
\]  

(10)

If the $G''$ is large, the sample is predominantly viscous.

**Figure 6 Phase shift between shear stress and corresponding strain by oscillation test**

For an oscillation with the constant stress rheometer, the range of amplitude of $\sigma_0$ and frequency is entered, and the software automatically converts the results of shear stress to the storage $G'$, and loss modulus $G''$.

### 2.3 Creep or Step Change Test

The creep test is a static method that determines the visco and elastic behaviour of the material. This technique applies a **constant stress** $\sigma_0$ and measures the effect of this stress as function of time. In the creep test, the **compliance $J_c$** (sometimes marked $J_c$) of the material is studied. The compliance of the material is defined from Equations 11.

\[
J = \frac{\gamma}{\sigma_0}
\]  

(11)

If we apply a small constant stress $\sigma_0$ to a visco-elastic material and hold it for a period of time whilst measuring the resultant strain we will see behaviour initially from elastic components followed shortly by viscoelastic effects. In a creep test, the selected shear stress is instantaneously applied to a sample and the resultant strain monitored as a
function of time. After some predetermined time the stress is removed and the strain is again monitored. The three typical response curves are shown in Figure 7.

When the stress is removed, the compliance $J$ (sometimes marked $J_r$) is followed a relaxation curve. It is important to note that the relaxation compliance uses $\sigma_0$ initial stress as constant in the Equation 11, although there is no actual stress present in the test.

![Figure 7 Compliance vs. time (a) Pure elastic; (b) Pure viscous; (c) Visco-elastic material](image)

### 2.4 Solder Paste Performance Prior to Reflow

Three aspects of solder paste performance are commonly measured: **print defect**, **tack**, and **slump**. Two print defects are identified to help evaluate the printability:

a) Smearing or bridging of the solder paste, Figure 8(a)
b) Insufficient solder paste, Figure 8(b)

![Figure 8 (a) Smear; (b) Insufficient solder paste (the dotted box represents ideal deposit)](image)

The tack is defined as the tackiness reading determined on freshly printed paste at room temperature. Unless otherwise specified, the test method of ANSI / IPC-SP-819 is used for determining the tack.

Slump is shown schematically in Figure 9. Slump can be characterised using a Slump Index (SI), which is evaluated by identifying the largest spacing bridged by paste for
both horizontal and vertical aperture patterns. The average of those ratios for the corresponding largest bridged spacing is than calculated and is used to represent the slump performance.

![Solder Paste Slump Diagram](image)

**Figure 9** Slump of the solder paste after stencil printing

### 2.5 Dimensional Solder Paste Measurement for Rheology

Assessing printability through rheological measurements requires reliable measurement systems to determine deposit size and shape. Visual inspection is helpful as a QC (Quality Control) tool but will not recognize subtle changes in shape usually indicating deterioration. Such a quantification tool is essential if meaningful correlation is to be established with rheological measurements. The measurement tool can be a laser scanning instrument measuring individual heights of deposits [1]. Precision of this instrument should be below that of a solder particle diameter, i.e. around ± 5 μm.

### 3. RECOMMENDATIONS

Gap size in parallel plate rotational rheometer for characterizing solder paste rheology should be set to 500-1000 μm. As mentioned before, for solder paste systems the use of roughened plates is advantageous, and prevents slippage. A lower gap can also cause slippage.

The oscillation test using a low frequency sweep is useful in measuring solder paste recovery (hysteresis loop).

Weakly thixotropic material (thickeners) can drop value of G’ (elastic modulus) down and sometimes even below G” (loss or viscous modulus). This can cause paste to become liquid-like and slump possibly forming wet bridges.

Moisture absorption can be critical to solder paste performance. Even with resin solvent-based paste systems hydroscopic solvents attract water and this deteriorates printing quality.

Probably the most important part in controlling the quality of a printing process is played by the stencil. A badly designed and/or produced stencil alone can spoil printing process.

Solder paste formulation is always a compromise between the requirements of printing, tackiness, and reflow, which means the composition is application dependent. The
preferred rheology methods should therefore be highly sensitive to slight changes in the solder cream properties.

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