IBM Research Report

Rheology and Stability of Highly Filled Thermal Pastes

C. Feger, M. McGlashan-Powell, I. Nnebe

IBM Research Division Thomas J. Watson Research Center P.O. Box 218 Yorktown Heights, NY 10598

D. M. Kalyon

Highly Filled Materials Institute Stevens Institute of Technology Castle Point on Hudson Hoboken, NJ 07030



Research Division Almaden - Austin - Beijing - Haifa - India - T. J. Watson - Tokyo - Zurich

LIMITED DISTRIBUTION NOTICE: This report has been submitted for publication outside of IBM and will probably be copyrighted if accepted for publication. It has been issued as a Research Report for early dissemination of its contents. In view of the transfer of copyright to the outside publication, its distributionoutside of IBM prior to publication should be limited to peer communications and specific requests. After outside publication, requests should be filled only by reprints or legally obtained copies of the article (e.g. payment of royalties). Copies may be requested from IBM T. J. Watson Research Center, P. O. Box 218, Yorktown Heights, NY 10598 USA (email: reports@us.ibm.com). Some reports are available on the internet at http://domino.watson.ibm.com/library/CyberDig.nsf/home

Rheology and Stability of Highly Filled Thermal Pastes

C. Feger, M. McGlashan-Powell, I. Nnebe, and D. M. Kalyon* IBM T. J. Watson Res. Cntr., P.O. Box 218, Yorktown Hts. NY 10598; *Highly Filled Materials Institute, Stevens Institute of Technology, Castle Point on Hudson, Hoboken NJ 07030

Thermal interface materials (TIMs) such as thermal pastes, films, pads, adhesives, and gels are an integral component of chip cooling assemblies. Of these, thermal pastes are capable of achieving the highest thermal conductivities, on the order of 5 W/m-K and - more importantly – can achieve some of the lowest thermal resistivities since as liquids – albeit of high viscosity - they can conform to any surface within the chip – cooling lid gap. One of the most important TIM properties is long-term stability of its thermal resistivity. This property is rather unique to thermal pastes, since most highly filled composites used in areas such as explosives, soaps or food products [1-8] exist in the liquid phase only for a short period during processing.

Most thermal pastes are formulations of solid, thermally conducting particles in a liquid matrix consisting of hydrocarbons or silicone oils [9]. Often other ingredients such as antioxidants and/or phase stabilizers are present in small amounts [10]. The solids loading of pastes tends to be very high, often close to the maximum packing fraction, since the degree of solids loading is related to the bulk thermal conductivity, k, of the paste [11]. High solids loading is achieved by tailoring the particle shape and size distributions, principally by employing bi- or multimodal particle size distributions [12]. The mixing process for such pastes is important since it determines the paste properties such as thermal conductivity and particularly paste rheology which determines the flow properties and thus the minimum bondline between solid surfaces achieved during the assembly process.

We investigated the rheological and fail behaviors of two thermal pastes which were described in detail elsewhere [13]. Two mixing methods, also described previously [13], were used to prepare these pastes. The failure behavior of other, commercial TIMs was also investigated and was found to generally show the same fail behavior described here. However, conditions leading to failure may vary between TIMs.

Rheological properties were measured using an ARES rotational rheometer (TA Instruments). Samples were characterized at 50 °C using 25 mm disks in parallel plate configuration. Dynamic properties were measured under small-amplitude oscillatory shear flow and steady flow behavior was characterized using steady torsional flow. Strain sweep tests were conducted at 1 rps frequency. Strain-sweep, time-sweep, frequency sweep, dynamic temperature sweep and steady shear tests were conducted. **The results were discussed in detail elsewhere** [13].

The rheological properties of thermal pastes can be affected by the mixing process - in particular the ultimate quality of the mixed state [13] – and other processing variables such as the amount of entrapped air. Highly filled materials such as the investigated thermal pastes show pronounced wall slip. This behavior is a universal characteristic of highly loaded systems [14, 15] such as TIMs [13]. Wall slip is characterized by the development of an apparent slip layer at the substrate – paste interface. This slip layer consists solely of the binder of the suspension, and its thickness is a fraction of the particle size of the solid phase [16, 18]. Wall slip increases with increasing thickness of this layer and decreasing shear viscosity of the binder [15, 17, 18]. The amount of air in the paste can also affect wall slip [1, 17, 19].

Experiments carried out without taking wall slip into account can lead to greatly distorted results since measured strain and actual strain of a sample can differ significantly. Figure 1 shows differing apparent wall slip and strain values for the identical thermal paste measured



Fig. 1: Extent of shear of a thermal paste in between top and bottom parallel plates of a rheometer using various shear rates. The marker angle indicates the extent of shear in the paste, the distance between the straight marker lines indicates the tool shear strain. 1a. Left: Negligible paste deformation, i.e., plug flow with wall slip; 1b. Right: Same paste being sheared however under still significant wall slip.

under varying strain rates. Wall slip is revealed by the appearance of discontinuities in the straight marker line at the material - wall interfaces of the parallel plate fixtures of the rotational rheometer in steady torsional flow. Figure 1a indicates pure plug flow with no deformation introduced into the paste (shear stress is smaller than the yield stress of the paste) and Figure 1b shows the wall slip under conditions that the paste is being deformed (at a true rate which is smaller than the intended).

Wall slip which can occur during thermal pumping of a TIM in the chip – cooling lid gap is a significant failure mode of thermal pastes and can lead to the loss of all or part of the thermal paste [14-20]. However, wall slip alone may not be the sole factor leading to paste failure.

Long-term stability of the thermal resistivity of the chip – TIM - cooling lid assembly depends on paste stability, i.e., the ability of the thermal paste to remain unchanged during thermal and mechanical cycling of the chip – lid gap. Besides wall slip behavior, paste stability depends on other factors such as the amount of entrapped air incorporated during the mixing process, the uniformity of the paste, and the rate of thermal or mechanical changes.

In order to study paste stability a silicon prism heat sink assembly was developed that enables IR imaging of the thermal interface in the actual packaging environment while gap tilt between chip and lid and force on the TIM paste was monitored (Figure 2). This assembly consists of two



Fig. 2: Schematic of the IR paste analysis tool. TP: thermal paste, TC: thermocouples, LPD: laser position detector, SiP: Silicon prism, LC: load cell

matching right angle prisms which are held against each other so that the gold coated surface of the hypotenuse of one prism acts as mirror, reflecting the IR from the heat source (e. g., the chip backside) into an IR camera (FLIR Systems Merlin Mid). The top surface of the silicon cube formed by the prisms is bonded to a circulating liquid cooled cold plate. Gap tilt was measured by four laser position sensors located at each corner. Force was measured through a force transducer located on the central pressure rod. The force could be varied using a piezo-driver. Further experimental details are given elsewhere [13].

IR imaging was performed on a Power4 microprocessor at power levels up to 140 Watt. The chip -TIM – heat sink stack was assembled by applying 1 – 2 mm of thermal paste to the backside of the chip and then pressing the prism on top of the paste until the desired gap of 100 μ m was obtained. IR images of the heat sink-paste interface were taken at various power levels from 0 watts (room temperature) up to 140 watts (80 – 100 °C).

Another method of studying paste stability involved the use of two glass slides between which the paste was compressed. Such assemblies were subjected to thermal and mechanical cycling and the paste behavior was observed through an optical microscope.

These investigations identified several distinct TIM failure modes:

Paste Voiding. This failure mode is characterized by air pockets which bridge the chip – heatsink gap (Figure 3). Voids develop over time but most quickly over hot spots where they also



Fig. 3: Schematic cross-section through the chip-paste-heat sink stack (left) and top view (right) of thermal paste showing paste voiding.

cause the greatest damage. These voids originate from air entrapped in the thermal paste during mixing. If significant amounts of entrapped air are included in the paste, voiding can be massive leading to significant increase in thermal resistance and subsequent catastrophic chip fails.

Interfacial Voiding. This failure mode (Figure 4) occurs during rapid contraction of the chip - TIM - heat sink stack, when the wall slip layer temporarily disconnects from one of the surfaces. These voids appear first as bands at the edges of the chip - heat sink gap but travel to the interface in the gap center over time. The size of these voids can be rather large but owing to



Fig. 4: Schematic description (left) of interfacial void movement and cross-section through the chip-paste-heat sink stack (right)

the fact that they are contained in the interface layer they tend to be thin. Unlike paste voids, interfacial voids do not span from one side of the gap to the other. Sometimes these voids may disappear spontaneously.

Paste Erosion. This failure mode (Figure 5) is very complex and not well understood. It is characterized by successive removal of paste from the chip – heat sink gap. Closer examination



Fig. 5: Schematic cross-section through the chip-paste-heat sink stack (left) and top view of the paste (right) showing massive paste erosion.

indicates that in the course of this failure process a channel pattern develops in the paste similar to a drainage system [13]. It is assumed – and we will present data showing - that the liquid component flows out of the paste eroding it with time. This process may begin at the wall – paste interface since the apparent slip layer consists of nearly pure paste binder (liquid phase) and may be driven by cyclical gap dimension variations (paste pumping). This failure mode eventually will cause catastrophic thermal resistance increases. Conditions that lead to the occurrence of this failure mode and acceleration factors are not known yet though rapid erosion has been observed with pastes of poor mix quality.

Conclusions

Critical properties of thermal pastes such as rheology and failure mechanisms affecting the thermal resistance stability were investigated. Processing of the paste can affect the paste rheological properties and their propensity to fail particularly when air is included in the paste during processing. Rapid chip – heat sink gap expansion can lead to interfacial voids. Wall slip layers and other yet unknown factors can lead to paste erosion.

Acknowledgments

We are grateful to many people including S. Iruvanti, N. Wier-Cavalieri, and M. Gaynes for providing TIM samples and M. Farinelli, J. Zinter, V. Khanna, and S. Sri-Jayantha for helping with various aspects of the IR set-up. The help and support by S. Buchwalter of IBM and H. Gevgilili and E. Birinci of HfMI are greatly appreciated.

References

- 1. D. M. Kalyon, R. Yazici, C. Jacob, B. Aral and S. W. Sinton, "Effects of Air Entrainment on the Rheology of Concentrated Suspensions during Continuous Processing," Polym. Eng. Sci., 31 (1991) 1386-1392.
- 2. R. Yazici and D. M. Kalyon, "Degree of Mixing Analyses of Concentrated Suspensions by Electron Probe and X-Ray Diffraction," *Rubber Chem. and Techn.* **66** (4), 527-537 (1993).
- 3. R. Yazici and D. M. Kalyon, "Quantitative Characterization of Degree of Mixedness of LOVA Grains," *Journal of Energetic Materials* 14 (1), 57-73 (1996).

- 4. B. L. Greenberg, D. M. Kalyon, M. Erol, M. Mezger, K. Lee and S. Lusk, "Analysis of Slurry-Coating Effectiveness of CL-20 using a Novel Grazing Incidence X-ray Diffraction Method," *Journal of Energetic Materials* **21** (1), 185 (2003).
- 5. D. Kalyon, E. Birinci, R. Yazici, B. Karuv, and S. Walsh, "Electrical Properties of Composites as Affected by the Degree of Mixedness of the Conductive Filler in the Polymer Matrix," *Polym. Eng. Sci.* **42** (7), 1609-1617 (2002).
- D. M. Kalyon, A. Lawal, R. Yazici, P. Yaras and S. Railkar, "Mathematical Modeling and Experimental Studies of Twin Screw Extrusion of Filled Polymers," *Polym. Eng. Sci.* 39 (6) 1139-1151 (1999).
- 7. M. Erol and D. Kalyon, "Assessment of the Degree of Mixedness of Filled Polymers: Effects of Processing Histories in Batch Mixer and Co-Rotating and Counter-rotating Twin Screw Extruders", International Polymer Processing, 20, 228-237 (2005).
- 8. D. Kalyon, H. Gevgilili, R. Yazici, A. Post and G. McFann, "Flow and structure development behavior of bar soaps containing synthetic detergent," *Rheologica Acta* **43**, 396-405 (2004).
- 9. S. Iruvanti, R. K. Gupta, and E. Ruckenstein, "Stable High Solids, High Thermal Conductivity Pastes," U. S. Patent **5 098 609**, March 24 (1992).
- 10. S. Iruvanti, K. S. Olsen, K. G. Sachdev, "Polyester Dispersants for High Thermal Conductivity Paste," U. S. Patent 5 591 789, January 7 (1997).
- 11. B. Bird, W. Stewart and E. Lightfoot, *Transport Phenomena*, 2nd edition, John Wiley and Sons, New York, 281-283 (2002).
- 12. T. Fiske, S. Railkar and D. M. Kalyon, "Effects of Segregation on the Packing of Spherical and Non-Spherical Particles," *Powder Technology* **81**, 57-64 (1994).
- C. Feger, J. D. Gelorme, M. McGlashan-Powell and D. Kalyon, "Mixing, Rheology and Stability of Highly Filled Thermal Pastes", IBM Journal of Research and Development, 49, 4/5, 699-707 (2005).
- D. M. Kalyon, P. Yaras, B. Aral, and U. Yilmazer, "Rheological Behavior of a Concentrated Suspension: A Solid Rocket Fuel Simulant," *Journal of Rheology* 37, 35-53 (1993).
- B. Aral and D. M. Kalyon, "Effects of Temperature and Surface Roughness on Time-Dependent Development of Wall Slip in Torsional Flow of Concentrated Suspensions," *Journal of Rheology* 38 (4), 957-972 (1994).
- 16. U. Yilmazer and D. M. Kalyon, "Slip Effects in Capillary and Parallel Disk Torsional Flows of Highly Filled Suspensions," *Journal of Rheology* **33**, 1197-1212 (1989).
- 17. B. Aral and D. M. Kalyon, "Rheology and Extrudability of Very Concentrated Suspensions: Effects of Vacuum Imposition," *Plast. and Rubber Comp. Proc. and Applications* **24**, 201-210 (1995).
- 18. D. Kalyon, "Apparent Slip and Viscoplasticity of Concentrated Suspensions", J. Rheology, 49, 3, 621-640 (2005).
- 19. D. Kalyon, H. Gokturk, P. Yaras and B. Aral, "Motion Analysis of Development of Wall Slip During Die Flow of Concentrated Suspensions," *Society of Plastics Engineers ANTEC Technical Papers* **41**, 1130-1134 (1995).
- 20. E. Bonaccurso, H.-J. Butt, and V. S. J. Craig, "Surface Roughness and Hydrodynamic Boundary Slip of a Newtonian Fluid in a Completely Wetting System," *Physical Review Letters* **90**, 144501-1 144501-4 (2003).