RHEOLOGY OF SOLDER PASTE: SHELF LIFE STUDY

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ABSTRACT
Can expired solder paste be used without an issue? Solder paste consists of powder and flux components that start chemical reactions immediately after blending. Therefore, during manufacturing, packing, transportation and storage, solder paste is continuously changing over time. Additionally, during usage varying temperature and humidity conditions can influence the reaction rate. Flux formulation is the key factor affecting the reaction between solder powders and flux, which will further impact the solder paste shelf life. Besides solder ball, slump and viscosity measurement, rheological analysis is one of the best methods to quantify the change of solder paste. In this paper, an accelerated shelf life prediction method is introduced to study the status of solder paste in a very short period. Several rheology test methods are developed to investigate the change of solder paste from different perspectives, including yield stress, shear sweep, strain sweep (oscillation mode) and axial force. Each rheological experiment has its limitation, and the responses are influenced by the test method used. This paper examines the accuracy and precision of rheological experiments through four different solder pastes. Both no-clean and water-soluble type pastes are included to illustrate the environmental contribution to the paste degradation. This study forms the background for a better understanding of the correlation between rheological properties and shelf life of solder paste exposed to extreme conditions.

Key words: Solder paste, flux, rheology, shelf life, printing

INTRODUCTION
Most of the solder paste products require low temperature storage between 4 ˚C and 10 ˚C with the shelf life of 6-12 months. The shelf life of solder paste products will vary based on the chemistry composition of the paste flux. Since the flux is in constant contact with the solder powder, it is continually acting on the oxides of the metal surfaces of the solder powders, and this action may reduce the activity levels of the fluxes. This is also why the paste manufactures always recommend refrigerating the solder paste to reduce this chemical reaction rate and give a longer shelf life to the paste. The shelf life of a solder paste typically is defined by many areas: IPC solder ball test, viscosity and tackiness measurement, as well as application evaluation such as printing and reflow test before and after the paste is stored in refrigerator (or room temperature) environment for certain amount of time. Specifically, the viscosity is highly correlated to the printability of the paste. [1] The current viscometer such as Malcom and Brookfield were designed for collecting viscosity at certain shear speed, which only provide single data point as a record. And all the paste suppliers adopt viscometer and use one data point to communicate with internal quality control and external customers. However, one data point can easily underestimate or overestimate the real viscosity because the solder paste has dynamic characteristics of fluidic performance.

Rheology has become a common tool in the qualification and development of electronics assembly products. [1-7] Rheology studies can help evaluate the solder paste performance and processability and predict product's long-term stability and shelf life. This study developed accelerated shelf life prediction method with several rheological test methods. These methods include yield stress, shear sweep, oscillation amplitude sweep, and axial force. A DOE analysis can be used together with these methods to understand the effect of temperature and time on the shelf life of solder paste by looking into fluidic characteristic parameters such viscosity, yield stress, modulus, phase angle and axial force.

MATERIAL AND EXPERIMENT
Accelerated Aging Test of Solder Paste
During the solder paste blending, the fluxes and powders are mixed and certain chemical reactions occurs, and temperature increases the rate of a reaction. Therefore, when a solder pasted is placed in elevated temperature environment, the shelf life of the paste would be significantly shortened, which can be used to predict the shelf life at low temperature.

All the paste samples were prepared with the same lot of Type 4 SAC 305 solder powders. The metal loading was 88.5 wt% for all solder paste samples. Each paste was blended in the same lot and separated into jars for different storage conditions. Fresh samples are stored at room temperature (22 ˚C) for 24 hours. To conduct the aging test, solder pastes were placed in the oven at elevated temperature, 30 ˚C and 40 ˚C for 1 day and 3 days, respectively, to accelerate the reaction between flux and solder powder to understand the storage condition effect on rheological properties of solder paste. There are four different solder pastes used for this shelf life study: no clean paste 1 (**NC P1**) and no clean paste 2 (**NC P2**), water-soluble paste 1 (**WS P1**) and water-soluble paste 2 (**WS P2**). Therefore, a three factor DOE can be designed to investigate the shelf life of different solder paste though accelerated shelf life study. The DOE was summarized in Table 1.

Table 1. DOE of Solder Paste Shelf Life Study

Factor	Levels	Values
Paste	4	NC P1, NC P2, WS P1, WS P2
Storage Temperature (˚C)	2	30, 40
Storage Time (Day)	2	1, 3

Rheometer and Experimental Parameters

TA Instrument discovery hybrid rheometer HR-3 mounted with a 40 mm diameter parallel plate was used to analyze all solder paste samples. The measurement temperature was controlled at 25 ˚C for most of test, except temperature dependent test method. All paste samples were measured at a 1000 µm gap. A pre-shear cycle was programmed in each experiment at 0.1 rad/s for 10 s, which is helpful to build similar rheological history of sample before collecting data and provide more reproducible result for analysis. [7] Two basic rheology measurement methods, flow mode and oscillation mode were used to understand the rheological performance of solder fluxes and pastes. Detailed experimental parameters were described in different test methods.

RESULT AND DISCUSSION

Flux not only provides the chemical role to clean the solder surface oxide during high temperature reflow, but also contributes physical role to make sure the paste can be printed and released properly during printing and jetting. When the solder pastes expired, it is possible that either the chemical performance degraded, such as solder ball test failed, poor wettings on board, or some physical performance changed and resulted in troubles of paste printing, such as shorter stencil life and inconsistent paste transfer efficiency. Typically, the pure paste flux has longer shelf life than paste with powders because there is no chemical reaction between flux and powders. During our study, the different flux formulations have been tried to blend with same powder and tested at accelerated temperature storage conditions. It is found that some fluxes will result in the paste dried out after aging at 40 ˚C over time, and some fluxes will survive. The dried-out solder pasted was further investigated. The powders were separated from dried paste and cleaned several times by solvent and compared with fresh powders. Figure 1(a) shows the SEM images of Type 4 SAC305 fresh powder used in three paste samples, a smooth surface has been observed before blending with chemical flux. Figure 1(b) shows the powder cleaned from dried paste. The powders turned to rough surfaces which is an evidence of reaction between metal oxide and flux. It is known that the powder always has few nanometer thick tin oxide layer during the powder manufacturing and storage, and the flux is usually acidic environment. Hence, at the elevated temperature, the reaction rate between metal oxide and chemical complex in the flux will speed up.

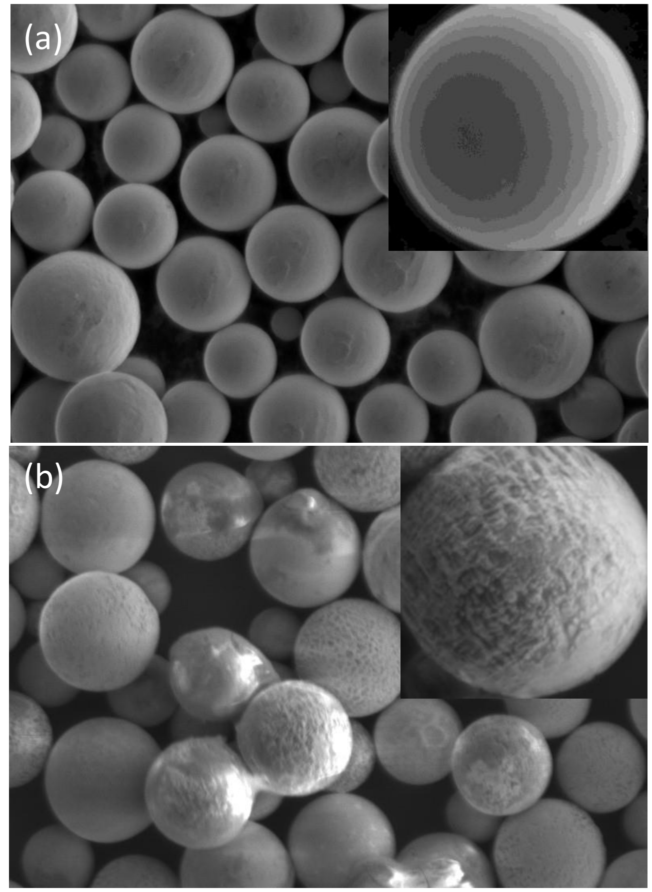

Figure 1. SEM images of SAC305 Type 4 solder powder. (a) Fresh solder powders before blending with paste flux; (b) solder powders cleaned from the dried paste which is resulted by inappropriate flux formulation and extreme storage condition.

With the improvement of flux formulation, the shelf life of solder paste can be extended to longer time, and the environment storage tolerance of solder paste raises. In this paper, both room temperature stable and low temperature stable paste fluxes are selected to make pastes and go through the rheology analysis, because it is difficult to work with dried-out paste to collect meaningful data. From the real data, **NC P1** has 1-year shelf life if stored in the refrigerator (<10 ˚C), **NC P2** has 1-year shelf life at room temperature storage.

Yield Stress Method

Yield stress is the minimum shear stress required to initiate flow which is an important parameter for all structured fluids. In solder paste application, the yield stress determines the force needed to start paste rolling during stencil printing, dispensing/jetting on board or filling a jar in solder paste production. The higher yield stress of the solder paste resulted in higher pressure required of printing or dispensing.

Figure 2 shows the most extensively used test method to measure the yield stress for solder pastes aged at different conditions. All four pastes presented different shapes of curve which is due to the different formulation of fluxes. A flow mode stress ramp test has been applied with the stress range from 0 to 800 Pa within 80 seconds. The stress at the maximum viscosity provides representative value for the yield stress. It is noticed that the solder paste typically needs a long time to recover after shear, the yield stress of solder paste without fully recovery may shift to smaller value, so 120 seconds recovery time has been applied after pre-shear. From the figures, **NC P1** shows most of the stress shift, from about 200 Pa (fresh) to 350 Pa (40 ˚C for 3 days), followed by **WS P2** changing between 76 Pa (fresh) to 150 Pa (40 ˚C for 3 days); **NC P2** and **WS P1** has minimum stress change, indicating better shelf life stability than the other two pastes. This result shows that the paste shelf life is not related to the flux type, both no clean and water-soluble type can be formulated to obtain room temperature (or higher temperature) storage stable. All samples showed the more increasing of viscosity at higher storage temperature 40 ˚C than 30 ˚C which indicates the storage temperature has greater impact than storage time.

It is noticed that this test method may cause wall slippage. There are many literatures reported the wall slip issue in yield stress analysis, especially at high stress range. [8-9] When wall slip occurs, the measured yield stress will be lower than the actual value. In addition, the measured yield stress value is dependent on the experimental stress ramp rate, so the test results are less reproducible.

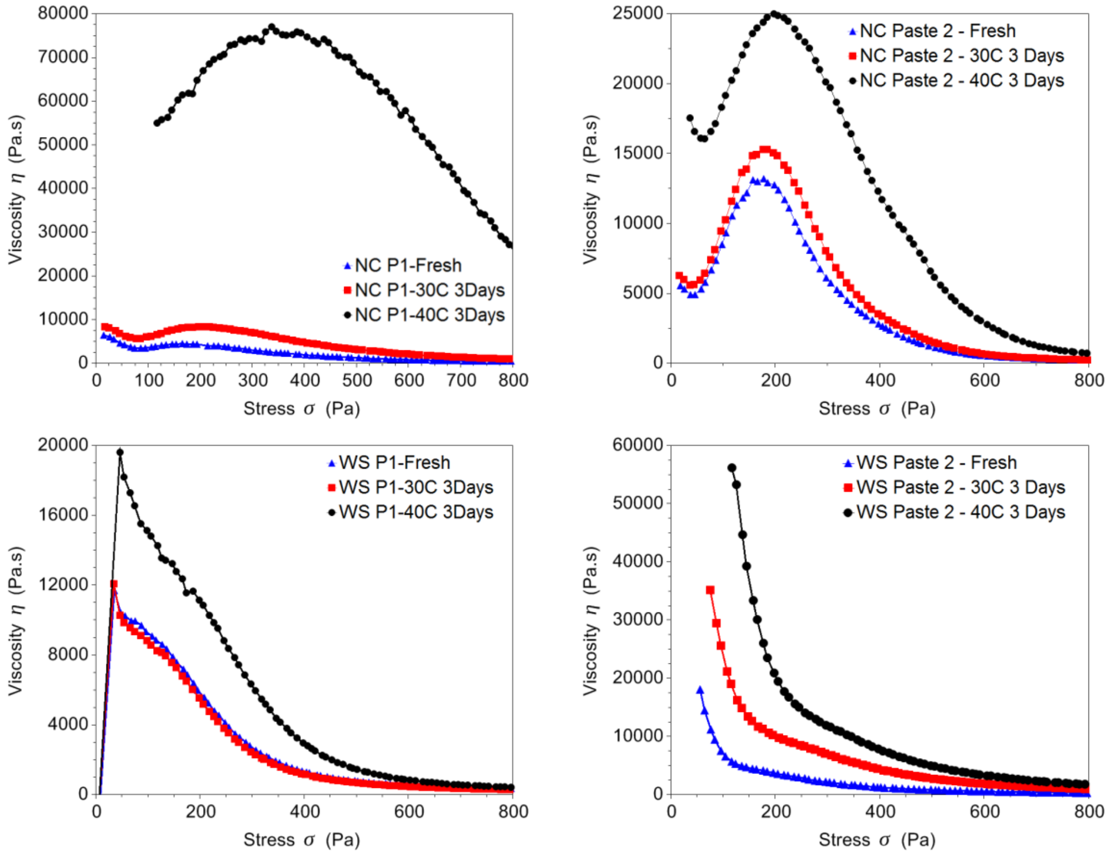

Figure 2. Yield stress analysis of four pastes.

Shear Sweep Method

Shear sweep is the most simple and reliable test to overall map the material viscosity over a wide range of shear rate. Compare to the single data point of viscosity reported by viscometer with fixed shear speed, shear sweep method can present not only viscosity, but also stress and thixotropy of the fluid. Due to the feature of flux, the solder paste exhibits shear thinning behavior, and each paste will show its characteristic curve in viscosity vs shear rate plot. Figure 3 shows shear sweep plots of each solder paste sample at five different conditions: fresh paste, paste aged at 30 ˚C for 1 day and 3 days, paste aged at 40 ˚C for 1 day and 3 days. **NC P1** was mostly impacted by storage condition, followed by **WS P2** which indicates the poor stability of solder paste at high temperature; both **NC P2** and **WS P1** shows minimum change of viscosity over accelerated temperature conditions which indicates good room temperature stability of these two pastes. The 40 ˚C storage condition can significantly increase the overall viscosity of **NC P1** within 1 day, and the viscosity is keep changing over time. In another word, the thixotropic index (TI) increased at high temperature storage. The viscometer is used to measure the viscosity at two speeds (by a factor of 10), which is difficult to see dramatic change compare to rheometer measurements which plots data into 4 or higher orders of magnitude of shear rate. It is also seen that the viscosity change is not sensitive enough at high shear rate range between 10 to 100 s^{-1}. In previous study, the value of viscosity measured at high shear rate has certain correlation to the Malcom viscometer measurement. [7] When the viscosity data reported by viscometer, it is possible that the viscosity change of solder paste cannot be found, or the minor change falls into the product specification range or system error of instrument. Although this minor change may not result in the difficulty during paste application, a false conclusion can be drawn that the viscosity of paste did not change.

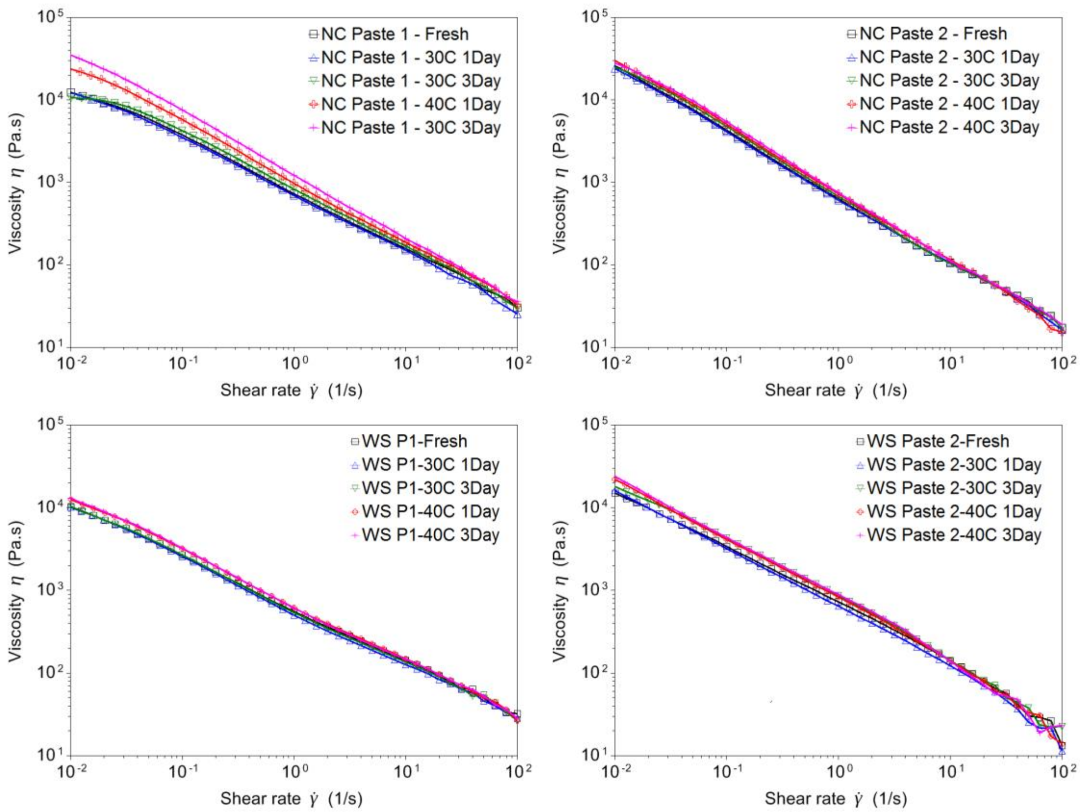

Figure 3. Viscosity measured by flow mode shear sweep method for 4 different pastes aged at different temperature and time.

Since each solder paste has its characteristic fluidic property, it will be inappropriate to compare the absolute viscosity value between each sample. To understand the significance of each factor of solder paste shelf life, including storage temperature, storage time and solder paste formulation, the value of viscosity increase ($\Delta\eta$) at shear rate of 1^{-s} between fresh and aged condition was quantitively studied through DOE analysis. Figure 4 shows the main effects plot and interaction plot for $\Delta\eta$, which indicates the different formulation of solder paste flux will significantly dominant the viscosity increasing of solder paste; storage temperature and time would both result in higher viscosity in general, and the effect of temperature is more significant than time. From the interaction plot, it is found that there is no interaction between storage temperature and time. Longer storage time and higher temperature will both result in the viscosity increase. **NC P1** and **WS P2** are more sensitive to temperature, which indicates the poor stability of storage at room temperature or higher. and **NC P2** and **WS P1** are very stable at 30 ˚C storage environment. Again, the simple shear sweep test can provide accurate and reliable data of viscosity values of solder paste which would benefit for statistical analysis with predictable storage condition of shelf life.

Strain Sweep Method

There are many oscillation mode rheology studies reported to understand the mechanical behavior of solder pastes, such as solid-like and liquid-like behaviors through relationship between storage modulus (*G'*) (elastic component), loss modulus (*G''*) (viscous component) and phase angle (δ). Basically, an oscillatory mode measurement applies a sinusoidal shear deformation (input) in the sample and measures the resultant stress response (output) between the two sinusoidal waves, which has been widely used in characterization of viscoelastic materials.

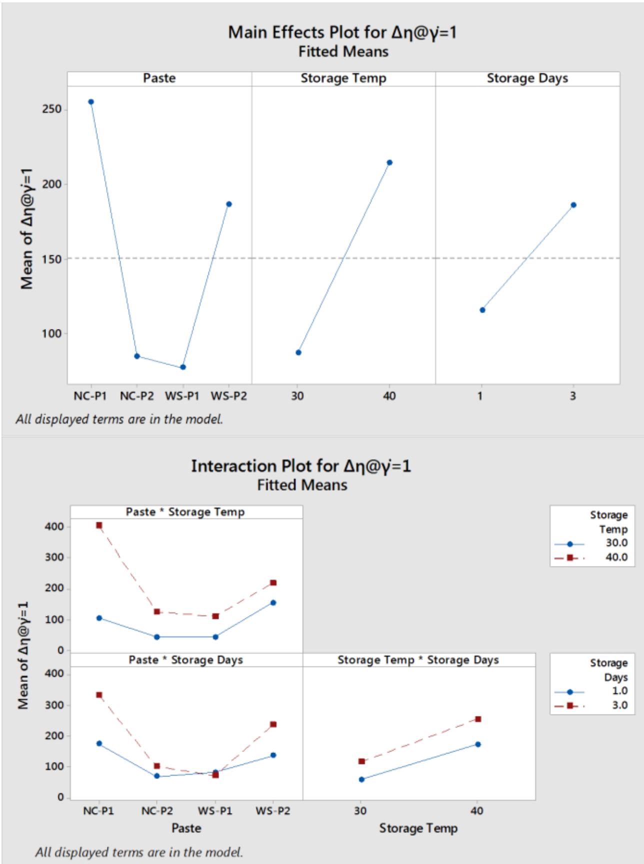

Figure 4. DOE analysis of viscosity changes of each paste sample aged at different temperature and time (data collected at shear rate=1^{-s}).

Figure 5 shows the oscillation mode strain sweep method of all four paste samples with modulus and phase angle plot for fresh and aged paste at 30 ˚C and 40 ˚C for 3 days. This strain sweep test was carried out at constant frequency of 1 Hz, and the strain% varied between $1x10^{-2}$ to $1x10^{3}$ in logarithmic sweep, and the material response to increasing deformation amplitude (strain or stress) was monitored. Since the solder paste usually has very low linear-viscoelastic range, less than 0.05%, [7] the entire sweep range is mostly running beyond the LVR. Comparing four pastes, they all show similar trend of the *G'*. It is seen that the poor stability paste, **NC P1** shows most increase of *G'* and *G''* and the modulus crossover point shifting to right, indicating the more solid like behavior of paste or drying out tendency, which is consistent with the conclusion above. However, **WS P2** still keeps good matching plots between fresh and aged conditions, although the yield stress test and shear sweep test pointed out the great change and poor stability. Similarly, **NC P1** shows minimum increase of modulus, followed by **WS P1**. It is noticed that all the paste samples, except **NC P1**, presented the minimum change of modulus and phase angle *Δδ*. It is possible that the oscillation mode does not break down the fluidic structure completely, so the signals from small amplitude oscillatory shear range ($1x10^{-2}$ to $1x10^{1}$) would be contributed more by the flux, other than the flux-powder interaction. If the flux does not change the its modulus, the overall behavior of the paste under oscillation mode test would not show significant change. The nonlinear response in large amplitude oscillatory shear range ($1x10^{1}$ to $1x10^{3}$) would partially affected by harmonics and hence not much difference can be found between fresh and aged paste samples.

Temperature Sweep Method

The solder pastes may be used in different manufacturing environment with higher or lower temperature, which would affect the performance of the paste printing. Constant shearing test method under flow mode would result in the continuous structure breakdown; when testing at higher temperature range, the paste thinned to lower viscosity would be squeezed out of the parallel plate and cause the inaccurate measurement. Therefore, the temperature sweep method tested under oscillation mode will be beneficial in the evaluation of the paste changing along the temperature. From the study above, the **WS P1** is the most stable solder paste with least change of rheological properties after accelerated temperature aging, which is selected to demonstrate temperature sweep method. The linear heating rate is applied on the paste between 16 ˚C to 40 ˚C with the temperature step of 1 ˚C to allow sample to equilibrate and achieve uniform temperature. The response is monitored at constant strain at 2% and frequency of 1 Hz. The condition time and sampling time are 2 seconds of each. The data are collected after the temperature is stabilized.

From Figure 6, both the modulus and complex viscosity are decreasing when temperature increases. Although the paste shows higher modulus (*G'* and *G''*) in aged paste, the difference of *G'* and *G''* shows similar trend that relative hard paste at lower temperature (*G''*> *G'* below 20 ˚C) and softer paste is obtained at higher temperature (*G'* > *G''* above 22 ˚C). The complex viscosity is frequency-dependent, since the constant frequency of 1 Hz is applied through the entire test, the complex viscosity may be correlated to shear viscosity, according to Cox-Merz relationship. [10] The trend that the viscosity of aged paste drops faster than the fresh paste is similar like the result in Figure 3 with more accurate prediction.

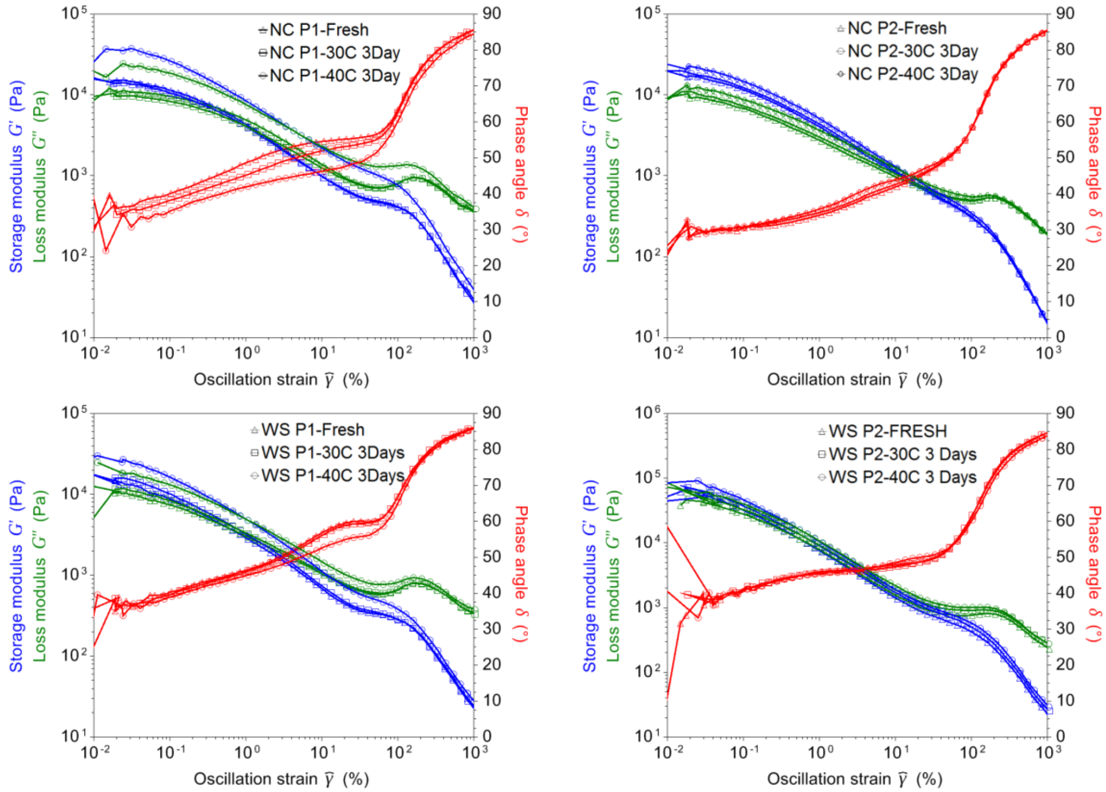

Figure 5. Oscillation mode strain sweep method of all four pastes with modulus and phase angle plot for fresh and aged paste at 30 ˚C and 40 ˚C for 3 days.

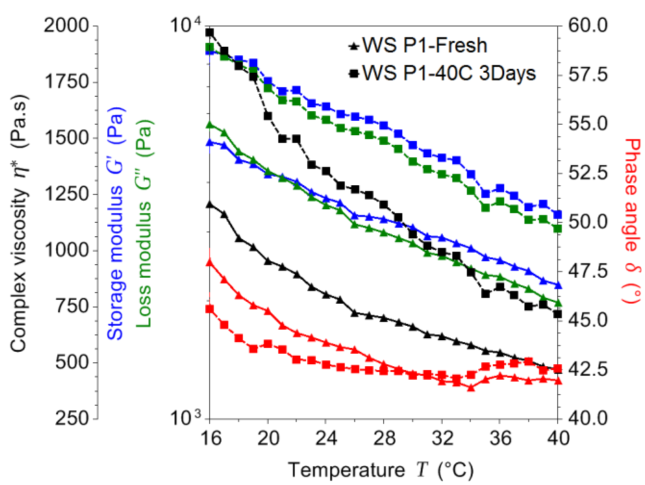

Figure 6. Temperature sweep test of **WS P1** at fresh and aged conditions under oscillation mode.

Axial Force Method

All the commercial solder pastes products provide the tackiness value, which measures the tensile force to extract the probe preloaded onto the printed solder paste and has been part of the quality control of product manufacturing for decades. The commercial tackiness test machine turns to be the industrial standard. The tackiness value of the paste can certainly correlate to the paste performance, for example, the significant change of tackiness would indicate the noticeable changes in paste printing. However, the tack test may not be accurate when the paste was printed with varied thickness or pressed on uneven printed area etc., as there are many manual operations during the test. Rheometer can be used as a more accurate and real-time tack tester, which is one of the more important but least utilized aspects of rheology — axial force. Axial force is a very sensitive and accurate measurement of the elasticity of a material and can generate useful information relating the internal structure to the material's flow behavior. It is noticed that the forces are sensitive to small variations in the instrument settings, such as the parallel plate size, compression and lifting speed, compression depth, etc., therefore, several trials might be needed to optimize the test parameters.

In this axial force test, the paste was firstly compressed down of 100 μm depth with the speed of 100 μm/s and then followed by a tension with the speed of either 10000 μm/s or 40 μm/s, which are close to the settings of JIS and IPC tack test standards, respectively. Figure 7 shows the axial force verses gap of two water soluble pastes at two different lift speeds. During the compression, the paste against the parallel plate pressed from top and the direction of the force can be defined as positive value. After that, the plate was lifted and due to the flux-powder cohesion, the material resisted the separation from pulling force in the opposite direction, which then would provide negative value. Fast speed lifting provides larger axial force and sharper peak than slow speed, because the paste usually needs long time to recover. The paste experienced more recovery in slow lift movement and hence partially cancelled the force from separation. The slow deformation result in the paste sustained and stretched at larger gap size, as seen in the figures that the axial force approaches to zero after near 1000 μm gap at 40 μm/s, while only roughly 500 μm gap is needed at 100000 μm/s. Comparing the difference of axial force at lowest reading, **WS P1** shows the minimum change and **WS P2** has noticeable difference of force, which again proved the better stability of **WS P1**.

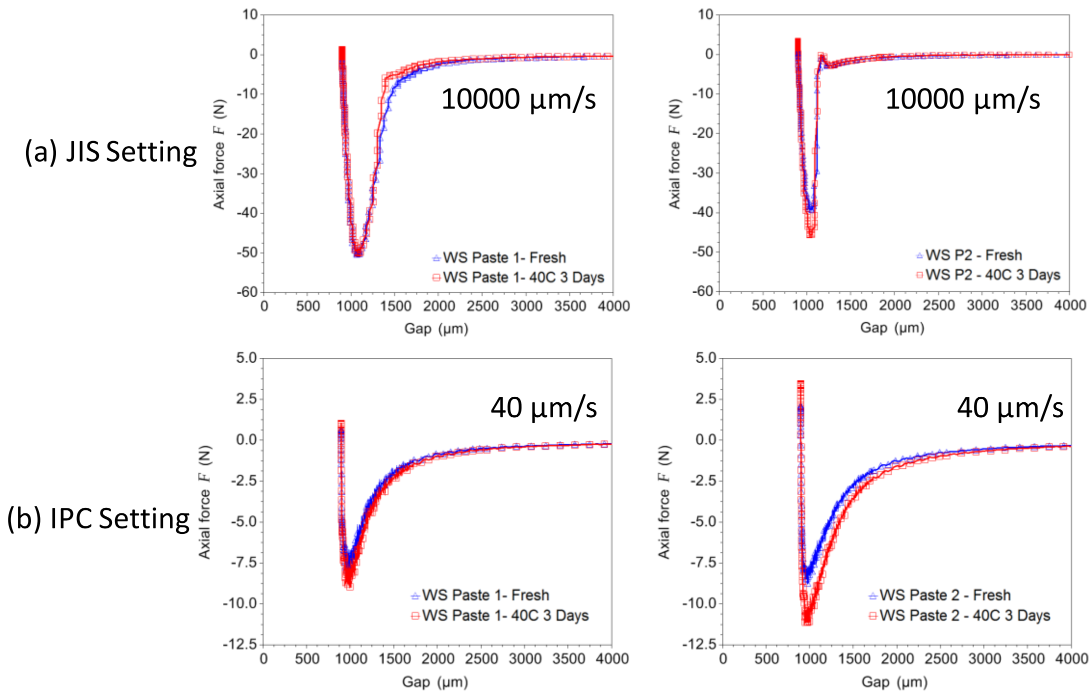

Figure 7. Axial force measured by two speeds following different industrial standards: (a) JIS setting and (b) IPC setting for two water-soluble pastes at fresh and aged conditions.

CONCLUSION

The accelerated solder paste aging method has been used to prepare paste samples and simulate the solder paste stored at high temperature environment. The reaction between flux and solder powder surface can be confirmed from the SEM imaging of dry paste. Several rheological test methods have been developed in this study to predict the shelf life of solder paste from the rheological measurements. In general, **NC P1** performed the shortest shelf life among all tested samples from all test methods, including yield stress, shear sweep, and oscillation strain sweep methods, after aging at 40 ˚C for 3 days. The DOE analysis shows the formulation effect on the paste flux shelf life is most significant, and the storage temperature will increase the paste viscosity more than the storage time. Since **NC P1** has 1-year shelf life in the refrigerator, all other samples will have longer shelf life. **NC P2** has approved 1-year shelf life at room temperature, which shows similar rheological results as **WS P1**. Therefore, it is predicted that **WS P1** has at least 1-year shelf life at room temperature. In summary, proper chemicals formulation can minimize the reaction between flux and solder powder and therefore provide very long shelf life solder paste, for both no clean and water-soluble type solder pastes, even storage at elevated temperature at 40 ˚C.

Two methods under flow mode — yield stress and shear sweep shows more sensitive responses than oscillation mode strain sweep method, which is possibly due to the less breakdown structure under oscillation mode so not much flux-powder interaction can be measured. Temperature sweep test under oscillation mode shows both the viscosity and modulus is decreasing when temperature increases, which also may be used to predict the shear viscosity. The axial force test can be used to correlate with tackiness value measured by tackiness tester.

The study in this work established the repeatable methods to understand flux and paste rheological behavior, which provide useful tools for further understanding many other aspects of the paste formulation contribution to shelf life. It also builds the fundamentals to develop a repeatable and reproducible standard method to be applied in the electronic assembly industry for quality control.

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