

Modeling the Structural Breakdown of Solder Paste Using the Structural Kinetic Model

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Solder paste is the most important strategic bonding material used in the assembly of surface mount devices in electronic industries. It is known to exhibit a thixotropic behavior, which is recognized by the decrease in apparent viscosity of paste material with time when subjected to a constant shear rate. The proper characterization of this time-dependent rheological behavior of solder pastes is crucial for establishing the relationships between the pastes' structure and flow behavior; and for correlating the physical parameters with paste printing performance. In this article, we present a novel method which has been developed for characterizing the time-dependent and non-Newtonian rheological behavior of solder pastes and flux mediums as a function of shear rates. We also present results of the study of the rheology of the solder pastes and flux mediums using the structural kinetic modeling approach, which postulates that the network structure of solder pastes breaks down irreversibly under shear, leading to time and shear-dependent changes in the flow properties. Our results show that for the solder pastes used in the study, the rate and extent of thixotropy was generally found to increase with increasing shear rate. The technique demonstrated in this study has wide utility for R&D personnel involved in new paste formulation, for implementing quality control procedures used in solder-paste manufacture and packaging; and for qualifying new flip-chip assembly lines.

Keywords advanced characterization, electronic materials, modeling processes

1. Introduction

Solder paste is one the most widely used interconnection material in the electronic assembly process which provides mechanical, electrical, and thermal bond between electronic components and the substrate. Solder paste can be categorized as a homogeneous and dense suspension of solder alloy particles suspended in a flux medium. For a typical solder paste, the typical metal content (solder alloy particles) lies between 88 and 91% by weight, and about 30-70% by volume (Ref 1). For lead-free soldering, the solder alloy can be made from the combination of a wide range of elements, including Sn, Ag, Bi, Cu, In, Sb, Zn in binary, ternary, or multi-component systems (Ref 2). The Sn-Ag-Cu (SAC) alloy combination is one of the most commonly used lead-free solder alloy system. The main constituent of flux medium is a naturally occurring rosin or resin which is used to facilitate soldering process by chemically cleansing the surfaces to be joined. A number of different ingredients including solvents, activators, thickeners, thixotropic agents, and tackifiers are normally added to the flux to provide the desired rheological properties to the solder paste.

The non-Newtonian flow properties exhibited by solder pastes during its manufacturing and application phases have been of practical concern to surface mount engineers and researchers for many years. With the increased miniaturization of the electronic products and to meet the challenges of making greener products a number of formulation, processing, and application problems have arisen which can, directly or indirectly, be related to the complex rheological behavior of solder pastes. The experimental characterization and a proper understanding of the rheological properties of solder paste and flux mediums, and the effect of these properties on the solder paste flow behavior will definitely aid in solving such problems.

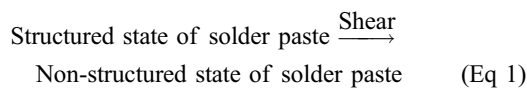
In order to understand rheological phenomena associated with the flow of solder pastes, it is necessary to understand time-dependent rheological behavior. Such behavior is common to many industrial fluids and consequently has been of interest to rheologists for many years. During both the manufacturing and application phases, solder paste experiences a continuous change in terms of breakdown and build up of its internal structure. Shear-induced breakdown of solder paste structure involves two contrasting processes. The application of shear force acts to break down the structural bonds between the primary solder particles or the aggregates of such particles. At the same time, however, shear-induced collisions of the separated structural elements tend to reform part of the broken bonds. The two opposite time-dependent phenomena give rise to overall break down of the paste structure and thus result in reduction in the viscosity with time of shear. An equilibrium state can be attained after some time—at the point when the bond breaking and bond forming rates are at balance. In this study, the thixotropic breakdown of solder paste with shear has been quantitatively examined using a rotational rheometer. The structural kinetic model (SKM) has been used to investigate the rate of structural change of solder paste and to correlate the experimental kinetic data with the model parameters.

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2. The Structural Kinetic Model

The observed time-dependent flow behavior of solder paste can be modeled using the so-called structural kinetic approach. The structural kinetic theory was first developed by Cheng and Evans (Ref 3), which was then extended by Petrellis and Flumerfelt (Ref 4) to describe the time-dependent behavior of shear degradable crude oils. Since then, the theory has been modified and simplified to describe the time-dependent flow behavior of various materials including mayonnaise (Ref 5), concentrated mineral suspensions (Ref 6), starch pastes (Ref 7), and more recently, for concentrated yogurt and semisolid foodstuffs (Ref 8, 9).

In this article, the model is used to study the solder paste behavior. As postulated by the SKM, the change in the time-dependent rheological properties of solder paste is associated with shear-induced breakdown of the internal structure. This structural change is quite analogous to that of a chemical reaction and the mechanism can be expressed as:



If λ is a dimensionless time-dependent structural parameter, the above reaction can be expressed as

$$\frac{d\lambda}{dt} = f(\lambda, \dot{\gamma}) \quad (\text{Eq 2})$$

The rate equation states that the rate of change of structure, or alternatively the structure parameter is a function of the shear rate as well as of the structural parameter. The model also assumes that the structure recovery after shear is negligible and the degradation of structure is irreversible.

Following Nguyen et al. (Ref 7), the decay of the structural parameter with time is assumed to obey an n -order kinetic equation:

$$\frac{d\lambda}{dt} = -k(\lambda - \lambda_e)^n \quad (\text{Eq 3})$$

where the rate constant, k , is a function of shear rate to be determined experimentally, and n is the order of the breakdown reaction. Initially, at the fully structured state, $t = 0 : \lambda = \lambda_0$ and at equilibrium state, $t \rightarrow \infty : \lambda = \lambda_e$.

Integration of Eq 3 can only be achieved in certain special cases. One of these is the case of constant shear-rate degradation. Under such conditions, k and λ_e are constants, and Eq 3 can be integrated from $\lambda = \lambda_0$ at $t = 0$ to $\lambda = \lambda$ at $t = t$ to yield

$$\begin{aligned} \int_{\lambda_0}^{\lambda} \frac{1}{(\lambda - \lambda_e)^n} d\lambda &= \int_0^t k dt \\ \Rightarrow \frac{1}{-n+1} (\lambda - \lambda_e)^{1-n} \Big|_{\lambda_0}^{\lambda} &= -kt \Big|_0^t \\ \Rightarrow \frac{1}{(1-n)} [(\lambda_0 - \lambda_e)^{1-n} - (\lambda - \lambda_e)^{1-n}] &= kt \end{aligned}$$

After rearranging this, finally we get

$$(\lambda - \lambda_e)^{1-n} = (n-1)kt + (\lambda_0 - \lambda_e)^{1-n} \quad (\text{Eq 4})$$

The determination of the rate constant k in Eq 4 as a function of shear rate is intricate because of the fact that the

structural parameter λ cannot be acquired explicitly from the experimental measurements. To overcome this difficulty, the structural parameter λ is defined in terms of apparent viscosity.

The apparent viscosity may be defined for any fluid by the equation:

$$\eta = \frac{\text{Shear stress, } \tau}{\text{Shear rate, } \dot{\gamma}} \quad (\text{Eq 5})$$

where η is a function of both shear rate $\dot{\gamma}$ and time of shear t . Following Nguyen et al. (Ref 7), the structural parameter λ may be defined in terms of apparent viscosity as

$$\lambda(\dot{\gamma}, t) = \frac{(\eta - \eta_e)}{(\eta_0 - \eta_e)} \quad (\text{Eq 6})$$

where η_0 is the initial apparent viscosity at $t = 0$ and η_e is the equilibrium apparent viscosity at $t \rightarrow \infty$. Note that, both η_0 and η_e are functions of applied shear rate only.

Substituting Eq 6 into Eq 4 we get, for a constant shear rate:

$$\left[\frac{(\eta - \eta_e)}{(\eta_0 - \eta_e)} \right]^{1-n} = (n-1)kt + 1 \quad (\text{Eq 7})$$

Equation 7 is valid only under the constant shear-rate condition. The form of Eq 7 is particularly useful for testing the validity of the model by checking the linearity of the $[(\eta - \eta_e)/(\eta_0 - \eta_e)]^{1-n}$ and t data and also to determine the model parameters n and k .

3. Experimental Design

3.1 Materials and Preparation

Four lead-free solder pastes (from A to D) formulated with two different flux systems were investigated. Both flux types are classified as water-based, rosin-containing, no-clean, and halide free. The solder particles for all the paste samples are made of same tin-silver-copper alloy (95.5Sn-3.8Ag-0.7Cu) with a melting point of 217 °C. All the solder paste samples had the same metal content of 88.5% by weight. Further details of these samples are outlined in Table 1.

As recommended, all the solder paste samples were stored at about 4 °C. In order to avoid condensation forming on the paste, the paste samples were always taken out from the cold storage a minimum of 4 hours prior to use and allowed to be restored to room temperature.

3.2 Rheological Measurements

All the rheological measurements were carried out using a Bohlin Gemini-150 controlled-stress/strain rheometer (Malvern Instruments Ltd., Worcestershire, UK). A serrated parallel plate geometry (with serrations on both upper and lower plates) of

Table 1 Test materials

Paste sample	Particle size, μm	Flux type
A	25-45	F1
B	20-38	F1
C	25-45	F2
D	20-38	F2

20-mm upper plate diameter was used to minimize the effect of wall-slip. Prior to loading a sample onto the rheometer, the solder pastes were hand mixed with a plastic spatula for about 30 s. A sample was loaded on the bottom plate, and the top plate was then lowered to the desired gap height of 500 μm by squeezing the extra paste out from between the plates. The excess paste at the plate edges was neatly trimmed with a plastic spatula. Then the sample was allowed to rest for about 1 min before starting the test. Identical loading procedures were followed in all the tests. All the tests were conducted at 25 $^{\circ}\text{C}$ (± 0.1 $^{\circ}\text{C}$) with the temperature being controlled by a Peltier-Plate system. The reproducibility of the experimental results were assured by doing two replicates for most of the tests, and the results were fairly reproducible with $\pm 5\%$ variation on average.

4. Results and Discussion

The solder paste samples and the fluxes used in this investigation had been subjected to prolonged shearing at constant shear-rate values. This is to ensure that the samples reached an equilibrium state at which the rheological behavior is no longer dependent on shear time.

4.1 Solder Paste Samples

As revealed in Table 1, the main differences in the solder paste samples were in particle size distribution and the flux system. The particle size distribution (PSD) is very important in achieving the desired rheological properties and performance of solder paste. The narrower PSD for pastes B and D (20–38 μm) than pastes A and C (25–45 μm) means that the former pastes would flow more easily through apertures in fine pitch (less than 120 μm) applications. On the other hand, if the PSD of the solder powder particles is reduced, the total surface area for the solder alloy particles within the paste may increase rapidly, which leads to increased oxidation. Poor rheological properties and associated poor printing performance can often be attributed to heavily oxidized solder alloy powder particles. Selection of flux system is also vital as the flux composition plays a key role in determining the soldering defect rate and the ultimate solder joint reliability. Although the compositions of the flux systems (F1 and F2) are not known (because of the proprietary nature of the information), solder pastes with different flux systems are expected to show different deformation behavior and flow characteristics.

Solder paste samples were sheared for a period of 8 h at different values of constant shear rates, namely 2, 4, 6, 8, and 10 s^{-1} . The effects of shear rate on the thixotropic behavior of solder paste samples were investigated. The results for pastes A and C are presented in Fig. 1 and 2, as a series of apparent viscosity versus shear-time curves and as a function of shear rate. Other paste samples have yielded similar results (not shown here). It was observed that the rate of change in viscosity increases with the increase in shear rate for all the paste samples. At a constant shear rate, the apparent viscosity decreases rapidly with time in the initial stage which was then followed by a constant flat plateau region. On average after a shearing period of 60 min, no significant changes in viscosity can be observed. This indicates that the solder paste is at an equilibrium state.

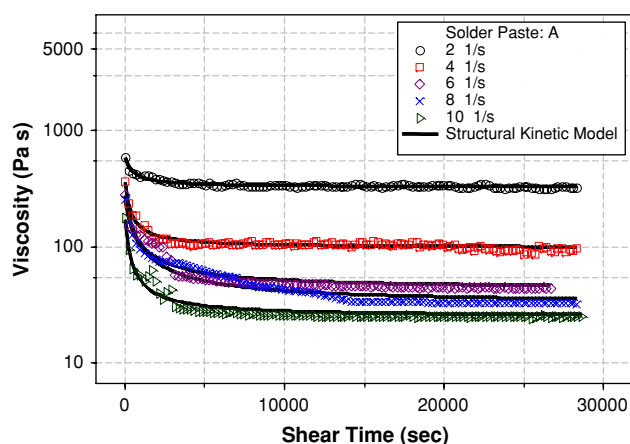


Fig. 1 Apparent viscosity data at constant shear rates for solder paste A at 25 $^{\circ}\text{C}$. Effect of shear rate

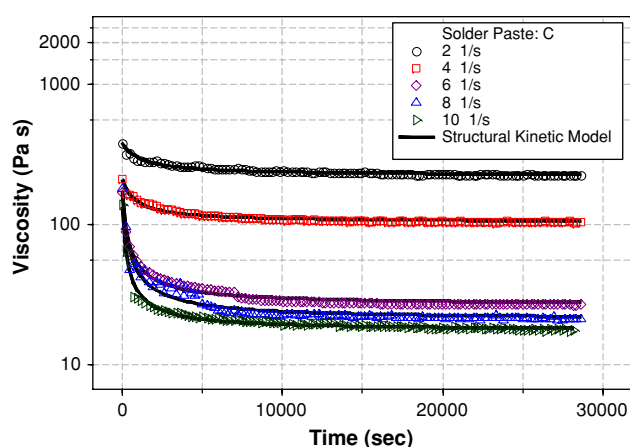


Fig. 2 Apparent viscosity data at constant shear rates for solder paste C at 25 $^{\circ}\text{C}$. Effect of shear rate

The results clearly demonstrate that the apparent viscosity can be drastically reduced from the initial unperturbed (structured) state to an equilibrium (de-structured) state with the application of shear. This indicates that the solder paste samples are highly shear thinning in nature. The rate of decay is quite rapid in the first hour of shearing, but reduces in magnitude as shearing is prolonged to approach the equilibrium state. If correlated to the solder paste printing process, this result would imply that the paste-printing performance will not be consistent until the solder paste reaches the equilibrium state of shearing.

The samples exhibited thixotropic behavior under all the investigated conditions. The observed thixotropic flow behavior of solder pastes was modeled using the structural kinetic approach. For all the solder paste samples studied, it was found that their apparent viscosity data at constant shear rates could be satisfactorily correlated using $n = 2$ in Eq 7, i.e., with a second-order structural kinetic model. This is obvious from Fig. 3 where the plots of $[(\eta - \eta_e)/(\eta_0 - \eta_e)]^{-1}$ versus t for different solder paste samples are linear, which confirms the applicability of the model according to Eq 7.

The observations (e.g., Fig. 1) show a good correlation of the model-fitted result (solid line) and viscosity-time data for all solder paste samples. Table 2 presents the values of rate

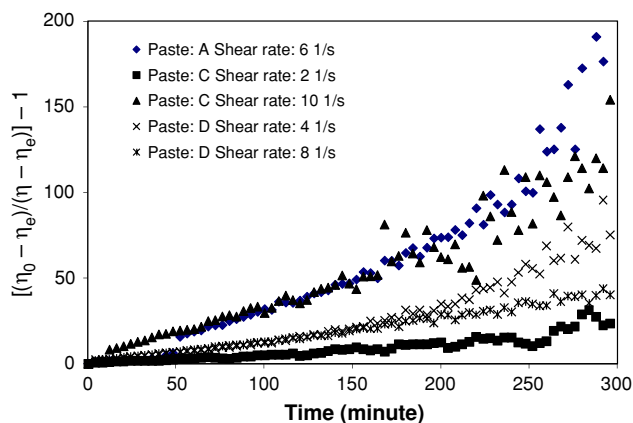


Fig. 3 Testing of the structural kinetic model with different solder paste samples at 25 °C

Table 2 The parameters from the second-order kinetic model for solder paste samples evaluated at different shear rates

Solder paste	Shear rate, s ⁻¹	<i>k</i> (×10 ⁻³)	η ₀ /η _e	η ₀	Correlation coefficient, <i>r</i>
A	2	2.360	1.789	584.9	0.960
	4	4.441	3.779	369.3	0.980
	6	2.735	6.448	279.3	0.970
	8	2.182	7.994	255.8	0.979
	10	4.766	7.118	176.8	0.984
B	2	2.371	1.421	406.4	0.946
	4	3.874	1.808	282.0	0.977
	6	2.962	3.064	250.0	0.988
	8	4.736	5.184	183.0	0.999
	10	6.765	6.274	193.8	0.990
C	2	1.029	1.710	379.7	0.970
	4	1.586	2.021	209.2	0.983
	6	4.560	6.353	169.0	0.996
	8	5.296	8.638	180.1	0.988
	10	6.627	7.945	138.4	0.995
D	2	0.680	1.721	328.1	0.984
	4	3.427	2.722	261.4	0.963
	6	4.937	3.849	211.4	0.973
	8	3.475	3.234	157.7	0.975
	10	3.158	3.554	120.2	0.984

constant, *k*, the ratio of initial to equilibrium viscosity, η₀/η_e, initial viscosity, η₀ and the correlation coefficient, *r* as a function of the applied shear rate for the solder paste samples. The rate constant, *k*, is a measure of rate of structural breakdown. The ratio of initial and equilibrium viscosity (η₀/η_e) on the other hand shows the extent of structural decay with shearing. For any time-dependent structured material, it is normally expected that the *k* values would increase with the increase in shear rate, as was the case for starch pastes (Ref 7) and yogurt (Ref 8). But this was not the case for solder paste samples investigated. As can be seen from Table 2, among the four solder paste samples only paste C has shown an increase in *k* values indicating an increase in the rate of structural breakdown with increasing shear rates. The rest of the solder paste samples (A, B, and D) showed no particular trend for the values of *k*. One of the reasons of this behavior might be because the constant shear-rate values applied on the solder

paste samples were quite close to each other and hence were not able to produce any big difference in terms of the *k* values. Meanwhile, the ratio of initial and equilibrium viscosity (η₀/η_e) was generally found to be increasing with increasing shear rate, indicating a shear thinning behavior. Considering the result of B solder paste, for example, for an applied shear rate of 10 s⁻¹, apparent viscosity can be lowered from an initial value of 194 Pas in the unperturbed state to a fairly constant value of 31 Pas in the equilibrium state after a shearing time of 8 h. The shear thinning nature of solder paste was also evident from the initial apparent viscosity values (η₀) which were generally found to be decreasing with increasing shear-rate values.

The kinetics of structural breakdown of solder paste is quite similar to that of red mud suspension as observed by Nguyen and Boger (Ref 6). It may be generally assumed that there are two types of bonds that exist in the solder paste: (i) bonds between the particles or inter-particle bond and (ii) bonds between the aggregates or inter-aggregate bond. The inter-aggregate bonds are responsible to maintain the strength and integrity of the system. When shear is applied in excess of the yield stress the inter-aggregate bonds first breaks down irreversibly. This leads to a collapse of the network and concurrently a dramatic reduction in the viscosity with time. The inter-particle bonds, however, break down reversibly in a way that they can both be broken and reformed during shear to an extent depending on the applied shear rate. Breaking of these inter-particle bonds results in breaking down of the aggregates into smaller flocs or particles and causing the system to be more dispersed with a further decrease in the viscosity. Another striking point to observe is that after long time of shearing, solder paste still exhibits finite viscosity values and shear thinning behavior. Similar structural behavior has been observed for red mud suspension (Ref 6), starch pastes (Ref 7), and semisolid foodstuffs (Ref 9). This type of behavior may indicate that the original solder paste structure cannot be destroyed completely by long-time shearing (unless the paste is subjected to a very high shear rate) but may only be broken down to a certain minimum or equilibrium state.

4.2 Flux Samples

In this section, the rheological time-dependent behavior of two fluxes (F1 and F2) are investigated. As mentioned before, these fluxes were used to prepare the solder paste samples as outlined in Table 3. So one of the key issues in this investigation was to find out if there is any correlation between paste and flux rheology with regards to breakdown behavior.

Similar to solder paste samples, the two fluxes were sheared for a period of 8 h at constant shear-rate values of 2, 4, 6, 8, and 10 s⁻¹. The results presented in Fig. 4 and 5 are showing the effect of shear rate on the time-dependent rheological properties of flux mediums. Although the fluxes have shown similar breakdown behavior to solder paste samples under the application of constant shear rates, the initial rate of decrease in viscosity were more rapid for the flux samples. Furthermore, the fluxes have generally taken more time to reach the equilibrium state compared to the solder paste samples.

It was found that the second-order structural kinetic model fits satisfactorily with the time-dependent behavior of the flux samples. Figure 6 shows the applicability of the model to the time-dependent rheological data of fluxes, where the plots of [(η - η_e)/(η₀ - η_e)]⁻¹ versus *t* are linear. Figures 4 and 5 illustrate that the second-order structural kinetic model provides

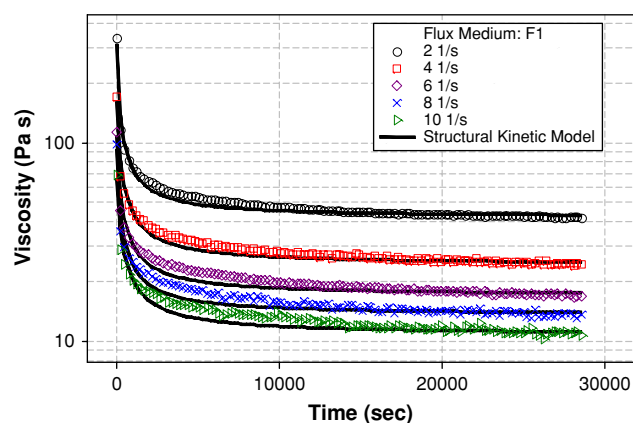


Fig. 4 Apparent viscosity data at constant shear rates for flux medium F1 at 25 °C. Effect of shear rate

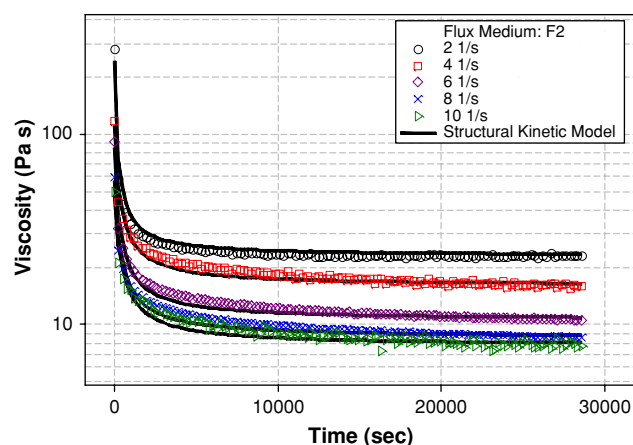


Fig. 5 Apparent viscosity data at constant shear rates flux medium F2 at 25 °C. Effect of shear rate

very good fit (solid lines) of the apparent viscosity versus time data for the flux samples. As shown in Table 3, the rate of structural breakdown, k , generally decreases with increasing shear rate for both of the flux samples. A similar trend was observed for the ratio of initial to final viscosity (η_0/η_e). This sort of quantitative behaviors is rather unexpected and do not match with the thixotropic behavior of the flux samples. As mentioned earlier, this might be due to the close range of the chosen shear-rate values. Further studies needs to be carried out with a wide range of applied shear rates. Table 3 also shows that the initial viscosity values (η_0) for fluxes F1 and F2 decreases with increasing shear-rate values, indicating shear thinning nature of the flux samples.

A comparative study of the data presented in Table 2 and 3 suggests that the rate of structural breakdown (judging from the values of k) for fluxes are greater than the corresponding solder paste samples for the same shear rate. Moreover, the values of (η_0/η_e) reported in Table 2 and 3 indicate that the amount of structural breakdown of the fluxes is mostly higher than that of the solder pastes. The flux samples also have shown lower values for the initial viscosities (η_0). These results imply that the addition of solder particles to the flux medium has made the system more viscous and more resistant to breakdown under the application of shear.

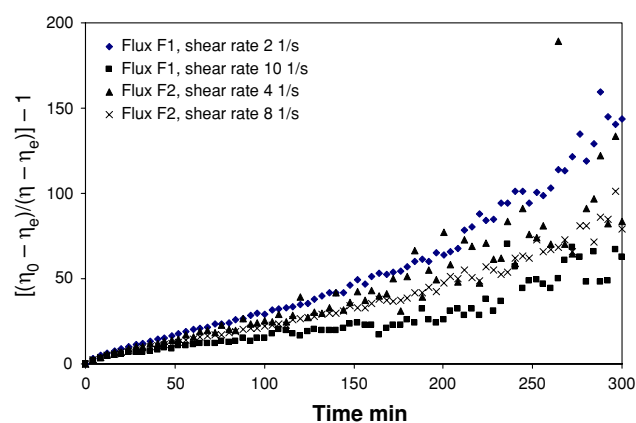


Fig. 6 Testing of the structural kinetic model with different flux samples at 25 °C

Table 3 The parameters from the second-order kinetic model for flux samples evaluated at different shear rates

Flux medium	Shear rate, s ⁻¹	$k (\times 10^{-3})$	η_0/η_e	η_0 , Pa s	Correlation coefficient, r
F1	2	8.296	7.995	335.3	0.993
	4	6.228	7.034	170.3	0.990
	6	6.053	6.698	113.4	0.987
	8	6.903	7.245	97.81	0.986
	10	5.042	6.437	69.07	0.981
F2	2	16.837	12.291	280.6	0.995
	4	7.121	7.326	116.7	0.991
	6	7.934	8.647	90.97	0.994
	8	6.130	7.007	59.46	0.991
	10	5.307	6.488	49.98	0.983

5. Conclusions

In this study, the time-dependent break-down behavior of solder pastes has been analyzed using a novel technique which was developed combining the experimental rheological data with the theoretical structural kinetic approach. On analyzing the experimental data, the rheological behavior of solder paste and flux mediums can be characterized as thixotropic and shear thinning. The thixotropic rheological behavior of solder paste has been satisfactorily modeled using a second-order SKM which demonstrates how the internal structure of solder paste can break down irreversibly under the application of shear. For the solder paste samples studied, the rate and extent of thixotropy was generally found to increase with increasing shear rate. The results from this investigation can be of great help for the solder-paste manufacturers and formulators in quantifying and predicting the effect of long-term shearing on solder paste samples. Nevertheless, the technique developed may be implemented for other similar materials such as solar pastes and conductive adhesives.

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