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New Improved Polyimides for Increased Reliability

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Abstract
A Design of Experiment (DOE) was conducted to determine the best filler, or combination of fillers that would offer the best reduction of CTE expansion from 50°C to 260°C without compromising electrical, chemical, mechanical or thermal performance of the base Polyimide resin. Our study here shows that a unique combination of fillers can reduce the percent z-axis expansion of a V0 Polyimide from 1.45% total expansion to 1.28% better than any single type of filler. Thus offering higher reliability in Printed Wiring Board (PWB) applications that continuously operate in conditions of severe thermal cycling.

Introduction
Polyimide substrates enjoy a niche marketplace in the Electronic Interconnect Industry. Due to their extraordinarily stable chemical nature, polyimides are found where traditional FR4 type material would otherwise fail. Polyimides are especially chemically and thermally resistant which makes them an attractive substrate for burn-in board applications as well as for industrial and military applications where field repairs are often performed in less than ideal conditions. Nonetheless, polyimides are not indestructible and can fail by many of the same mechanisms as typical FR4 wiring boards.

For higher reliability, any composite composed of a strong fibrous substrate impregnated with a resin matrix, as found in PWBs, the CTE must be reduced or it will eventually delaminate due to the long-term interfacial stress build-up due to thermal cycling.[1] One remedy to this failure mode is to decrease the laminate's thermal expansion. Still another advantage of polyimides over FR-4 materials is it's exceptionally inherently low expansion in the z-axis. The total z-axis expansion, from 50°C to 260°C, for traditional FR-4 materials are in the 3-4% range. The incorporation of fillers can lower the FR-4's value to 2.2-3%; while typical V0 flame rated polyimides have a total expansion on the order of 1.5-2.0%. The incorporation of fillers can have both positive and negative effects. Among the positive are an increase in Flexural Strength and Modulus, an increase in Impact resistance and reduction in CTE and warpage. Some of the drawbacks of fillers include lower peel strength and possible increase drill wear.[2] What we set out to do is find the best balance of properties that can increase the reliability of polyimides in high performance PWB applications.

Materials and Methods
All formulations were based upon standard, commercially available electronic grade polyimide resin to which 15 pph of an organic flame retardant was added. This ensuring a V0 flame rating. All samples were treated onto e-type 7628 style glass. A two level three factorial DOE was designed using three different fillers, herein fillers "A", "B" and "C", each at either 0 pph loading or 15 pph loading, plus combinations thereof. Further, all fillers used had a mean particle size of 1-10 microns. Test coupons were prepared from each sample using an 8-ply build-up and both Standard Grade 3 (HTE) copper and very low profile reverse treatment DSTF coppers. Samples were then pressed for 60 minutes at 360°F under normal laminating pressures. Coupons from the laminates were then taken to test Glass Transition Temperature (Tg), Copper Peel Strength and Percent Co-efficient of Thermal Expansion (CTE). The laminates were then post baked in a force draft oven at 430°F with the coupons being sampled and tested every 30 minutes for 180 minutes.

The Glass Transition Temperatures (Tg) were monitored via Differential Scanning Calorimetry (DSC) using a TA Instrument model 2920. The percent expansion, measured from 50°C to 260°C, was recorded using a DuPont TMA model 2940. Peel strength testing was performed in accordance with standard IPC procedures. Table 1 shows the descriptions and modifications made to the test samples.

Results
Before analyzing the CTE expansion it had to be ensured that there was sufficient cure of the Polyimide samples. The Tg developed during post-bake reaching a steady Tg of 260-265°C after 90 minutes. Figure 1 shows the effect of post-bake upon Tg for all samples.

Table - 1 Modification and Sample Description

Sample Code	Filler "A"	Filler "B"	Filler "C"
1	0 pph	0 pph	0 pph
2	7.5 pph	7.5 pph	0 pph
3	0 pph	7.5 pph	7.5 pph
4	7.5 pph	0 pph	7.5 pph
5	5 pph	5 pph	5 pph
6	0 pph	0 pph	15 pph
7	15 pph	0 pph	0 pph
8	0 pph	15 pph	0 pph

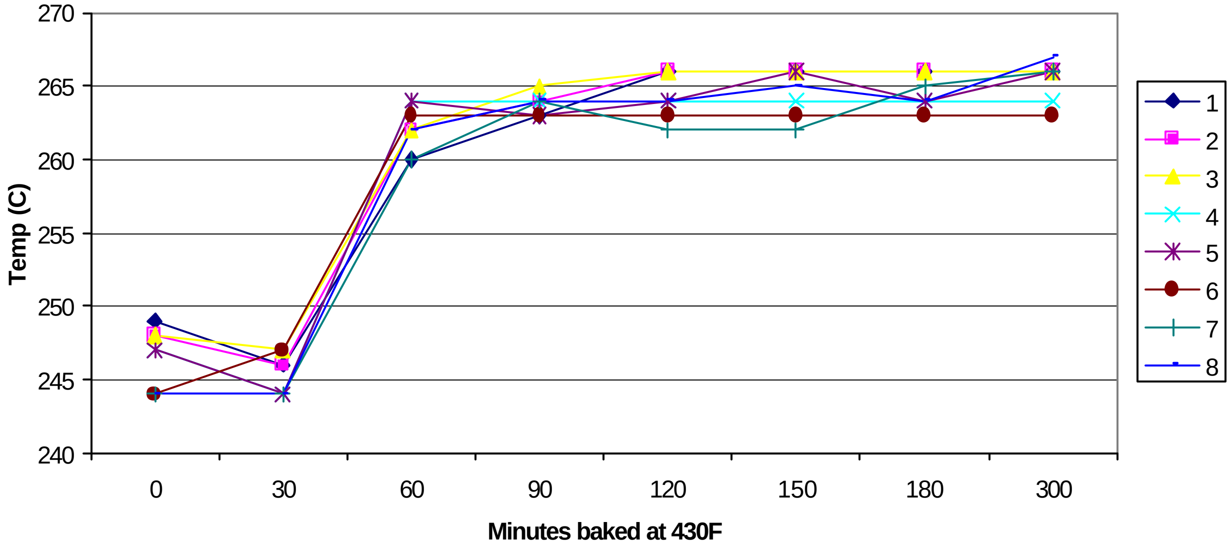

Figure 1 - Tg Build-Up as a Function of Post-Bake Time

Next, the percent expansion of all samples were recorded at 180 minutes, this when the Tg buid-up had reached a steady state. Figure 2 shows the percent z-axis expansion from 50°C to 260°C.

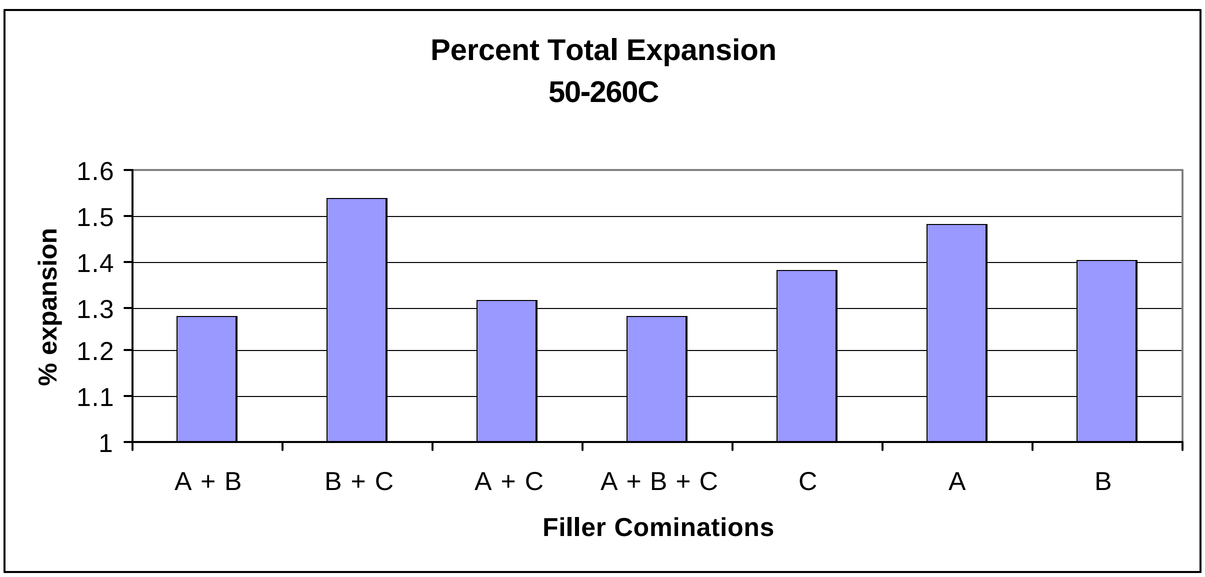

Figure 2 - Bar Chart Showing the Percent to Expansion of the Filled Polyimide Samples

Figure 3 shows the effects the various fillers had upon CTE. This is the over all effect of the fillers and their combinations.

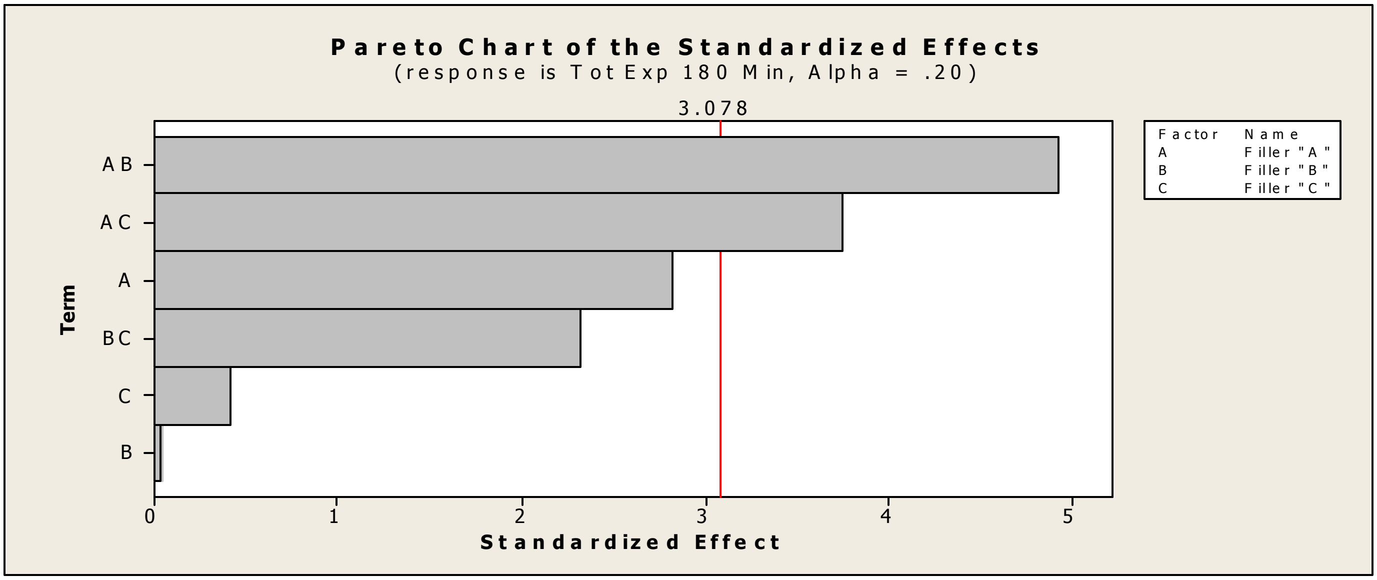

Figure 3 - Pareto Chart Showing the Overall Effects

Figure 3 shows that the greatest impact upon percent expansion for this polyimide system is filler "A" in combination with either "B" or "C", this at an alpha risk of 0.2, that is, with a 20 percent chance we detected a difference among samples where none actually exists. Analysis of Variance (ANOVA) showed the residual error to be <2.0%.

The Pareto chart showed the greatest impact of expansion. A Main Effects and Interaction Chart are used to determine if indeed filler "A" in combinations with "B" and or "C" caused the greatest reduction of total expansion. Figure 4 shows the Main Effects for z-axis expansion for our Polyimide system.

From Figure 4, it is clear that with the addition of filler "A" the percent expansion is reduced. Also what the Figure 4 shows is that filler "B" and "C" by themselves do not affect the percent expansion. The slight increase effect shown for filler "C" is within experimental error. Figure 5 shows the interactions of all the fillers.

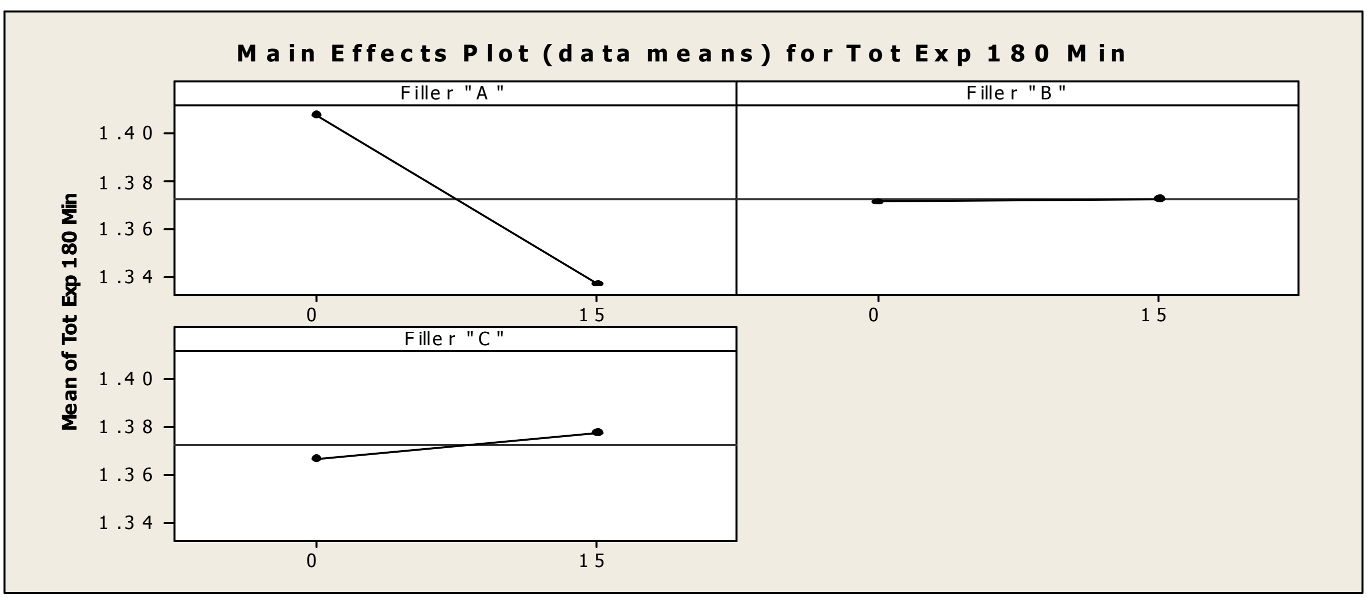

Figure 4 - Main Effects Plot Chart Showing the Impact of Fillers on Z-Axis Expansion

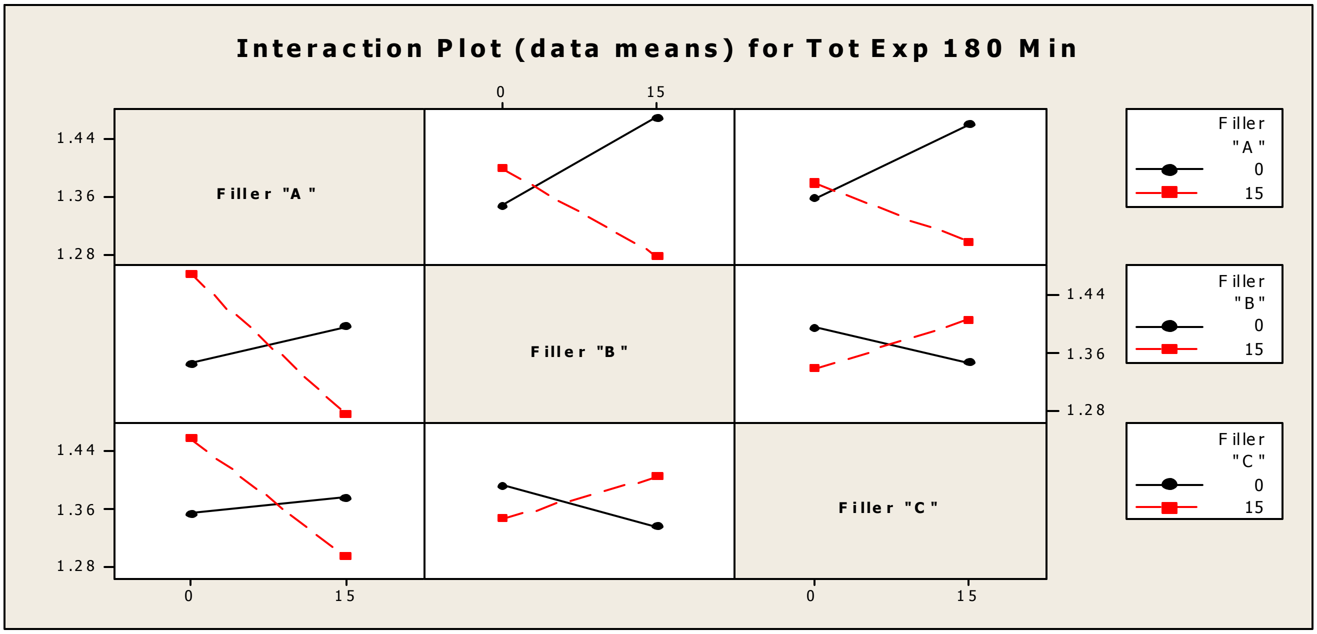

Figure 5 - Interaction Plot Chart Showing the Impact of Combinations of Fillers on Z-Axis Expansion

The above Figure 5 shows that the samples with the least z-axis expansion are the samples with filler "A" in combination with fillers "B" or "C". Also evidenced are the strong interactions all samples had with each other.

Likewise the copper peel strengths of both the HTE copper and DSTF coppers were plotted verses post-bake times. Figures 5 and 6 show the peel strength build-up as a function of post-bake and cure.

From the previous two figures, the samples that had the best peel strengths were samples 1 (control), sample 4 (filler "A" and "C") and sample 6 (filler "C"). Overall the lowest peel strength values were had in sample 8 (filler "B").

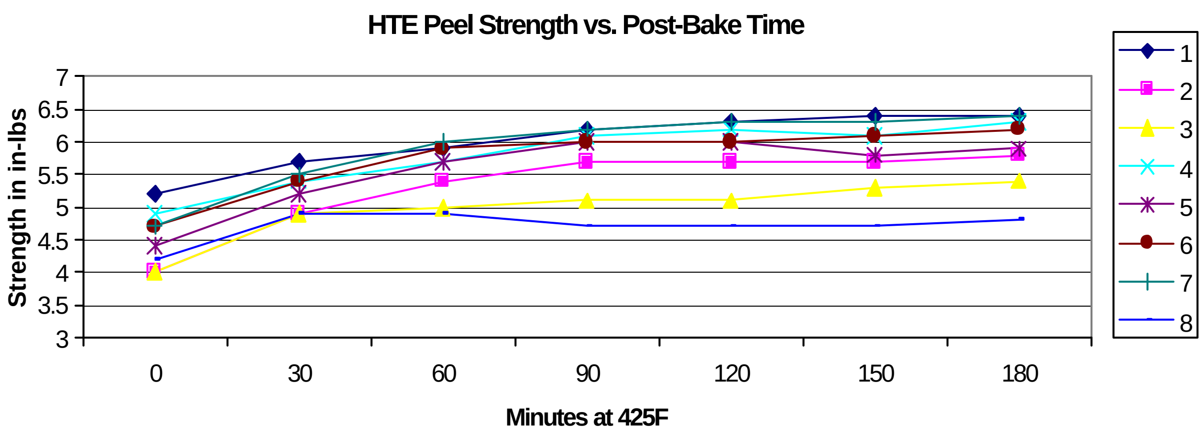

Figure 6 - Copper Peel Strength Build-Up for HTE Copper as a Function of Time of Post-Bake

Discussion

We have shown here that by using a combination of different fillers it is possible to reduce the z-axis expansion greater than using any single filler. Also of importance is that in our selection of materials we do not significantly compromise any other properties, especially Cu peel strength. (Figure 7)

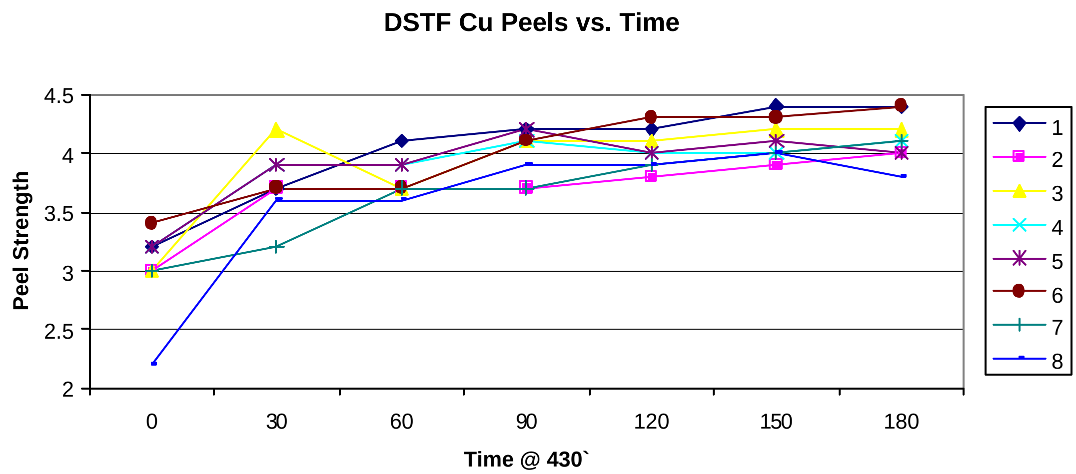

Figure 7 - Copper Peel Strength Build-Up for DSTF Copper as a Function of Time of Post- Bake

The surprising find here is that no particular filler stood out for the reduction of CTE, but rather filler “A” in combination with filler “B” or “C” offered the greatest reduction in expansion in the z-axis. Also of note is that aside from the three fillers used here, “A”, “B” and “C”, all samples also had an additional 15 pph of an organic flame retardant, this for a total of 30 pph filler for all samples reported. Most likely the contributing factors to CTE reduction is the interaction of the particle sizes and or shapes during cure allowing for the greatest packing density. Also of note is the rather poor Cu peel performance of the sample using filler “B” and the strikingly good peel strengths using filler “C”, this is believed to be attributed to particle shape rather that particle size. By no means was the choice of filler materials selected here exhausted, but rather offered here is evidence that a greater reduction of CTE can be had with different combinations of filler shapes and filler particle sizes as opposed to just one type of filler.

Conclusions

For this study, the best reduction of CTE is found by using a combination of fillers “A” and “C”, this not only for low z-axis expansion but also for acceptable copper peel strength. All this was accomplished while maintaining all the chemical, electrical and mechanical properties of a V0 Polyimide.

Acknowledgements

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References

1. Lin, S. and Pearce E. “High-Performance Thermosets”, Hanser Publishers, 1994
2. Wypych, G. “Handbook of Fillers” 2^{nd}. Edition, ChemTec Publishing, 1999