Impact of Moisture Content on Printed Circuit Board Laminate Thermal Properties

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Abstract

Moisture plays an important role in the integrity and reliability of printed circuit boards (PCBs). The presence of moisture in a PCB alters its thermo-mechanical properties, induces hygroscopic stress through differential swelling, reduces interfacial adhesion strength, induces corrosion, causes internal shorts through metal migration, and affects the performance of PCB. Past studies on thermal property measurements of PCB materials were conducted as per IPC test methods, including preconditioning of test samples. Some measurement results did not match the values quoted in manufacturers' datasheets.

This experimental study examines the dependence of out-of-plane coefficient of thermal expansion and glass transition temperature on the moisture content in halogenated and halogen-free PCB materials. Furthermore, this study establishes the suitability of IPC-TM-650 preconditioning steps for thermal property measurements. Commercially available PCB materials from two manufacturers, including materials containing halogen-free and halogenated flame retardant, were tested in this study. One set of test coupons were preconditioned and tested per IPC-TM-650 2.4.24 (Glass Transition Temperature and Z-Axis Thermal Expansion by TMA) and IPC-TM-650 2.4.25 (Glass Transition Temperature and Cure Factor by DSC) test methods, and held as controls. Two additional sets were preconditioned at 105°C and, 85°C and 85% RH for varying periods. The results showed that glass transition temperature and thermal expansion coefficient are affected by both moisture and temperature. Tg decreased with increase in the moisture content in laminates, while it increased with an increase in the duration when exposed to thermal conditions. Moisture dominated the trends before laminate materials reached a moisture saturation point; while temperature dominated the trend post saturation point. Also, the results showed that there was no significant effect of moisture content on out-of-plane coefficient of thermal expansion values below and above Tg, while the values between 100ºC and the glass transition temperature were affected by moisture content, specifically in halogen-free materials.

Key words: laminate, moisture, glass transition temperature, coefficient of thermal expansion, halogen-free

1 Introduction

The reliability of printed circuit board (PCB) laminates is strongly influenced by the presence of moisture. Moisture can be initially present in the epoxy glass prepreg, absorbed during the wet processes in the manufacturing of the printed circuit boards, or diffuse into the printed circuit board during storage [1]. Moisture may reside in the resins, resin/glass interfaces, and micro-cracks or voids due to defect. Moisture can cause internal shorts through metal migration, interfacial degradation resulting in conductive filament formation, and changes in dimensional stability [2]. Moisture also reduces the glass-transition temperature and increases the dielectric constant, leading to a reduction in circuit switching speeds and an increase in

propagation delay times**Error! Reference source not found.**.

Due to the shift in market trends toward halogen-free products, halogen-free PCB materials have recently gained popularity. Halogen-free PCBs rely on less well-understood flame retardants compared to halogenated materials. There are many studies on the moisture behavior of halogenated PCBs [1][3][5][6], but less data available on the use of halogen-free flame retardants in PCBs. Demaree et al. [7] evaluated the thermal stability of halogen-free laminated materials, but did not characterize the effect of moisture on the thermal properties of halogen-free materials. Rajoo et al. [8] reported that halogen-free materials absorb more moisture than halogenated materials; however, they did not characterize the effect of moisture on the thermal properties of halogen-free materials. Therefore, it is necessary to understand the moisture behavior of halogen-free PCB materials and the effect of moisture on material thermal properties when compared to halogenated PCB materials.

In the past CALCE has conducted material property measurements on halogen-free PCB materials, including glass transition temperature (T_g), coefficient of thermal expansion (CTE), decomposition temperature (T_d), time-to-delamination (T-260, T-288), and water absorption. Some measurement results were not in accordance with manufacturers' datasheets. Such as in some control set, T_g results were more than 5°C lower than datasheet and T_d results were 20°C higher than datasheet [9]. In the previous CALCE study, the control sets were conducted as per IPC methods, including preconditioning of test samples.

This paper examines the dependence of out-of-plane coefficient of thermal expansion, glass transition temperature, time to delamination, and decomposition temperature on the moisture content in halogenated and halogen-free PCB materials. Furthermore, this study establishes the suitability of pre-conditioning steps for thermal property measurements in IPC-TM-650 test methods.

2 Experimental Details

2.1 Materials

Four PCB materials—two halogen-free (A, C) and two halogenated (B, D) —were tested. These laminates were acquired from two manufacturers (A and B from manufacturer I, and C and D from manufacturer II). Suppliers were chosen from different geographic locations, with suppliers I and II from Taiwan and Japan, respectively. Laminate properties are shown in Table 1 according to their datasheets.

Table 1: Test material properties (datasheet)

Test Method IPC-TM-650	Properties		A	B	C	D
2.4.24	z-CTE ppm/°C	below T_g	30-50	50-70	40-55	55-70
		above T_g	200-230	270-300	170-250	170-300
2.4.24 (TMA) 2.4.25 (DSC)	T_g (°C)		150 ±5 (DSC)	140 ±5 (DSC)	140-150 (TMA)	135-145 (TMA)
2.4.24.6	T_d (°C)	5%	345	312 (ASTM D3850)	>340	340-360 (2.3.40)
2.6.2.1	Water absorption (%)		0.05-0.10	0.1	0.02-0.04	0.04-0.06

2.2 Test Methods

The test methods and equipment used for measuring the properties are listed in Table 2. The measurement procedure for each of the property is discussed in the following sections.

Table 2 Measurement methods

Property	**Units**	**Test standard**	**Equipment**
Glass transition temperature (T_g)	^oC	IPC-TM-650 2.4.25	Differential scanning calorimeter (DSC)
Coefficient of thermal expansion(CTE)	ppm/ ^oC	IPC-TM-650 2.4.24	Thermo-mechanical analyzer (TMA)
Decomposition temperature (T_d)	^oC	IPC-TM-650 2.4.24.6	Thermo-gravimetric analyzer (TGA)
Time to delamination (T-260, T-288)	minutes	IPC-TM-650 2.4.24.1	Thermo-mechanical analyzer (TMA)

Coefficient of thermal expansion (CTE)

The coefficient of thermal expansion (CTE) of a laminate system is the fractional change of linear dimensions with temperature. Out-of-plane CTE (z-CTE) is dominated by the resin system, whereas in-plane CTE is dominated by the glass fabric. Out-of-plane CTE influences failure mechanisms such as barrel cracking and delamination, and in-plane (warp/fill) CTE affects shear failures of solder joints.

Three samples of each material, each approximately 6.35 mm × 6.35 mm in size, were tested in this study. The samples were polished to ensure parallel edges, and the copper cladding was etched off using sodium per sulfate solution. The CTE of laminate materials along the out-of-plane directions (z-CTE) was measured using a Perkin-Elmer thermo-mechanical analyzer (Pyris TMA 7). The TMA heated the sample from 30^{o}C to 200^{o}C at a 10^{o}C/minute ramp rate. The instrument measures z-CTE by monitoring the sample's change in thickness. The laminate had one z-CTE below its T_g and another above the T_g, each of which were measured from the TMA results. Typical out-of-plane CTE measurement plot is shown in Figure 1.

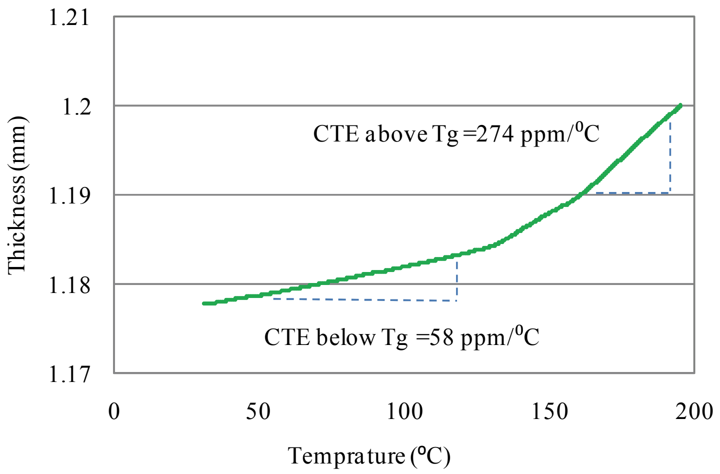


Figure 1 Out-of-plane CTE measurement plot

Glass transition temperature (T_g)

The glass transition temperature (T_g) of a resin system is the temperature at which a material transforms from a rigid and glass-like state to a rubbery and compliant state due to the reversible breakage of Van Der Waals bonds between the polymer molecular chains. Certain properties such as thermal expansion, Young's modulus, heat capacity, and dielectric constant undergo a change around T_g. Therefore, it is very important to determine the glass transition temperature under ambient and moisture conditions in order to define the temperature range in which these systems can be used without decreasing their properties at the service temperature.

Three samples from each material type weighing 15 mg–30 mg each were tested. The edges were smoothed and burrs were removed by sanding, and the copper cladding was etched off using sodium per sulfate solution. T_g was measured using a Perkin-Elmer differential scanning calorimeter (Pyris 1 DSC). Specimen were subjected to a temperature scan of 30°C to 200°C at a rate of 20°C/min. At T_g the heat capacity of a material changes, and this is captured by a step transition in the DSC measurement curve. T_g is identified as the midpoint of the step transition (across which the heat capacity of the material changes) in the DSC measurement plot (Figure 2).

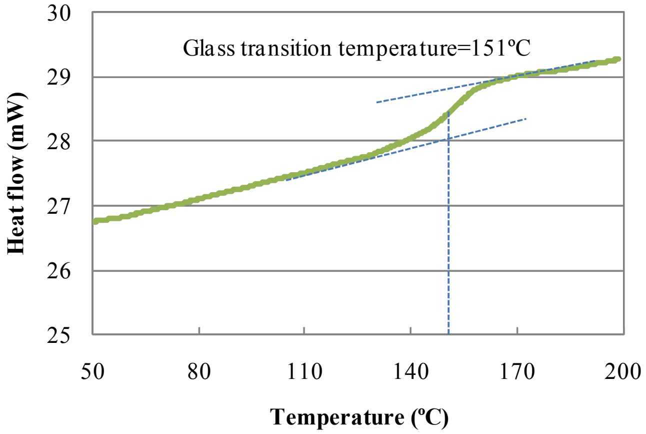


Figure 2 Glass transition temperature measurement plot

Decomposition temperature (T_d)

Decomposition temperature (T_d) is the temperature at which a resin system irreversibly undergoes physical and chemical degradation with thermal destruction of the cross-links, resulting in weight loss of the material. Two samples from each material type weighing 10 mg–20 mg each were tested. The edges were smoothed and burrs were removed by sanding, and the copper cladding was etched off. The T_d was measured using a thermo-gravimetric analyzer (Shimadzu TGA 50). The specimens were subjected to a temperature scan of 25°C to 550°C at a rate of 10°C/min. The change in weight of the sample was obtained as a function of temperature, and T_d was recorded at 2% and 5% weight loss compared to the sample weight at 50°C.

Time-to-delamination (T-260, T-288)

Time-to-delamination is the time taken by a laminate material to delaminate (defined as the separation between layers of prepregs and copper clad cores in a multilayered structure), when exposed to a constant temperature. The temperature of 260°C (T-260) is being used in the industry as a metric for assessing lead-free process compatibility of laminates. The T-288 delamination time provides a more appropriate level of performance given the process temperature required for lead-free soldering. Both parameters were tested in this study. Four samples, each 6.35 mm x 6.35 mm in size, were tested using a thermo-mechanical analyzer (Pyris TMA 7). The samples were subjected to a temperature scan of 25°C to 260°C or 288°C at a ramp rate of 10°C/minute and then held at 260°C or 288°C until an irreversible change in thickness of the sample was observed or 30 minutes elapsed, whichever came first[10]. Time-to-delamination was determined as the time between the onset of isotherm (260°C or 288°C) and the onset of delamination.

2.3 Experiments

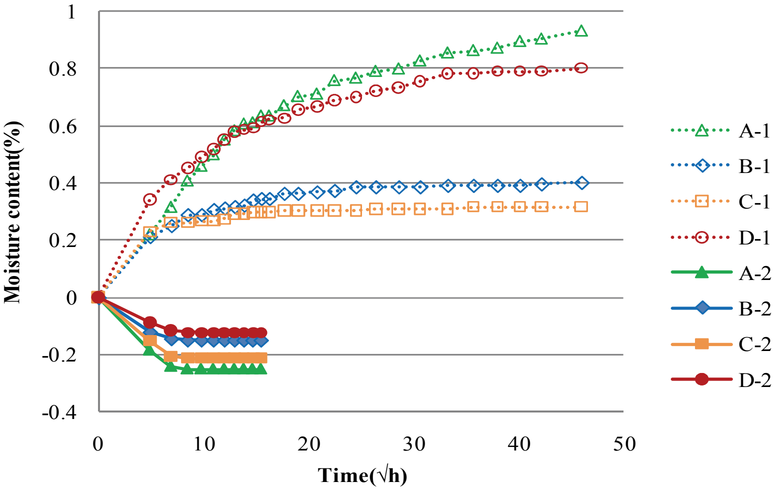
Copper cladded materials which were cut from some laminate were etched to remove copper from the laminate surface. The samples were placed in a solution of water and sodium per sulfate on a hotplate until all the copper was etched from the surface and were then cleaned under running water. The concentration of the solution and the operating temperature were noted on the package of the sodium per sulfate. After etching the samples were dried in an air-circulating oven for two hours at 105°C. Then four coupons of each material were prepared by cutting the laminate material into 20mm×20mm in square for studying the moisture absorption and desorption behavior.

2.3.1 Moisture Absorption and Desorption Experiments

Moisture absorption and moisture desorption experiments were conducted on four coupons of each PCB material. These experiments were conducted in order to characterize the moisture absorption and desorption behavior of the samples at different exposure times. The test started with the laminate from shelf. Two coupons were exposed to 85ºC and 85% RH and another two coupons were baked at 105°C in an air-circulating chamber from room storage conditions, respectively. The moisture content of each in laminate was measured at increasing time intervals. The weight of laminate samples was measured with an analytical balance (Mettler AE100) having a resolution of 0.1 mg. After measuring the weight, the test coupons were put back to their chambers within 5 minutes. The moisture absorption and desorption results of four PCB laminates are graphically displayed in Figure 3. Weight gain and weight loss were expressed as a percentage of the laminate's initial mass, M_t, which is determined by:

$$M_t(wt\%) = \frac{m_t - m_0}{m_0} \times 100\%$$

where m_t and m_0 are the weights of a specimen at exposure time, t, and of the initial specimen, respectively.



*-1: moisture absoption in 85ºC and 85% RH ; *-2: moisture desorption at 105ºC

Figure 3 Rate of moisture absorption and moisture desorption of test materials

The results showed that the moisture absorption and desorption rates in 4 laminates were fairly rapid in the early stages, and the rates decreased with time. Based on the results from the absorption and desorption experiments, time intervals were selected for testing z-CTE and T_g of 4 laminates.

Moisture diffusion rate in PCB laminate is effected by temperature and humidity [1][3][3]. For accelerating the experiment process, the moisture absorption experiments were also conducted using boiling water. Results are shown in Figure 4. All test materials were saturated after immersing in boiling water for 240 hrs.

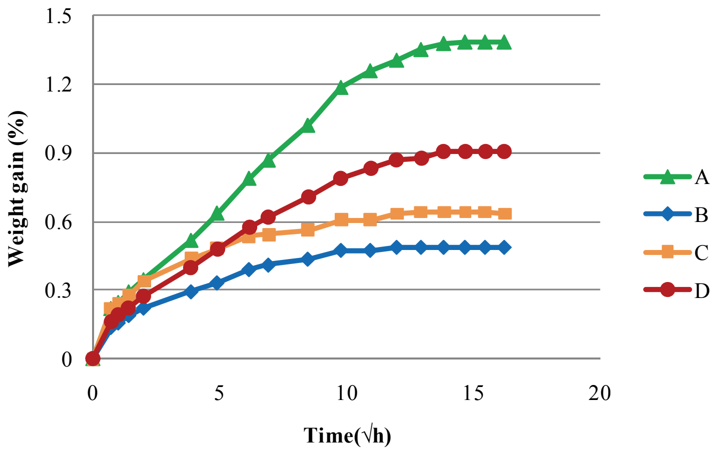


Figure 4 **Rate of moisture absorption of test materials in boiling water**

2.3.2 Impact of Moisture Absorption on z-CTE and T_g

Based on the results from the absorption and desorption experiments, ten sets of test coupons of each sample were prepared (Table 3). One set was preconditioned and tested according to the IPC-TM-650 2.4.24 (TMA) [11] and IPC-TM-650 2.4.25 (DSC) [12] test methods as a control coupon. Coupon sets 2-4 were baked at 105°C for 24, 48, and 72 hrs, respectively followed by cooling in a desiccator to room temperature before measurement. Coupon sets 5-10 were exposed to 85°C and 85% RH for 24, 48, 96, 192, 504, and 1200 hrs, respectively, to induce different moisture contents. Some of the coupons were tested directly without preconditioning, and the others were baked at 105°C for 2 hrs in an air-circulating oven followed by cooling in a desiccator to room temperature as per the IPC method before measurement.

Table 3 Preconditioning process of test coupons before z-CTE and T_g measurements

Sets No.	Name	85°C/85% RH (hrs)	105°C (hrs)
1	Control	×	2
2	b-24 hrs	×	24
3	b-48 hrs	×	48
4	b-72 hrs	×	72
5-1	a-24 hrs	24	×
5-2	a24-b2 hrs	24	2
6-1	a-48 hrs	48	×
6-2	a48-b2 hrs	48	2
7-1	a-96 hrs	96	×
7-2	a96-b2 hrs	96	2
8-1	a-192 hrs	192	×
8-2	a192-b2 hrs	192	2
9-1	a-504 hrs	504	×
9-2	a504-b2 hrs	504	2
10-1	a-1200 hrs	1200	×
10-2	a1200-b2 hrs	1200	2

2.3.3 Impact of Moisture Absorption on Decomposition Temperature and Time to Delamination

Four sets of test coupons of each material were prepared. Set 1 and Set 2 were preconditioned and tested according to the IPC-TM-650 2.4.24 (time to delamination) [10] and IPC-TM-650 2.4.24.6 (decomposition) [13] test methods, respectively, as controls. For accelerating the moisture absorption process, Set 3 and Set 4 coupons were immersed in boiling water for moisture absorption. Then the test coupons were preconditioned as per IPC test method before measurement for studying the impact of moisture absorption on decomposition temperature and time to delamination.

3 Results and Discussion

3.1.1 Moisture Absorption and Desorption

The moisture concentration in laminate increases with the exposure time and approaches equilibrium after several days when exposure to a humid enviroment. The time to reach equilibrium depends on the thickness of the laminate and the ambient temperature. The laminate samples were assumed to be relatively thin. So diffusion from the laminates' edges is negligible. Moisture diffusion in laminate follows one-dimensional Fickian equation. For Fickian diffusion in a laminate with thickness ℓ exposed on both sides to the same environment, the moisture content, M_t, at time t, is given by the expression

$$\frac{M_t}{M_\infty} = \frac{4}{\ell}\left(\frac{Dt}{\pi}\right)^{1/2}$$

Where M_∞ is the equilibrium moisture content, and D is the diffusion coefficient, or diffusivity, given in $(\text{length})^2(\text{time})^{-1}$[3].

Moisture diffusion will only occur through the epoxy, as the reinforcement glass does not readily absorb moisture. And, epoxies can inherently also absorb different moisture content; Also, the varying glass/resin ratios between different PCB constructions will result in a varying moisture concentration and maximum moisture uptake. As a result, the moisture absorption characteristics of PCB materials will vary by epoxy type, construction, and epoxy/fiber content [14].

A thermo-gravimetric analyzer (TGA) was used for measuring the glass/resin ratio for each material. Based on past experience, specimens were subjected to a temperature scan of 25°C to 540°C at a rate of 10°C/min, then held at 540°C for 60 minutes to make the epoxy resin decompose entirely. Calculated results are shown in Table 4.

Table 4 Thickness and glass/resin ratio of four materials

Material	*A*	*B*	*C*	*D*
Thickness	0.95	1.16	0.69	1.16
Glass/resin ratio	3:1	3:1	4:1	2:1

As we can see from Table 4, Figure 3 and Figure 4, material A and B have same glass/resin ratio, but material A absorbed more moisture since it is different halogen-free epoxy resin system. Material D absorbed more moisture since it has more epoxy resin in its system. After normalizing the glass/resin ratio, moisture absorption results were plotted in Figure 5. From Figure 5, we can see halogen-free system materials A and C absorbed more moisture in boiling water than halogenated materials B and D.

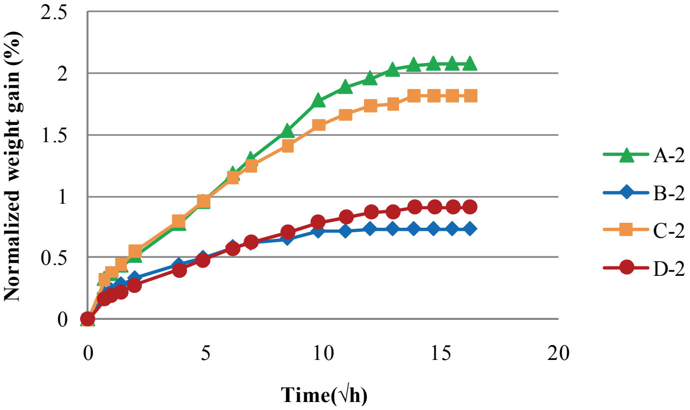
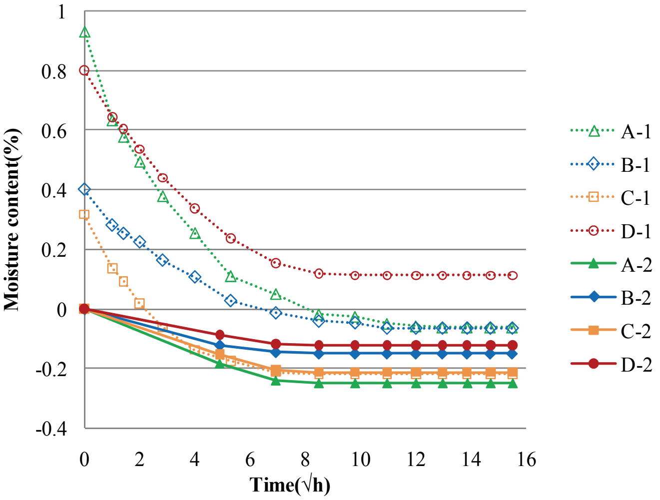


Figure 5 normalized results of moisture absorption in boiling water

Moisture desorption experiments were conducted on both the coupons exposed to 85°C and 85% RH for 2112 hrs and the coupons prepared from room storage condition(Figure 6). During 10 days of moisture desorption experiments, the moisture content decreased rapidly in the first 24 hrs. As shown in Figure 6, halogen-free materials A and C released more moisture than halogenated materials B and D in the desorption process starting from the room storage conditions. In other words, halogen-free materials A and C absorb more moisture in room storage conditions. None of the room storage specimens lose weight after baking for 72 hrs, while the specimens which exposure to 85°C and 85% RH for 2112 hrs did not lose weight after baking for 120 hrs. And after baking process, the final weight of specimens which baking after exposed to 85°C and 85% RH for 2112 hrs were higher than the specimens baking from room storage condition. The water molecules absorbed into the epoxy can be classified into two types [15][16]: bound water and free water. Bound water is trapped at polar sites and is usually bonded to hydroxyl groups in the epoxy network. Free water is clustered in the free volume or voids inside the epoxy. The "free volume" of the polymeric resin is defined as the volume of the resin without the volume of the polymer chains and the volume due to thermal vibrations of the polymer chains. The bound water which bonded to hydroxyl groups in the epoxy network will not released in baking process. As a result, the moisture content values of coupons which subject to 85°C and 85% RH are higher than the coupons in room storage conditions after baking process, as shown in Figure 6 .



*-1: baked after being in 85/85 chamber for 2112 hrs; *-2: baked from room storage condition

Figure 6 Rate of moisture desorption of laminates at 105˚C

3.1.2 Effect of Moisture on z-CTE

The z-CTE values (below T_g and above T_g) of four PCB laminates with different moisture contents are plotted in Figure 7. And datasheet regions are also illustrated. Figure 8 displays the CTE curves of sample A with different moisture condition. After exposed sample A to 85°C and 85% RH for 24 hrs, one part was preconditioned as per IPC-TM-650 2.4.24 test method, then measure the CTE. The other part was tested whitout preconditioning. Two results compared with control set were plotted in Figure 8. Figure 9 shows CTE curves of four samples which absorbed moisture in 85°C and 85% RH for various times, then preconditioned as per IPC-TM-650 2.4.24 test method before measurement.

There is no obvious trend in the z-CTE values calculated from the data below or above the glass transition region as shown in Figure 7. However, there is appreciable deviation on z-CTE curves around the glass transition region, as shown in Figure 9 and Figure 8. Preconditioning as per IPC test methods can reduce the effect of moisture on z-axis expansion. However, the swelling in the glass transition region increased with the increase of moisture content especially in halogen-free material A, which absorbing more moisture than other materials according to moisture absorption experiments.

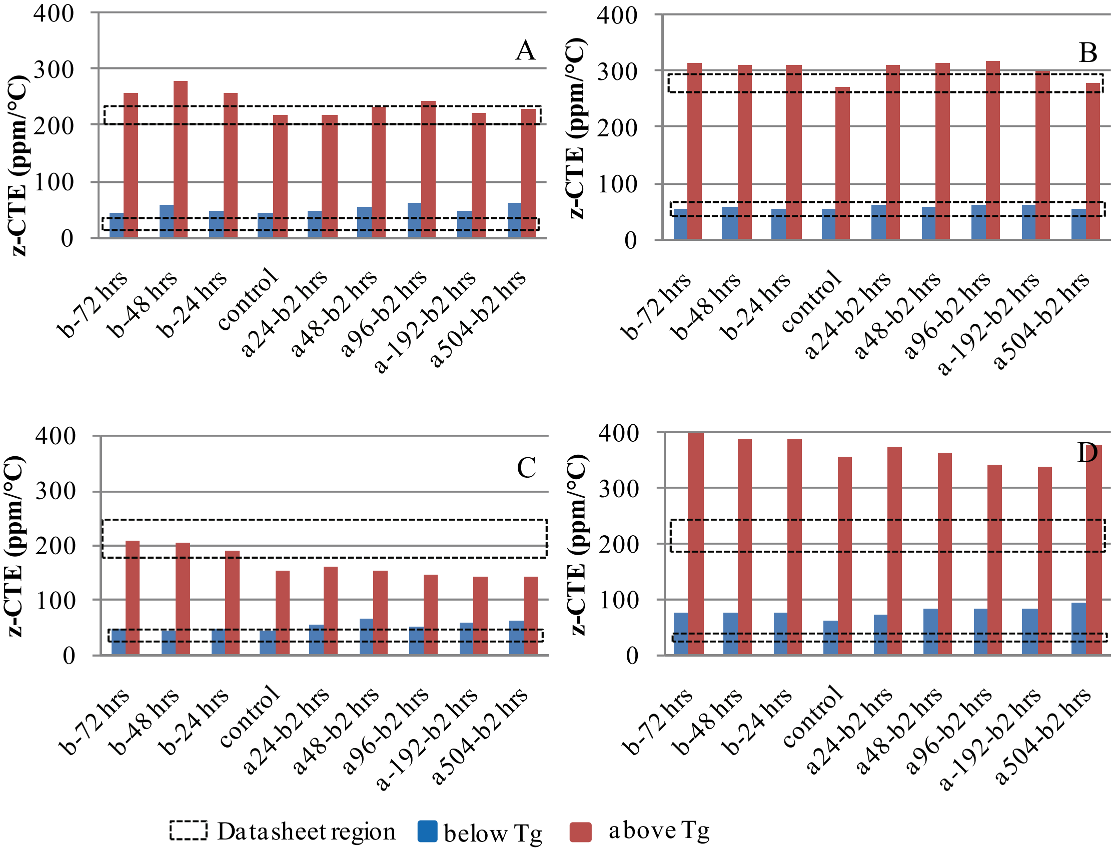


Figure 7 z-CTE values of samples with various moisture contents and datasheet regions

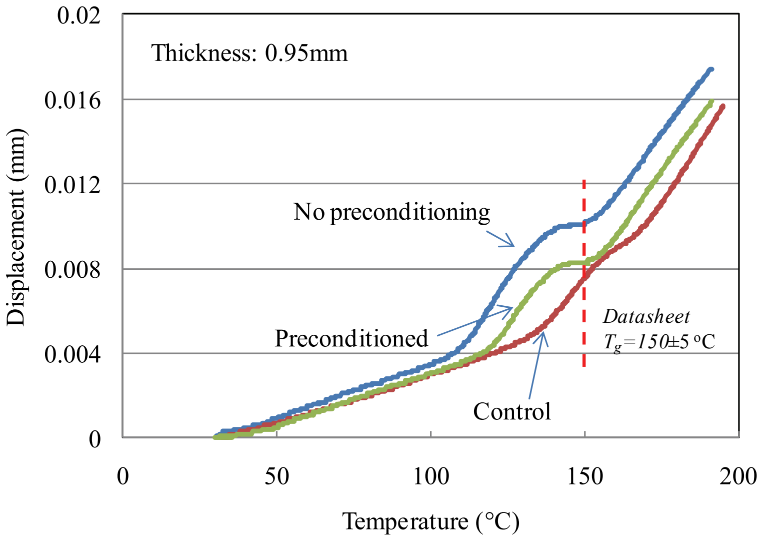


Figure 8 CTE curves of sample A after exposure to 85°C and 85% RH for 24 hrs, and later one part was preconditioned as per IPC-TM-650 2.4.24 test method before measurement compared with no preconditioning and control sets

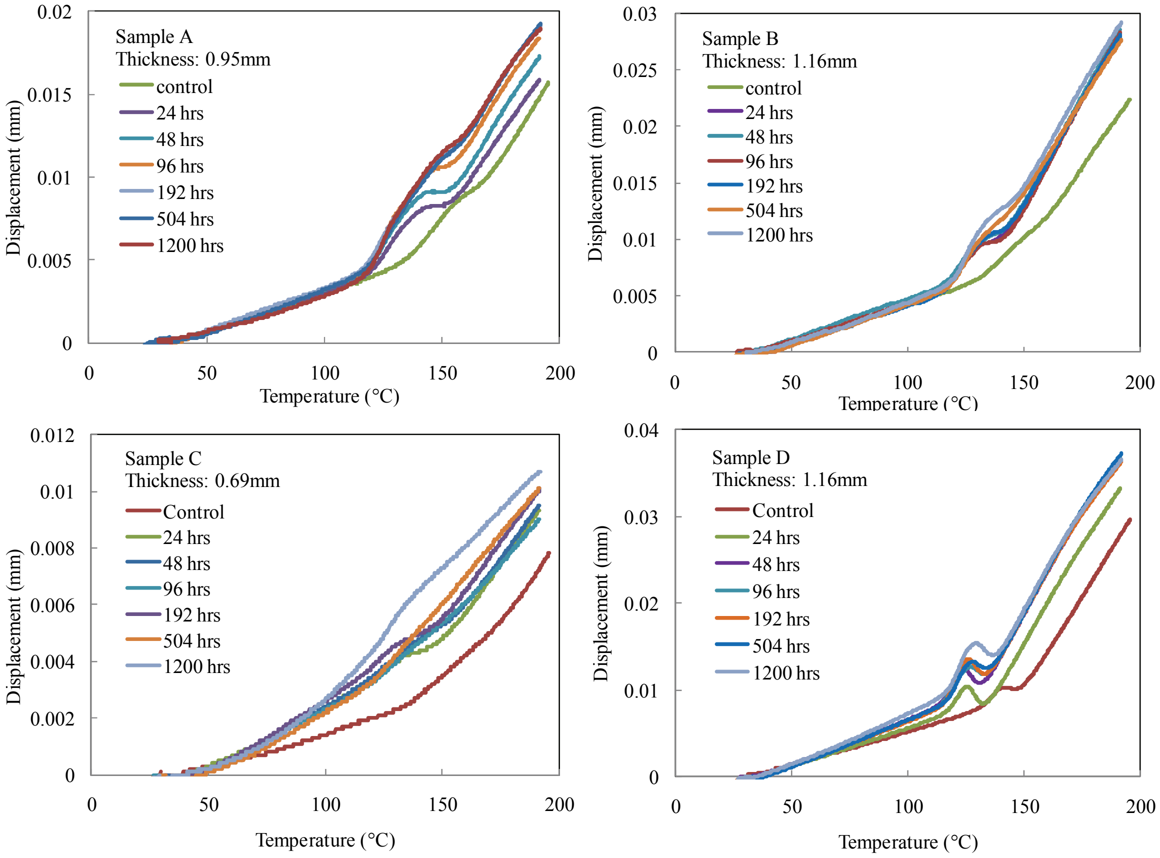


Figure 9 CTE curves of four samples after exposure to 85°C and 85% RH for various times, and later preconditioned as per IPC-TM-650 2.4.24 test method before measurement

It can be inferred from CTE curves in Figure 8 that there are three phases with each showing different thermal expansion rates. Phase 1 z-axis expansion is dominated by the resin, and hence the CTE values below T_g are close to that of epoxy resin (~60 ppm/^{o}C). In phase 3, materials expand because an increase in temperature leads to greater thermal vibration of the atoms in a material, and hence to an increase in the average separation distance of adjacent atoms. Therefore, the material has a large expansion rate, and material becomes more viscous above $T_{g,}$. In phase 2, there are two factors that cause appreciable deviation in z-CTE values. Firstly, moisture causes swelling in PCB laminate above 100ºC, and increases the z-axis expansion below the original T_g point. Secondly, water acts as a plasticizer in the epoxy system, increasing the viscosity of epoxy resin, and resulting in a reduction of T_g. Hence, the expansion rate becomes large below the original T_g point. As a result, the total z-axis expansion of the laminate increases with an increase of moisture content in the laminate.

3.1.3 Effect of Moisture on T_g

Previous work reported that the absorbed water in epoxy materials would lead to a decrease of the glass transition temperature due to the plasticizing effect of water [17]-[20]. DSC results from our experiments prove that the Tg of epoxy samples does indeed decrease with a moisture increase in the early stages (until around 192 hours except for sample D) as shown in Figure 10. However, T_g increases in the later stages (post 192 hours except sample D), after exposure for a long time to 85°C and 85% RH.

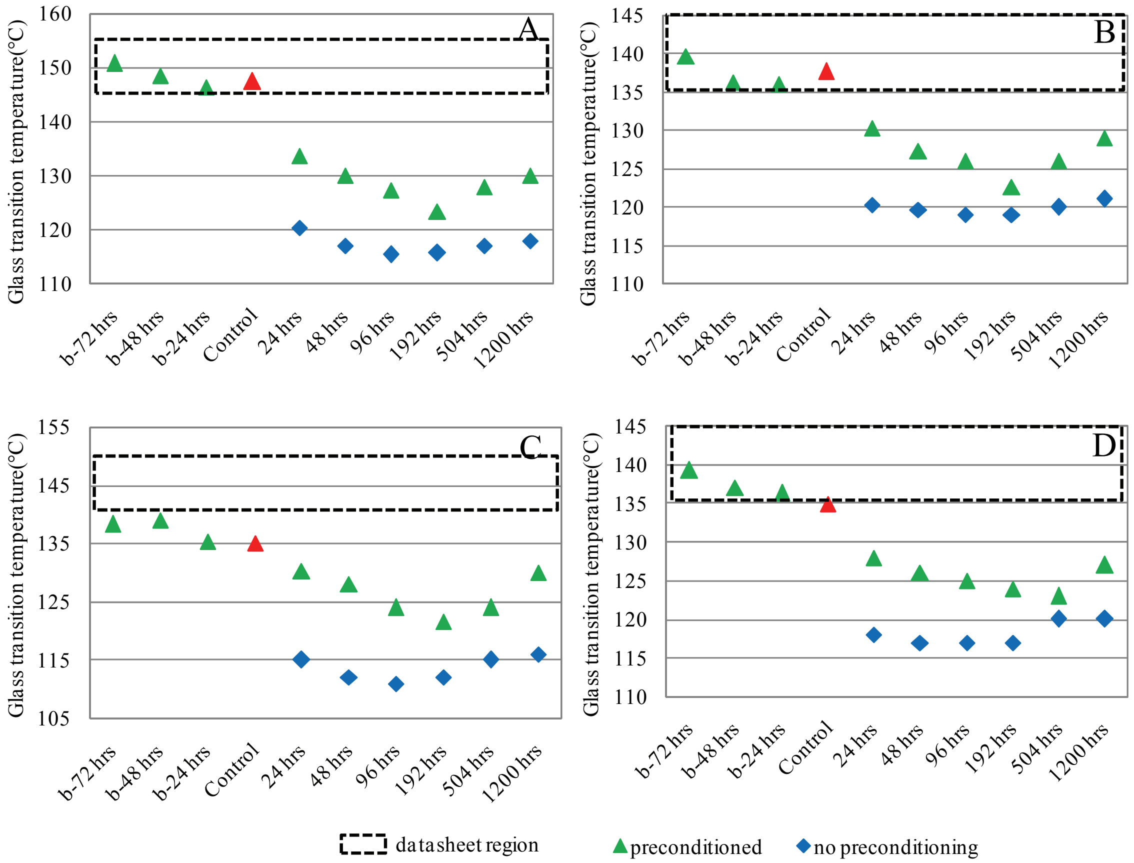


Figure 10 T_g results of four samples after exposure to 85°C and 85% RH for different durations

In order to verify that the T_g results obtained from this experiment were also influenced by temperature exposure, T_g tests were repeated on specimens A and B which were immersed in boiling water. Boiling water was used to accelerate the sample moisture absorption rate. The results are shown in Figure 11.

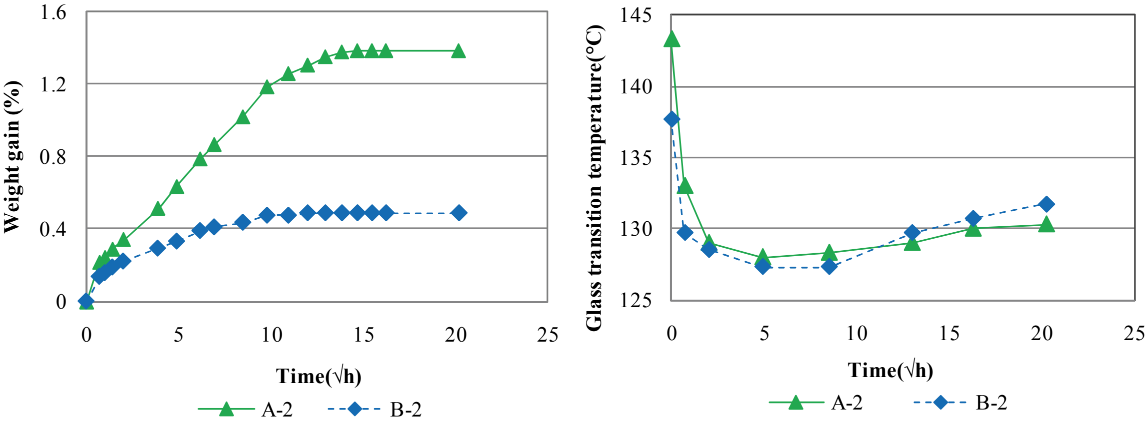


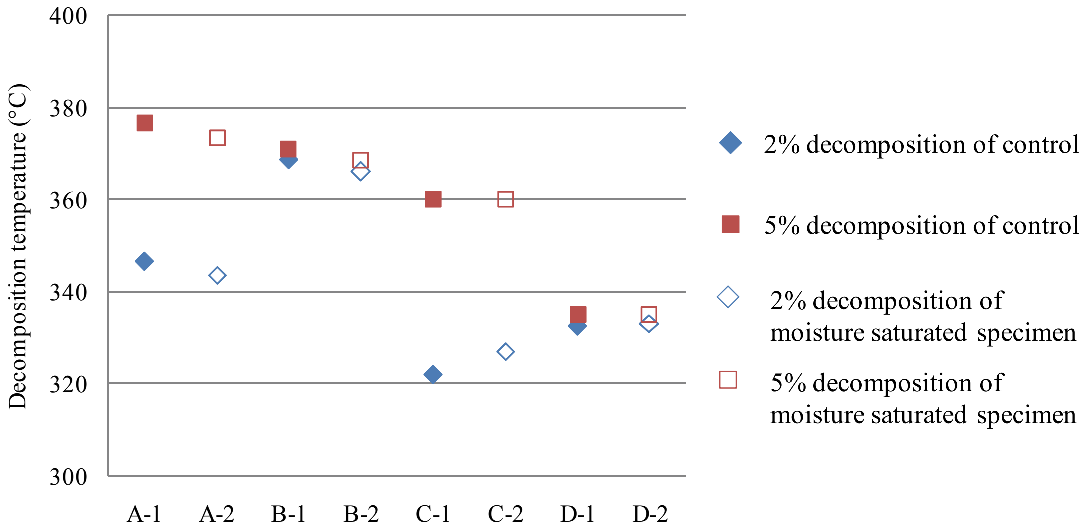
Figure 11 Moisture absorption and T_g results of samples A and B in boiling water

The same trends were found in samples A and B when immersed in boiling water. The results indicate that the Tg of a water-saturated epoxy depends strongly on exposure time and temperature. At the time when the hygrothermally exposed materials almost reach saturation, the depression of Tg is greatest. However, Tg begins to gradually recover post-saturation. A higher immersion temperature and longer duration induce a greater degree of recovery of Tg.

A decrease in T_g of an epoxy system is usually associated with entrapped plasticizers. Water typically acts as a plasticizer in the epoxy systems resulting in a reduction of T_g. An increase in T_g is associated with an increase in cross-linking density. Heat facilitates the chemical reactions that result in cross-linking of polymers, thus increasing the T_g. According to the T_g results both in 85°C and 85% RH condition and boiling water, we can see that during the early stages the test samples absorb more moisture, T_g decreases rapidly, and moisture dominates the trends. In the later stages, samples are nearly saturated, T_g increases with time under thermal condition, and temperature dominates the trends. This kind of behavior can also be explained by the findings of Zhou [21]. They have claimed that absorbed water molecules forming double hydrogen bonds would cause an increase of T_g. According to their findings, water molecules bind with epoxy resins through hydrogen bonding. Two types of bound water were found in epoxy resins. The binding types are classified as Type I or Type II bonding, depending on differences in the bond complex and activation energy. These two types bound water have quite different influences on T_g variation. Type I bound water disrupts the initial interchain Van der Waals force and hydrogen bonds, resulting in increased chain segment mobility acting as a plasticizer and thus decreases T_g. In contrast, Type II bound water contributes, comparatively, to an increase in T_g in water-saturated epoxy resin by forming a secondary crosslink network. Experimentally determined T_g values represent the combined effect of the two mechanisms.

3.1.4 Effect of Moisture on T_d

The decomposition temperature measurement was conducted by exposing specimens to a temperature scan of 25°C to 550°C under a flow of nitrogen at a heating rate of 10ºC /min. The decomposition temperature measurement results for four materials corresponding to 2% and 5% weight loss are plotted in Figure 12. After preconditioning according to IPC-TM-650 2.4.24.6, the T_d for specimen, which was saturated in boiling water, did not show noticeable variation compared with the control set. In other words, moisture has no obvious effect on T_d after preconditioning as per the IPC standard for all materials in this study. Further, typical TGA curves for four test materials are plotted in Figure 13. Halogenated materials (B & D) start to decompose at 320ºC and 370ºC, respectively, and subsequently experience a rapid degradation. Materials B & D underwent degradation from 2% to 5% within a narrow temperature range, which is not the case with halogen free materials (A & C). Halogen free materials (A & C) experience a slope degradation which indicated halogen-free materials have better thermal stability than halogenated materials. The possible reason is that the halogen-free and halogenated materials have different epoxy resin system as they use different flame retardant. The mechanism was not clear yet.



**-1) prepared as per IPC test method*

**-2) specimens saturated after 10 days in boiling water, then preconditioned as per IPC test method*

Figure 12 T_d results of four samples after being saturated in boiling water compared with control set

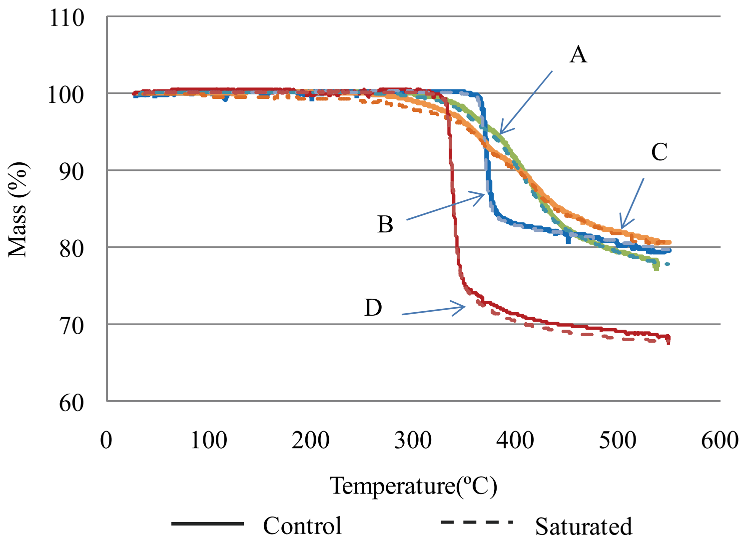


Figure 13 Typical TGA curves for four laminates

3.1.5 Effect of Moisture on Time to Delamination

Two sets of samples were prepared in this test. One set was prepared and tested as per IPC-TM-650 2.4.24 as a control. The other set was immersed in boiling water for 10 days. The weight of each laminate was measured before and after immersion with an analytical balance. The laminate thickness was measured with a digital vernier caliper with a 0.01mm least count. This test ramps the sample from 25 ºC to 260 ºC or 288 ºC at 10 ºC /minute and holds the sample at 260 ºC or 288 ºC until an irreversible change in thickness of the sample is observed or 30 minutes, whichever occurs first. The results are shown in **Error! Not a valid bookmark self-reference.**.

Table 5 Time to delamination results of four samples after absorbing moisture in boiling water compared with control set

Time to delamination	Laminate Thickness (mm)	Control		Immersed in boiling water		
		260 ºC	288 ºC	260 ºC	288 ºC	Moisture content
A	1.30	17 min	1 min	Delaminate at 235 ºC	—	1%
B	2.37	>30 min	5 min	24 min	4 min	0.5%
C	1.15	>30 min	>30 min	>30 min	>30 min	1.5%
D	2.31	14 min	< 10 s	< 5 s	Delaminate at 260 ºC	1%

The time to delamination is a measure of the ability of the dielectric bond line to absorb stresses. As we can see, time to delamination decrease obviously when materials A, and D were immersed in boiling water and absorbed around 1% moisture. T260 and T288 of material B decrease slightly after absorbing 0.5% moisture. Material C does not show any delamination within 30min neither control set or moisture absorption set. A degradation in time to delamination results showed that the moisture absorption have affected the bond line.

4 Conclusions

This study examines the effect of moisture on out-of-plane coefficient of thermal expansion, glass transition temperature, time to delamination, and decomposition temperatures. Four types of PCB materials were studied from two manufacturers, including two halogen-free and two halogenated. Furthermore, this study investigates the suitability of IPC-TM-650 pre-conditioning steps for thermal property measurements.

The results showed that glass transition temperature of all test materials was affected by both moisture content and exposure temperature. T_g decreases with an increase in the moisture content in laminates, and also it increases with an increase in the duration when exposed to thermal conditions. In the early stages, moisture dominated the trends before laminate materials reached the saturation point, while temperature dominated the trends in the later stages. The result showed that exposure to humidity has no obvious effect on z-CTE values (below 100ºC and above T_g). However, moisture causes swelling in PCB laminates between 100ºC and the T_g point, and increases z-axis expansion. Further, T_g and z-CTE results varied with different moisture contents, though the tests were conducted exactly as per the IPC test methods. Pre-conditioning steps outlined in IPC-TM-650 2.4.24 and 2.4.25 cannot account for varying moisture contents. The time to delamination of laminate was degraded by absorbing moisture. Moisture had no obvious effect on T_d after preconditioning as per the IPC test methods. However, halogenated materials underwent degradation from 2% to 5% within a narrow temperature range compared with halogen-free materials.

5 Acknowledgments

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6 References

[1] P.C. Liu, D.W. Wang, E.D. Livingston, and W.T. Chen, “Moisture Absorption Behavior of Printed Circuit Laminate Materials”, *Advances in Electronic Packaging*, Vol. 4, pp 435-442, 1993.

[2] B. Rudra, M. Pecht, and D. Jennings, “Assessing Time-to-Failure Due to Conductive Filament Formation in Multi-Layer Organic Laminates”, *IEEE Transactions on Component, Packaging, and Manufacturing Technology*, Vol. 17, pp 269-276, August 1994.

[3] M. Pecht, H. Ardebili, Anand A. Shukla, John K. Hagge, and D. Jennings, "Moisture ingress into organic laminates", *IEEE Transactions on Components and Packaging Technologies*, Vol. 22, No. 1, pp 104-110, March 1999.

[4] E.H. Wong, R. Rajoo, "Moisture absorption and diffusion characterisation of packaging materials — Advanced treatment", *Microelectronics Reliability*, Vol. 43, No. 12, pp 2087-2096, December 2003.

[5] M. Akay, S.K.A Mun, and A. Stanley, "Influence of Moisture on the Thermal and Mechanical Properties of Autoclaved and Oven-Cured Kevlar-49/Epoxy Laminates", *Composites Science and Technology*, Vol. 57, pp 565-571, 1997.

[6] J. Lundgren, and P. Gudmundson, "Moisture Absorption in Glass-Fiber/Epoxy Laminates with Transverse Matrix Cracks", *Composites Science and Technology*, Vol. 59, pp. 1983-1991, 1999.

[7] R. Demaree, "Halogen-free systems in current PCB practice", IPC EXPO, pp S11-3-1 to S11-3-4, 2001.

[8] E.H. Wong, and R. Rajoo, "Trends and Challenges of Environmentally Friendly Laminates", PC FAB, March 2003.

[9] R. Sanapala, B. Sood, D. Das, and M. Pecht, "Effect of Lead-Free Soldering on Key Material Properties of FR-4 Printed Circuit Board Laminates", *IEEE Transactions on Electronics Packaging Manufacturing*, Vol. 32, No. 4, pp 272-280, October 2009.

[10] IPC-TM-650 2.4.24.1, "Time to delamination by TMA", *The Institute for Interconnecting and Packaging Electronic Circuits,* Northbrook, IL, December 1994.

[11] IPC-TM-650 2.4.24, "Glass transition temperature and z-axis thermal expansion by TMA", *The Institute for Interconnecting and Packaging Electronic Circuits,* Northbrook, IL, December 1994.

[12] IPC-TM-650 2.4.25, "Glass transition temperature and cure factor by DSC", *The Institute for Interconnecting and Packaging Electronic Circuits,* Northbrook, IL, December 1994.

[13] IPC-TM-650 2.4.24.6, "Decomposition temperature of laminate material using TGA", *The Institute for Interconnecting and Packaging Electronic Circuits,* Bannockburn, IL, April 2006.

[14] P. Hamilton, G. Brist, B. Guy Jr and J. Schrader; "Humidity-Dependent Loss in PCB Substrates," Proceedings of IPC Printed Circuit Expo, February 2007.

[15] H. Zhao, and Robert K.Y. Li, "Effect of water absorption on the mechanical and dielectric properties of nano-alumina filled epoxy nanocomposites", *Composites: Part A, Applied Science and Manufacturing*, Vol. 39, No. 4, pp 602-611, 2008.

[16] C. Maggana, and P. Pissis, "Water sorption and diffusion studies in an epoxy resin system", *Journal of Polymer Science: Part A, Polymer Chemistry*, Vol. 37, No. 11, pp 1165-1182, 1999.

[17] P. Moy, F. E. Karasz, "Epoxy-water interactions", *Polymer Engineering Science*, Vol. 20, pp 315-319, 1980.

[18] S. Luo, J. Leisen, C. P. Wong, "Study on Mobility of Water and Polymer Chain in Epoxy and Its Influence on Adhesion", *Journal of Applied Polymer Science*, Vol. 85, pp 1-8, 2002.

[19] E. L. Jr. McKague, J. D. Reynold, J. E. Halkias, "Swelling and glass transition relations for epoxy matrix materials in humid environments", *Journal of Applied Polymer Science*, Vol. 22, pp 1643-1654, 1978.

[20] E. S. W. Kong, M. J. Adamson, "Physical ageing and its effect on the moisture sorption of amine cured epoxy, *Polymer Comm.*, Vol. 24, pp 171-173, 1983.

[21] J. M. Zhou, J. P. Lucas, "Hygrothermal effects of epoxy resin Part I: the nature of water in epoxy", *Polymer*, Vol. 40, No. 20, pp 5505-5512, 1999.

Impact of Moisture Content on PCB Laminate Thermal Properties

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Introduction

Moisture plays an important role in the integrity and reliability of PCBs, presence of moisture in PCB [1, 2]

- —Alters thermo-mechanical properties
- —Induces hygroscopic stress through differential swelling
- —Reduces interfacial adhesion strength
- —Induces corrosion
- —Cause internal shorts through metal migration

[1] Liu, P.C., Wang, D.W., and Livingston, E.D., "Moisture Absorption Behavior of Printed Circuit Laminate Materials", Advances in Electronic Packaging, v 4-1, pp: 435-442,1993.
[2] Wong, E.H., and Rajoo, R., "Moisture absorption and diffusion characterization of packaging materials - advanced treatment", Microelectronics Reliability, v 43, n 12, pp: 2087-2096, 2003.

Background and Motivation

- CALCE has been conducting material property measurements on PCB materials:
  - Most measurements are conducted as per IPC test methods, including sample preconditioning.
  - Some measurement results are beyond ranges specified in manufacturers' datasheets.
- This study estimates dependence of thermal properties* on moisture content, compares the effect of moisture on halogen-free and halogenated PCBs, and establishes suitability of preconditioning steps for thermal property measurements.

Thermal properties tested in this paper include glass transition temperature (T_g), coefficient of thermal expansion (CTE), decomposition temperature (T_d), and time-to-delamination (T-260, T-288).

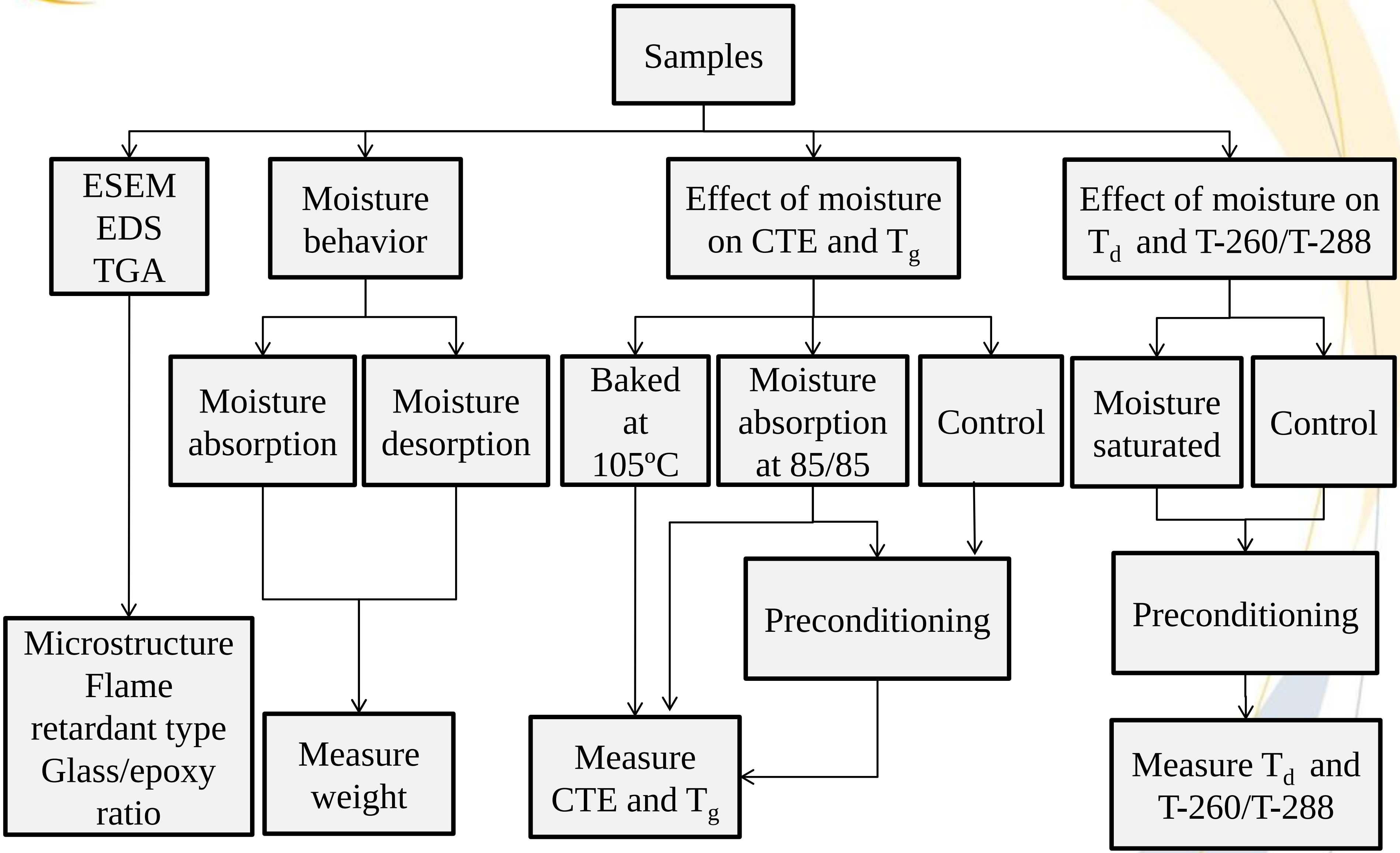
Materials

Four PCB materials — two halogen-free (A, C) and two halogenated (B, D) — were tested. These laminates were acquired from two manufacturers (A and B from manufacturer I and C and D from manufacturer II).

Datasheet values of test materials

Test Method IPC-TM-650	Properties		A	B	C	D
2.4.24	z-CTE ppm/ ^{o}C	below T_g	30-50	50-70	40-55	35-45
		above T_g	200-230	270-300	170-250	180-240
2.4.24 (TMA) 2.4.25 (DSC)	T_g (^{o}C)		150 ±5 (DSC)	140 ±5 (DSC)	140-150 (TMA)	135-145 (TMA)
2.4.24.6	T_d (^{o}C)	5%	345	312	>340	340-360
2.6.2.1	Water absorption (%)		0.05-0.10	0.1	0.02-0.04	0.04-0.06

Experiments



Samples

ESEM
EDS
TGA

Microstructure
Flame retardant type
Glass/epoxy ratio

Moisture behavior

Moisture absorption

Moisture desorption

Measure weight

Effect of moisture on CTE and T_g

Baked at 105ºC

Moisture absorption at 85/85

Control

Preconditioning

Measure CTE and T_g

Effect of moisture on T_d and T-260/T-288

Moisture saturated

Control

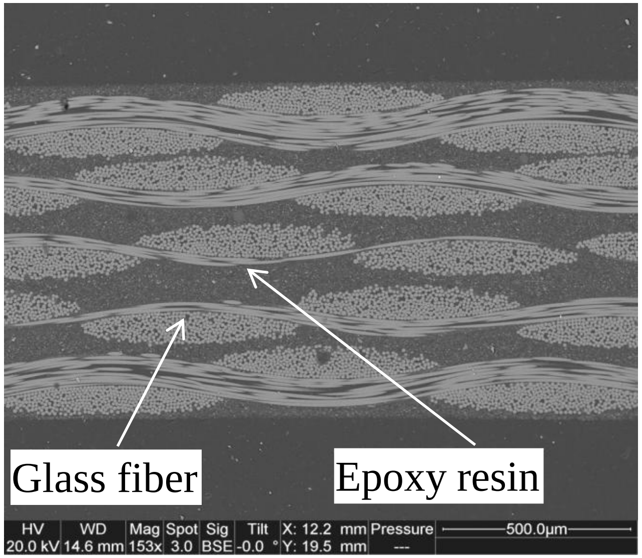
Preconditioning

Measure T_d and T-260/T-288

ESEM/EDS and TGA Results

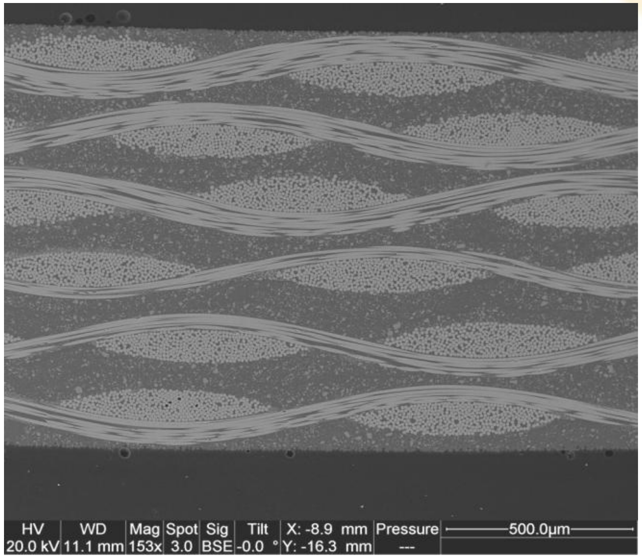
A:
5 plies
0.95 mm total
Halogen-free

Glass/epoxy
=3:1



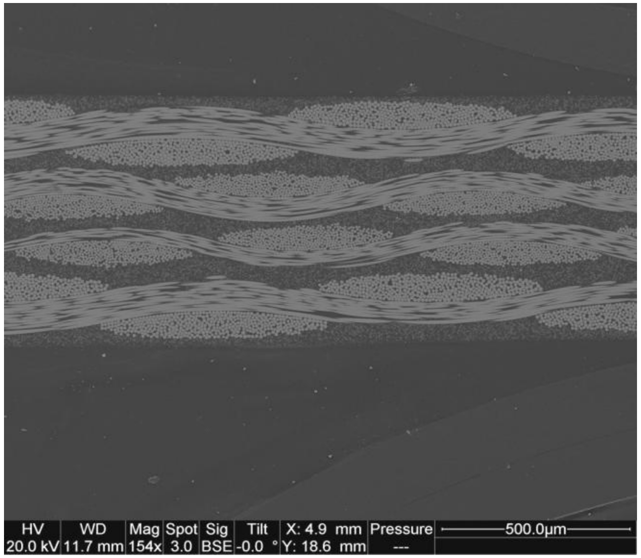
B:
6 plies
1.16 mm total
Brominated

Glass/epoxy
=3:1



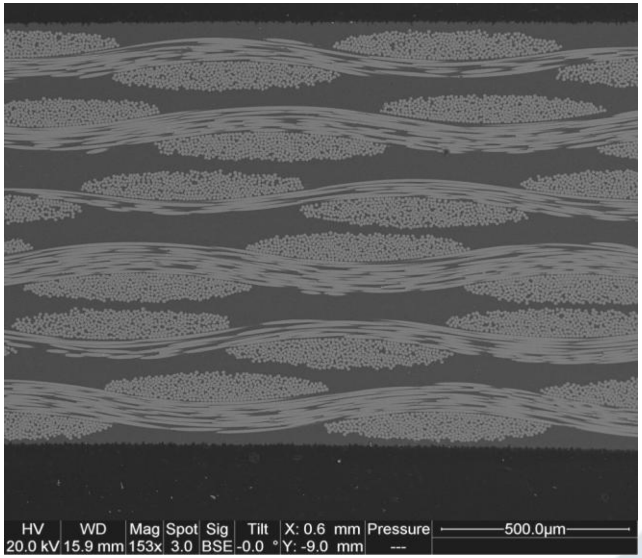
C:
4 plies
0.69 mm total
Halogen-free

Glass/epoxy
=4:1

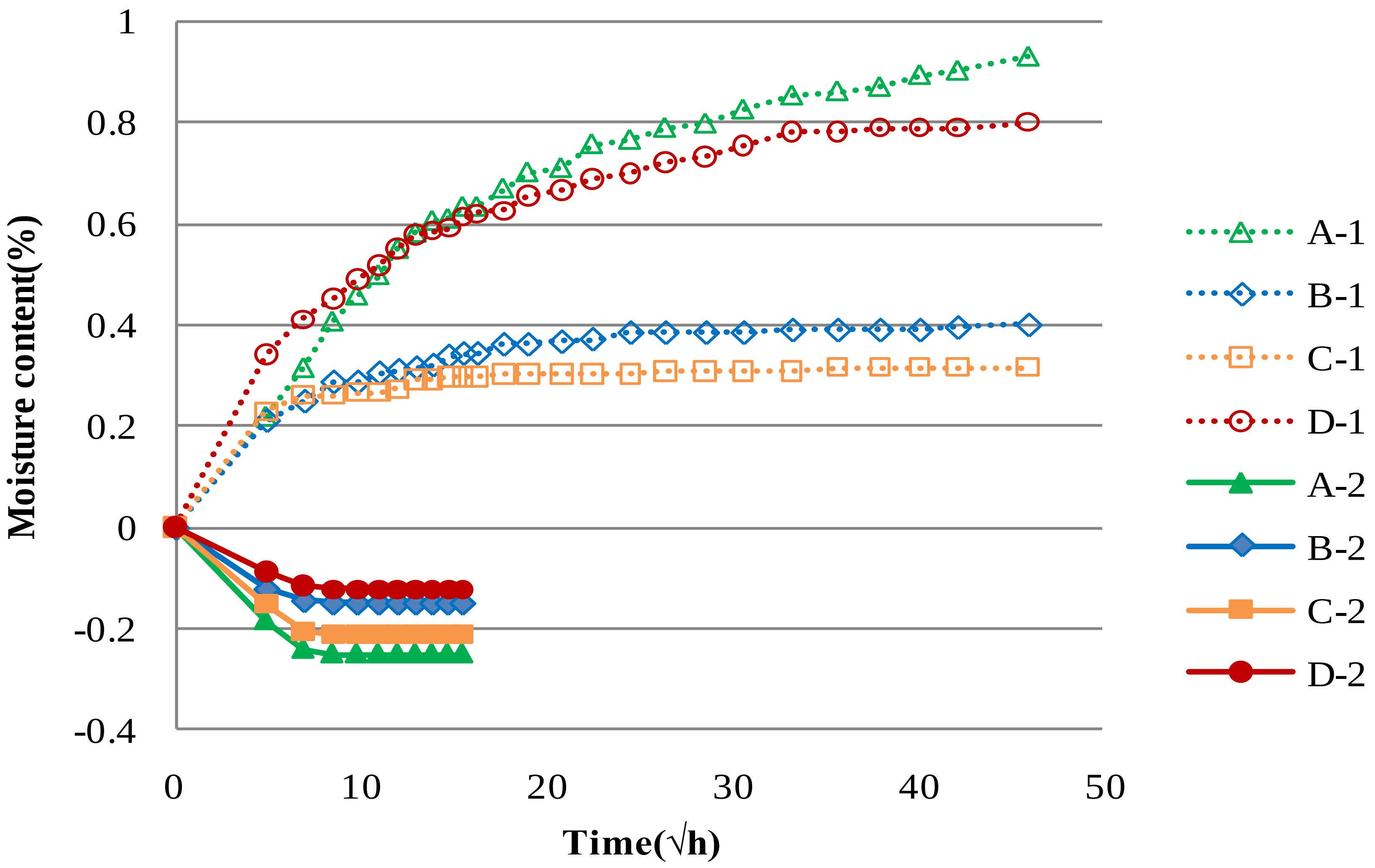


D:
6 plies
1.16 mm total
Brominated

Glass/epoxy
=2:1



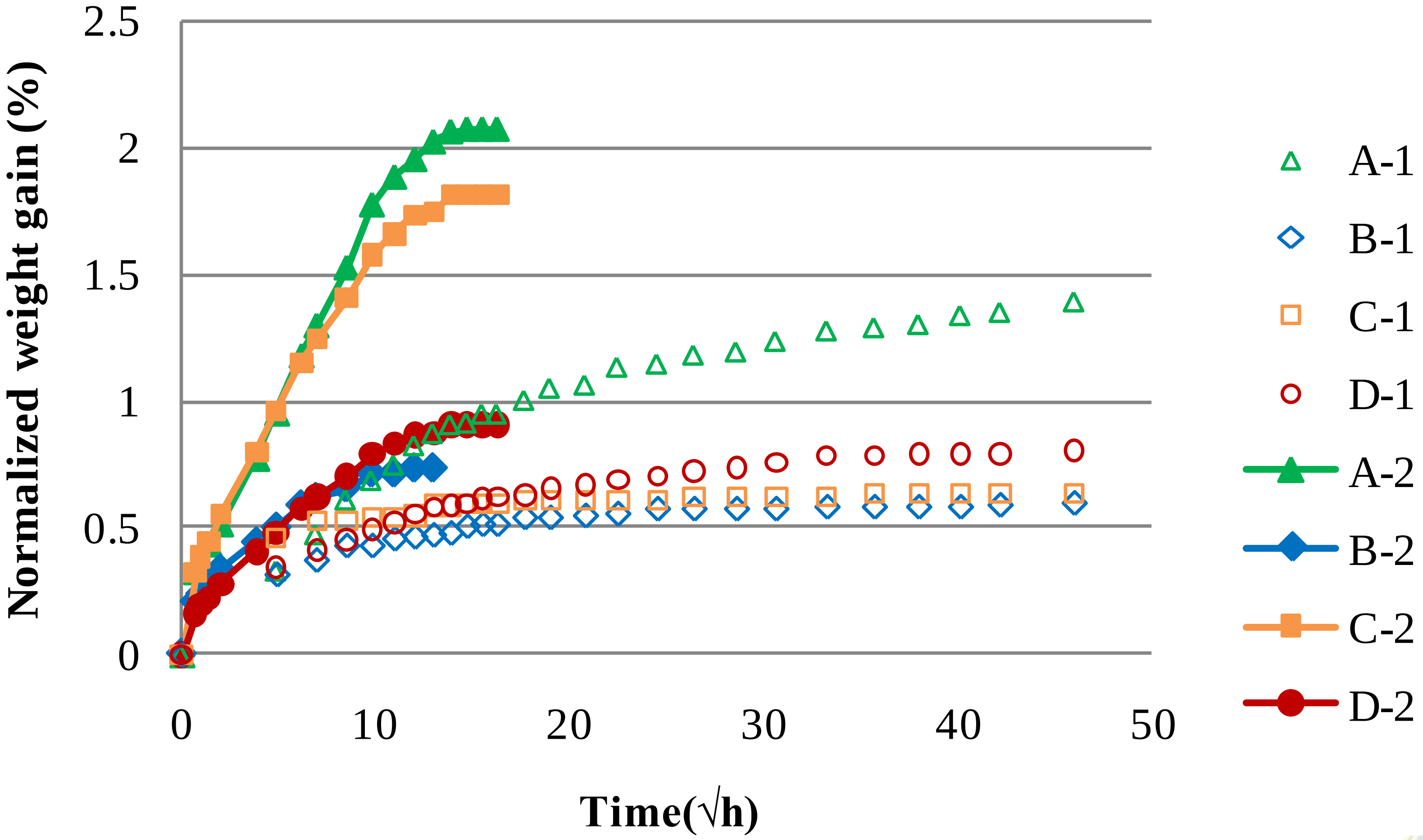
Absorption and Desorption



*-1: moisture absoption in 85°C and 85% RH ; *-2: moisture desorption at 105°C

Halogen-free materials (A & C) release more moisture after room storage.

Normalized Moisture Absorption



△ - exposed in 85ºC and 85% RH condition (no prebake)

▲ - baked at 105ºC for 2 hours, then immersed in boiling water.

Halogen-free materials (A & C) absorb more moisture in boiling water.

Moisture Absorption

- Moisture diffusion primarily occurs in the epoxy, reinforcement glass does not readily absorb moisture [1].
  - As a result, the moisture absorption characteristics of PCB dielectric materials will vary by construction and glass fiber/epoxy resin content.
  - The glass reinforcement will act as a barrier to restrict flow and impact the diffusivity between different constructions.
  - Also, the varying glass/epoxy ratios between PCB of different constructions will result in a varying moisture concentration and maximum moisture uptake.
- Epoxies inherently have different moisture content.

[1] Hamilton, P.; Brist, G.; Guy Jr, B.; and Schrader, J., "Humidity-Dependent Loss in PCB Substrates," Proceedings of IPC Printed Circuit Expo, February 2007.

Impact of Humidity on CTE and T_g

- Prepare 10 sets of each sample.
- Set 1 preconditioned and tested per IPC-TM-650 2.4.24 (TMA) and IPC-TM-650 2.4.25 (DSC) as a control.
- Sets 2-4 preconditioned at 105° C for 24, 48 and 72 hours followed by cooling in desiccators to room temperature before measurement.
- Sets 5-10 coupons were conditioned at 85° C and 85% RH chamber.
  - They were taken out of chamber after 24, 48, 96, 192, 504, and 1200 hours by turn.
  - One set measured directly without preconditioning and the other baked at 105° C for 2hrs per IPC test method.

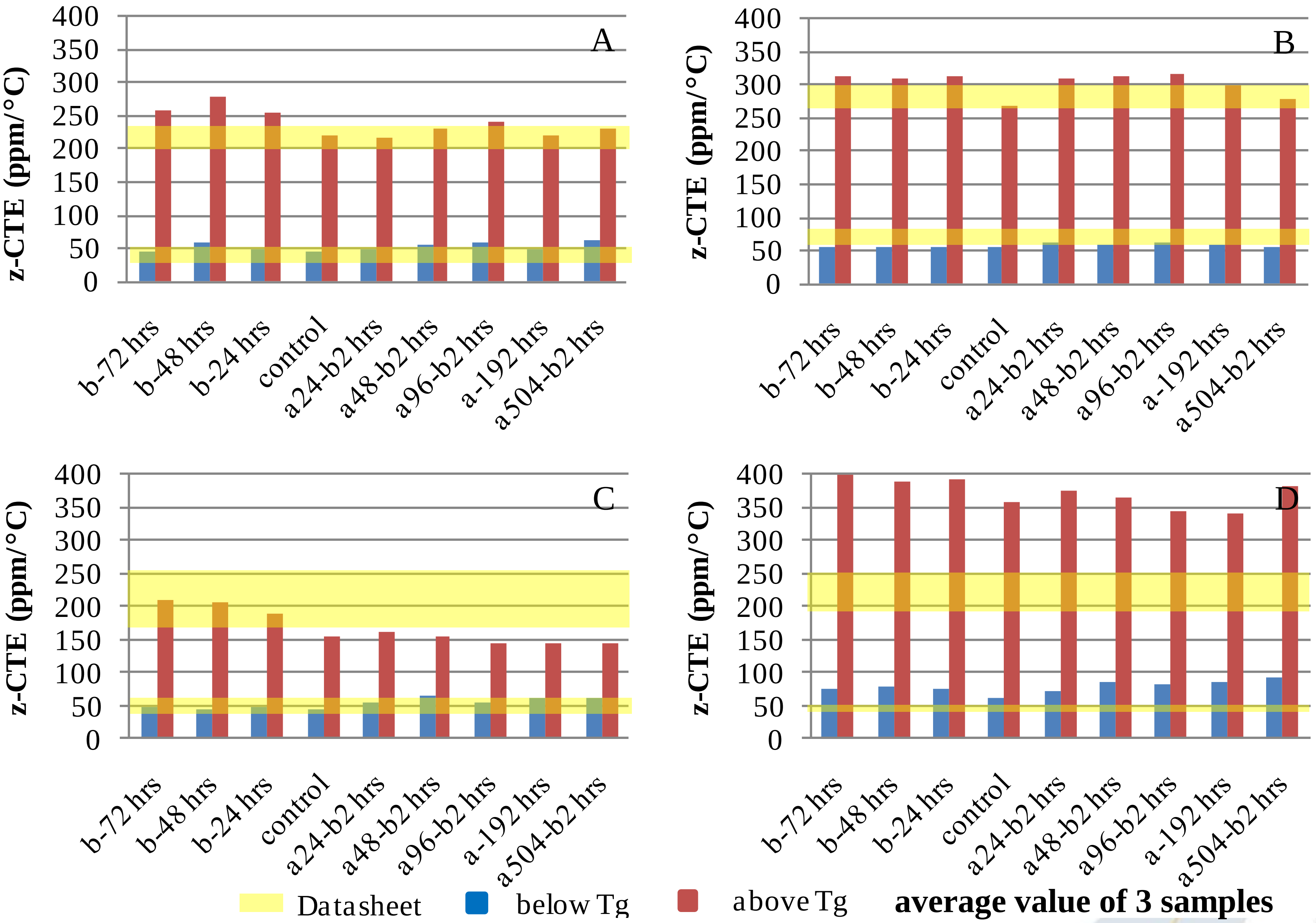
Preconditioning Process
z-CTE and T_g measurements

Sets No.	Name	85° C/ 85% RH (hrs)	105° C (hrs)
1	Control	×	2
2	b-24 hrs	×	24
3	b-48 hrs	×	48
4	b-72 hrs	×	72
5-1	a-24 hrs	24	×
5-2	a24-b2 hrs	24	2
6-1	a-48 hrs	48	×
6-2	a48-b2 hrs	48	2
7-1	a-96 hrs	96	×
7-2	a96-b2 hrs	96	2
8-1	a-192 hrs	192	×
8-2	a192-b2 hrs	192	2
9-1	a-504 hrs	504	×
9-2	a504-b2 hrs	504	2
10-1	a-1200 hrs	1200	×
10-2	a1200-b2 hrs	1200	2

Coefficient of Thermal Expansion (CTE)

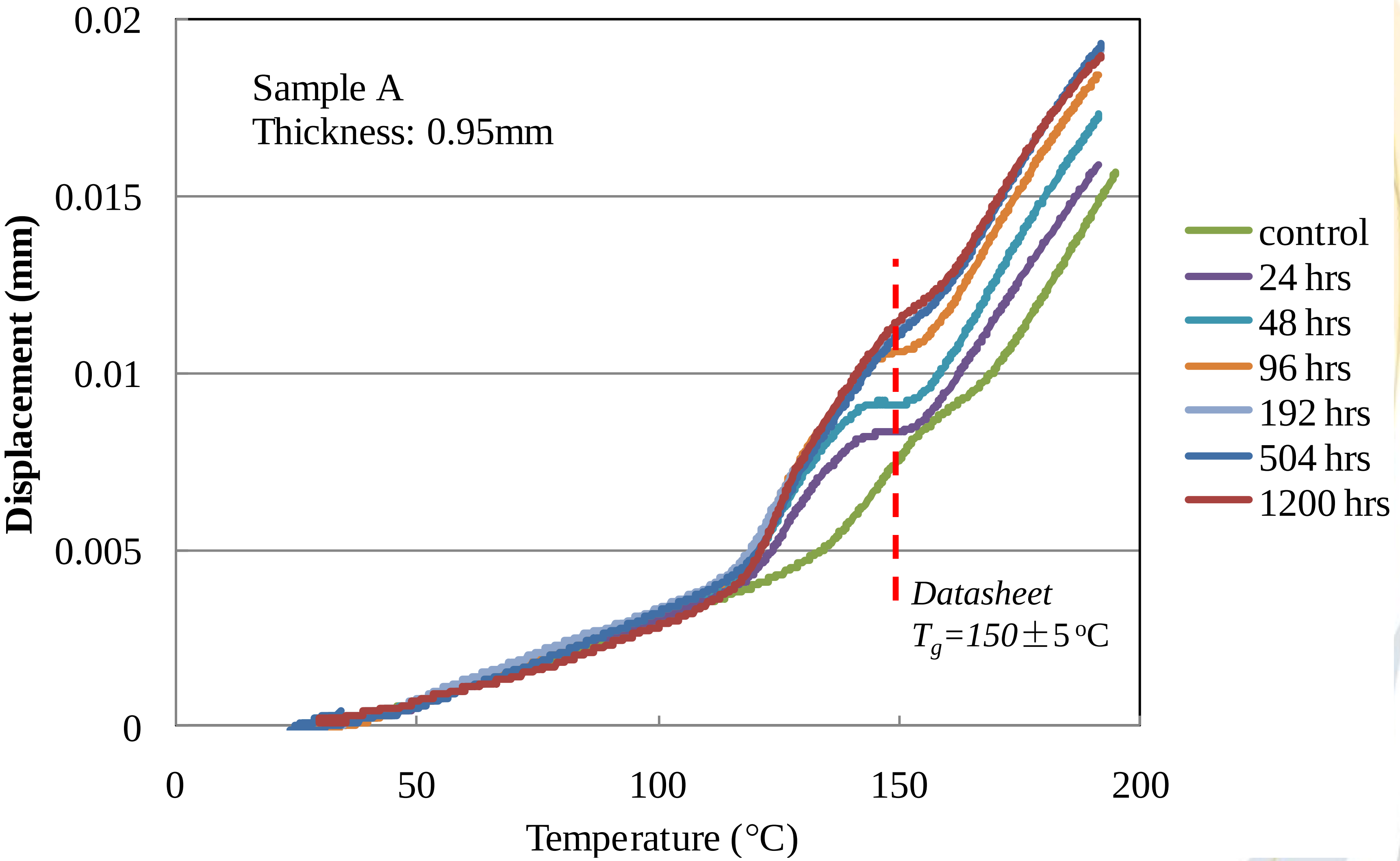
- **Definition:** CTE is the fractional change in linear dimensions with temperature of a material, expressed in ppm/^{o}C
- **Test method:** IPC-TM-650 2.4.24
- **Preconditioning:**
  - 2 hours at 105° C
  - cooled to room temperature in a dessicator
- **Equipment:** Thermo-mechanical analyzer (Perkin Elmer- TMA 7)
- **Temperature scan:** 30^{o}C to 200^{o}C @ 10^{o}C/minute
- **Sample dimensions:** 6.35 mm x 6.35 mm
- **Sample size:** 3 specimens per material type
- **Measurement method:** CTE was measured by choosing two points in a linear region of the TMA plot below and above T_g (T_g was identified as the temperature at which the slope of TMA measurement plot change)
- Out-plane CTE values

CTE : Varying Moisture Conditions



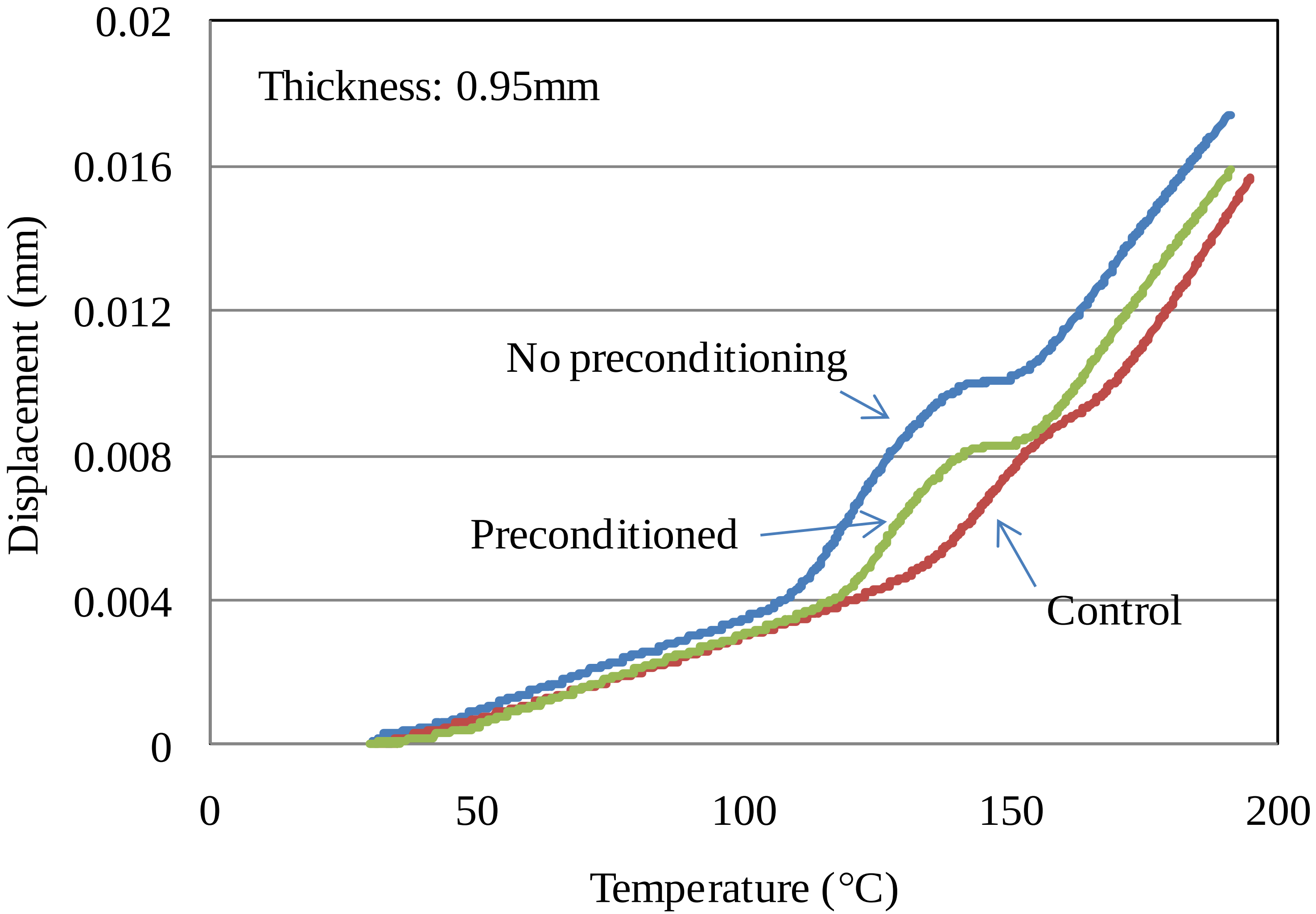
average value of 3 samples

Z-CTE Results (A)



CTE curves of sample A after moisture absorption in 85°C and 85% RH for different times and bake at 105°C for 2 hours

Z-CTE Results (A)



CTE curves of sample A after moisture absorption in 85ºC and 85% RH for 24 hrs, no preconditioning or preconditioned, compared with control.

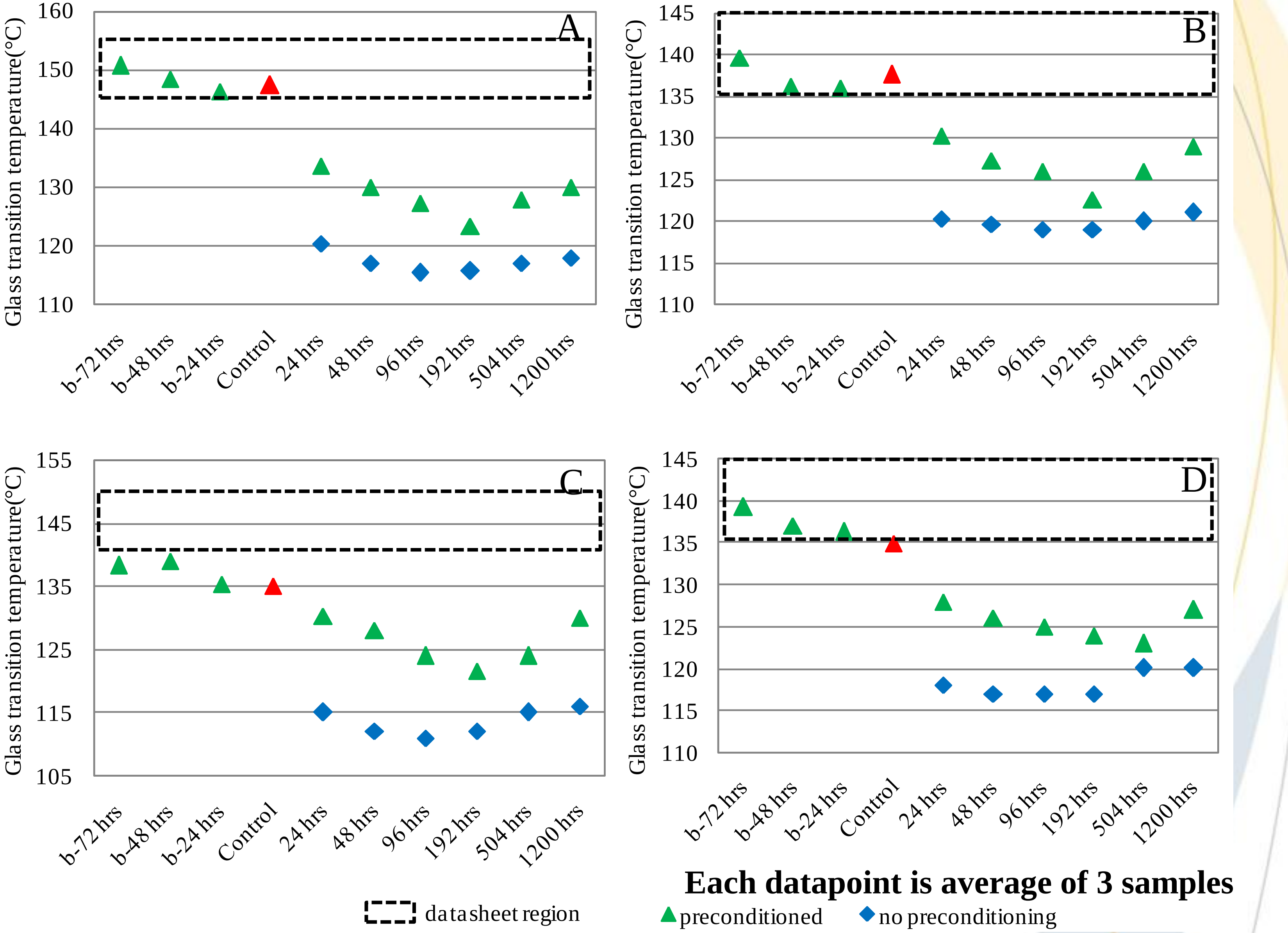
Moisture Effect on z-CTE

- Exposure to humidity has no obvious effect on z-CTE values (below 100ºC and above T_g).
- However, moisture causes swelling in PCB laminate above 100ºC, increase the z-CTE below T_g point.
- Preconditioning steps outlined in IPC test method help in reducing moisture in test samples, but residual moisture influences measurement results.

Glass Transition Temperature (T_g)

- **Definition:** Temperature at which the laminate material transforms from rigid and glass like state to rubbery and compliant state
- **Test method:** IPC-TM-650 2.4.25
- **Preconditioning:**
  - 2 hours at 105° C
  - cooled to room temperature in a dessicator
- **Equipment:** Differential Scanning Calorimeter (Perkin Elmer- Pyris 1 DSC)
- **Temperature scan:** 30^{o}C to 200^{o}C @ 20^{o}C/minute
- **Sample weight:** 15 - 25 mg
- **Sample size:** 3 specimens per material type
- **Measurement method:** T_g was identified as the midpoint of step transition (across which heat capacity of the material change) in the DSC measurement plot.
- T_g of FR4 materials primarily depends on the type or percentage composition of the epoxy resin
- Properties such as thermal expansion, Young's modulus, heat capacity, and dielectric constant undergo a change at T_g

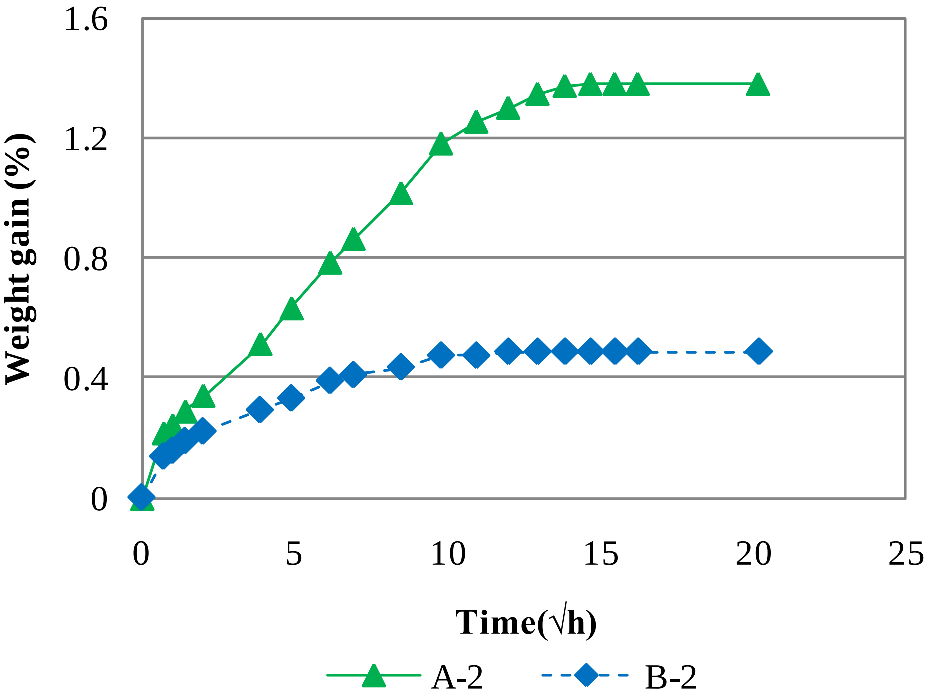
T_g Results for 85/85

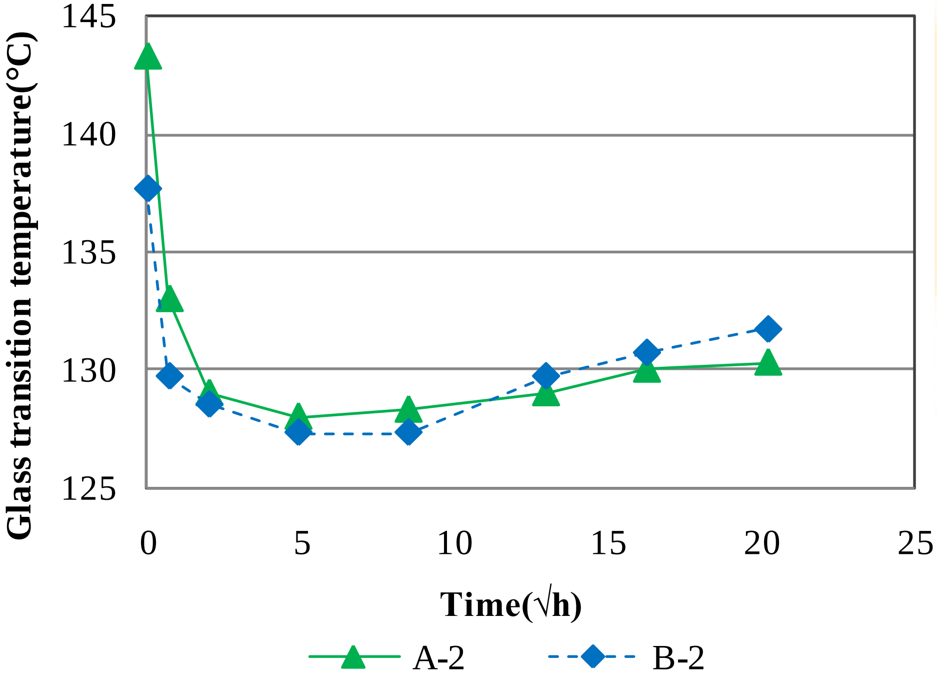


Each datapoint is average of 3 samples

T_g Results – Boiling Water Soak

For verifying the effect of moisture and temperature on T_g, tests were repeated on specimens that were immersed in boiling water.





During the early stages, test samples absorb more moisture, T_g decreases rapidly, and moisture dominates the trends. In the later stages, samples are saturated, T_g increases with time under thermal condition, and temperature dominates the trends.

Effects of Moisture and Temperature on T_g

- A decrease in T_g of an epoxy system is usually associated to the entrapped plasticizers. Water typically acts as a plasticizer in the epoxy systems resulting in a reduction of T_g.
- An increase in T_g is associated with the increase in cross-linking density. Heat facilitates the chemical reactions that result in cross-linking of polymers, thus increasing the T_g.

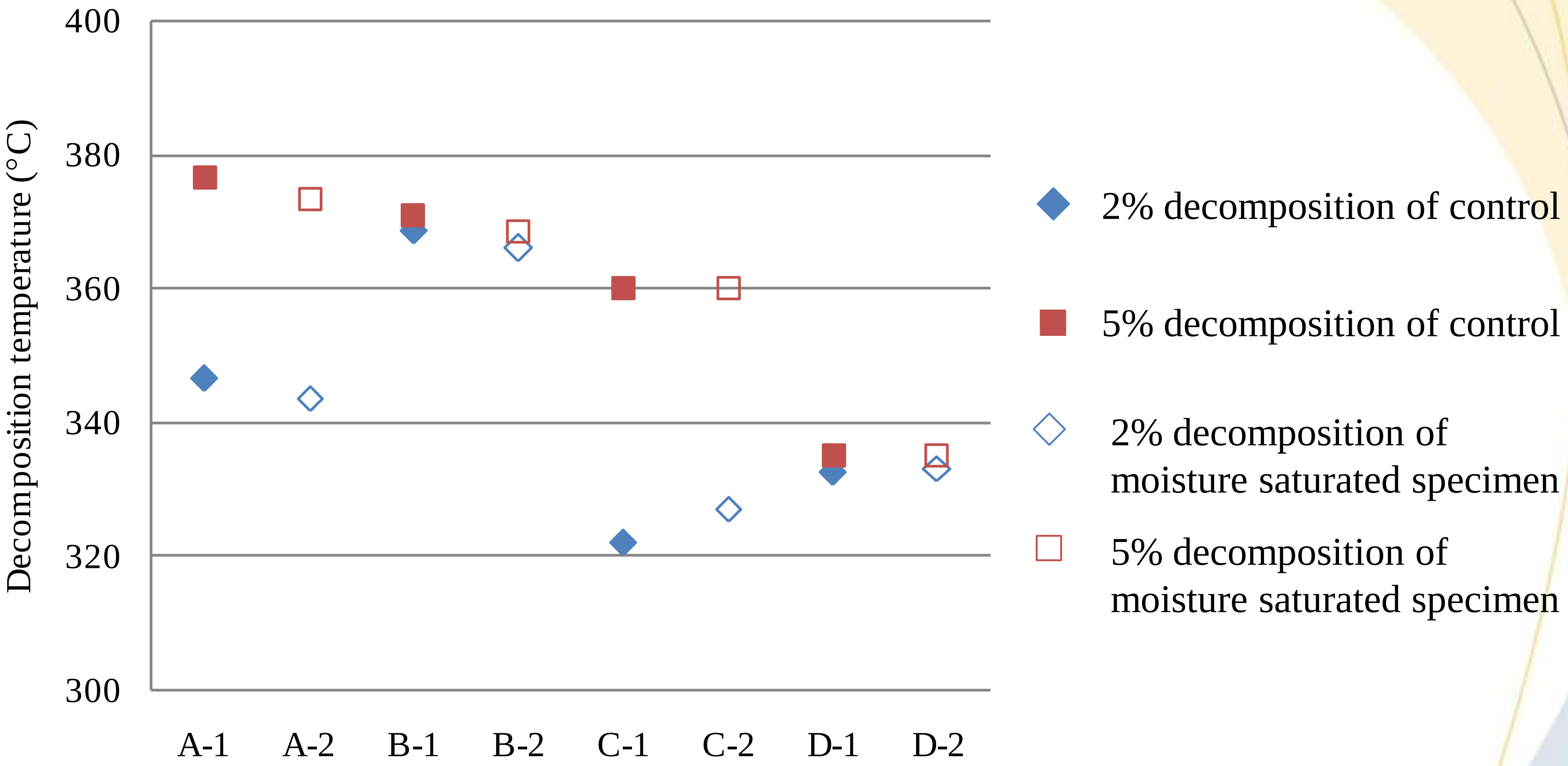
Moisture Effect on T_d

- Prepare 2 test coupons of each sample.
- Set 1 was preconditioned and tested according to IPC-TM-650 2.4.24.6 test method as a control.
- Set 2 was saturated in boiling water, then baked at 110° C for 24hrs followed by cooling in desiccators to room temperature as per IPC test method before measurement.

Decomposition Temperature (T_d)

- **Definition:** T_d is the temperature at which a resin system permanently degrades (physical and chemical) and some chemical bonds are thermally broken
- **Test method:** IPC-TM-650 2.4.24.6
- **Preconditioning:**
  - 24 hours at 110^{o}C
  - cooled to room temperature in a desiccator
- **Equipment:** Thermo-gravimetric analyzer (Shimadzu TGA 50)
- **Temperature scan:** 25^{o}C to 550^{o}C @ 10^{o}C/minute
- **Sample weight:** 10-20 mg
- **Sample size:** 2
- **Measurement method:** The change in weight of the sample was obtained as a function of temperature and T_d was recorded at 2% and 5% weight loss (compared to sample weight at 50^{o}C as per the test method)

Moisture Effect on T_d

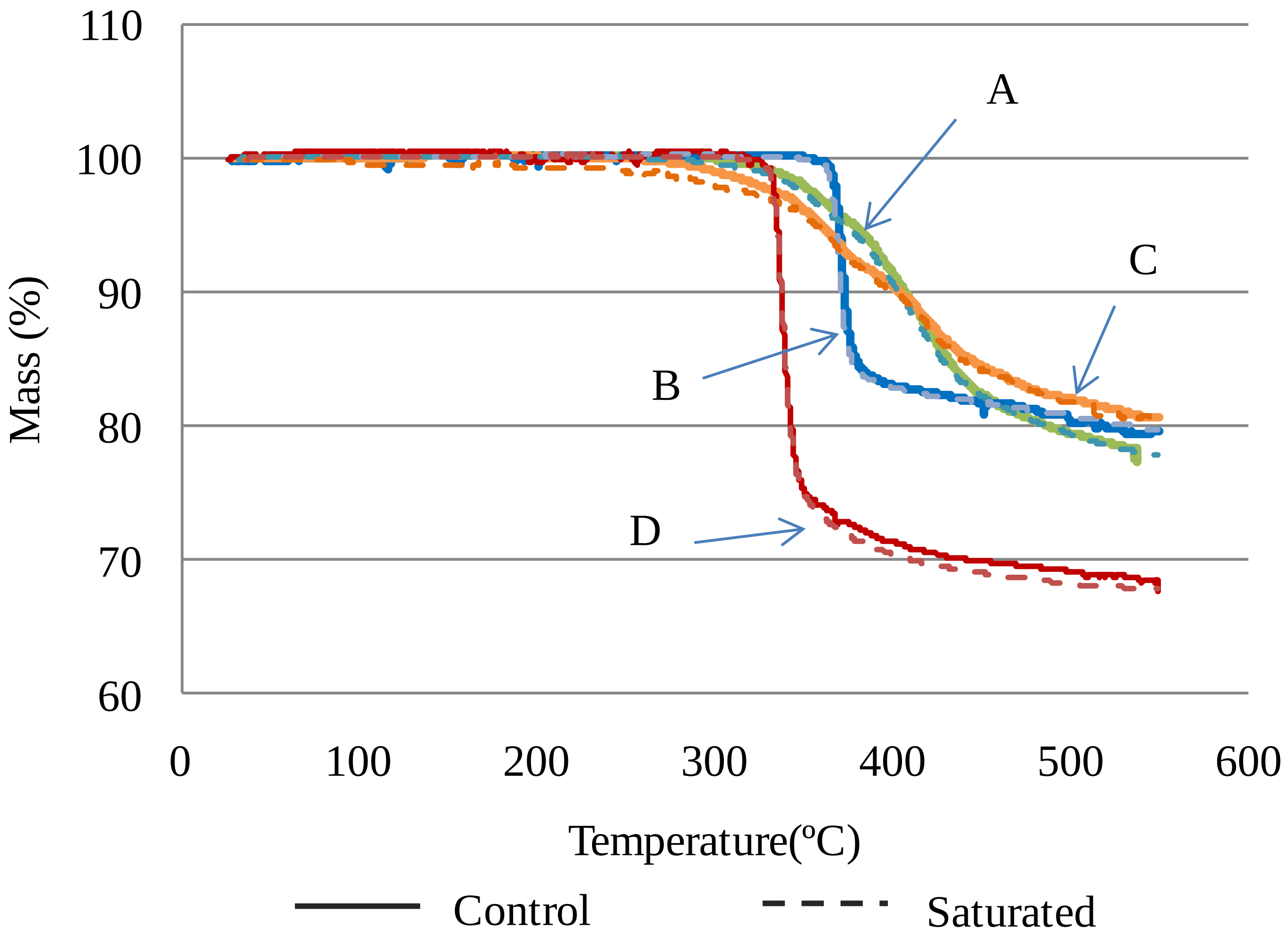


**-1) prepared as per IPC test method*

**-2) specimens saturation in boiling water, then preconditioned as per IPC test method*

Moisture has no obvious effect on T_d after preconditioning per IPC methods.

Moisture Effect on T_d



Halogenated materials (B & D) underwent degradation from 2% to 5% within a narrow temperature range, which is not the case with halogen free materials (A & C)

Moisture Effect on Time to Delamination

- Prepare 2 sets test coupons of each sample.
- Set 1 was preconditioned and tested according to IPC-TM-650 2.4.24.1 test method as a control;
- Set 2 were saturated in boiling water, then baked at 105° C for 2hrs followed by cooling in desiccators to room temperature as per IPC method before measurement.

Time to Delamination (T-260, T-288)

- **Definition:** Time to delamination is the time taken by a laminate material to delaminate (defined as the separation between layers of prepregs and copper clad cores in a multilayered structure), when exposed to a constant temperature.
- **Test method:** IPC-TM-650 2.4.24.1
- **Preconditioning:**
  - 2 hours at 105° C
  - cooled to room temperature in a dessicator
- **Equipment:** Thermo-mechanical analyzer (Perkin Elmer- TMA 7)
- **Temperature scan:** 30^{o}C to 260^{o}C or 288^{o}C @ 10^{o}C/minute, then hold at 260^{o}C or 288^{o}C
- **Sample dimensions:** 6.35 mm x 6.35 mm
- **Sample size:** 2 specimens per material type
- **Measurement method:** hold the specimen at 260^{o}C or 288^{o}C until an irreversible change in thickness of the specimen was observed or 30 minutes elapsed, whichever came first

Moisture Effect on Time to Delamination

Time to delamination	Laminate Thickness (mm)	Control		Immersed in boiling water		
		260 ºC	288 ºC	260 ºC	288 ºC	Moisture content
A	1.30	17 min	1 min	Delaminated at 235 ºC	—	1%
B	2.37	>30 min	5 min	24 min	4 min	0.5%
C	1.15	>30 min	>30 min	>30 min	>30 min	1.5%
D	2.31	14 min	< 10 s	< 5 s	Delaminated at 260 ºC	1%

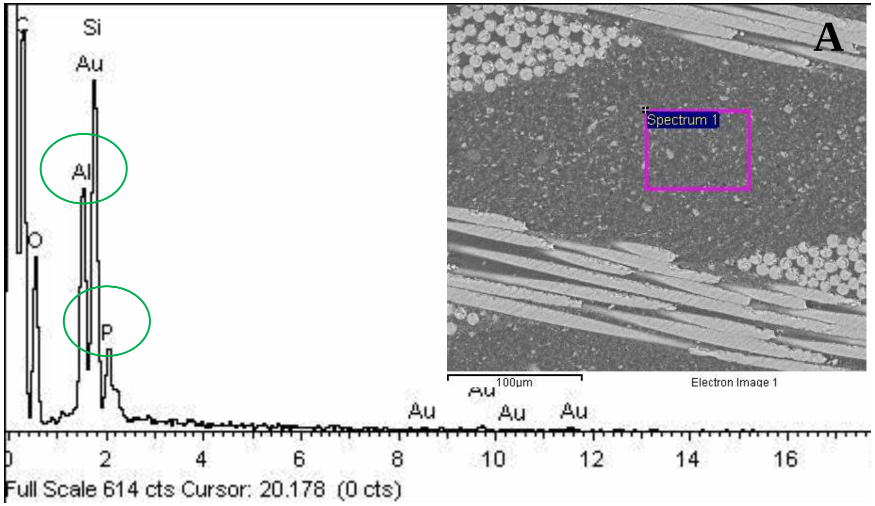
- **Td decreases for materials A and D (immersed in boiling water, absorbed around 1%).**
- **T260 and T288 of material B decrease slightly after absorbing 0.5% moisture.**
- **Material C does not show any delamination within 30min neither control set or moisture absorption set.**

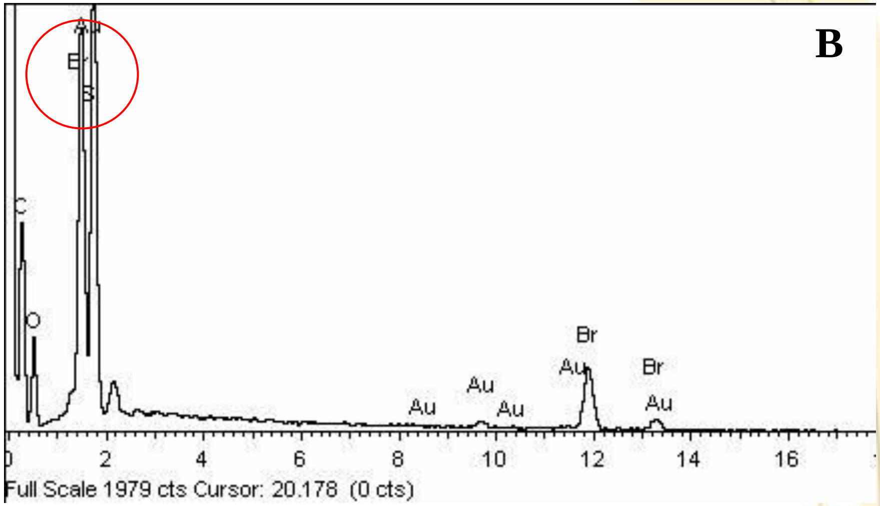
Summary

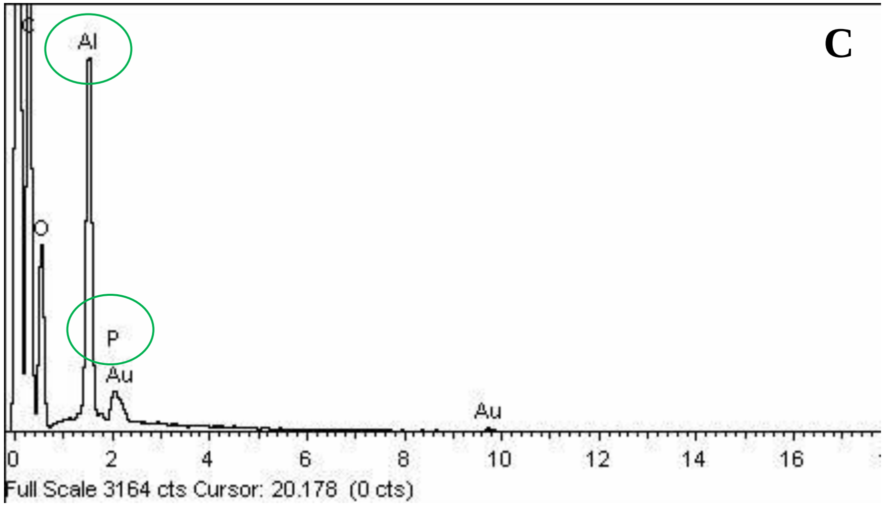
- Exposure to humidity has no obvious effect on z-CTE values (below 100ºC and above T_g). However, moisture causes swelling in PCB laminates between 100ºC and the T_g point, and increases z-axis expansion.
- Glass transition temperature of all test materials was affected by both moisture content and exposure temperature.
  - T_g decreases with an increase in the moisture content in laminates and,
  - T_g increases with an increase in duration of thermal duration
  - In the early stages, moisture dominated the trends before laminate materials reached the saturation point, while temperature dominated the trends in the later stages.
- Moisture has no obvious effect on T_d
  - Halogenated materials undergo degradation from 2% to 5% within a narrow temperature range compared to halogen free materials.

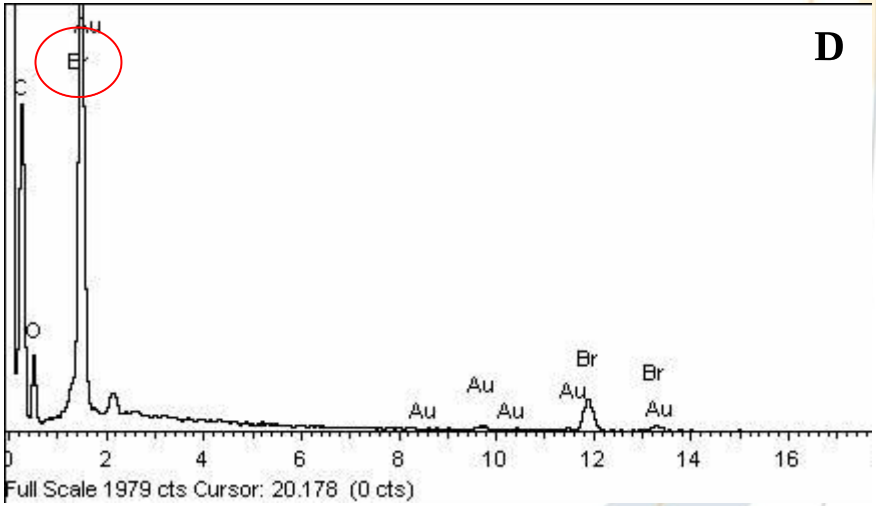
Back up

EDS Results



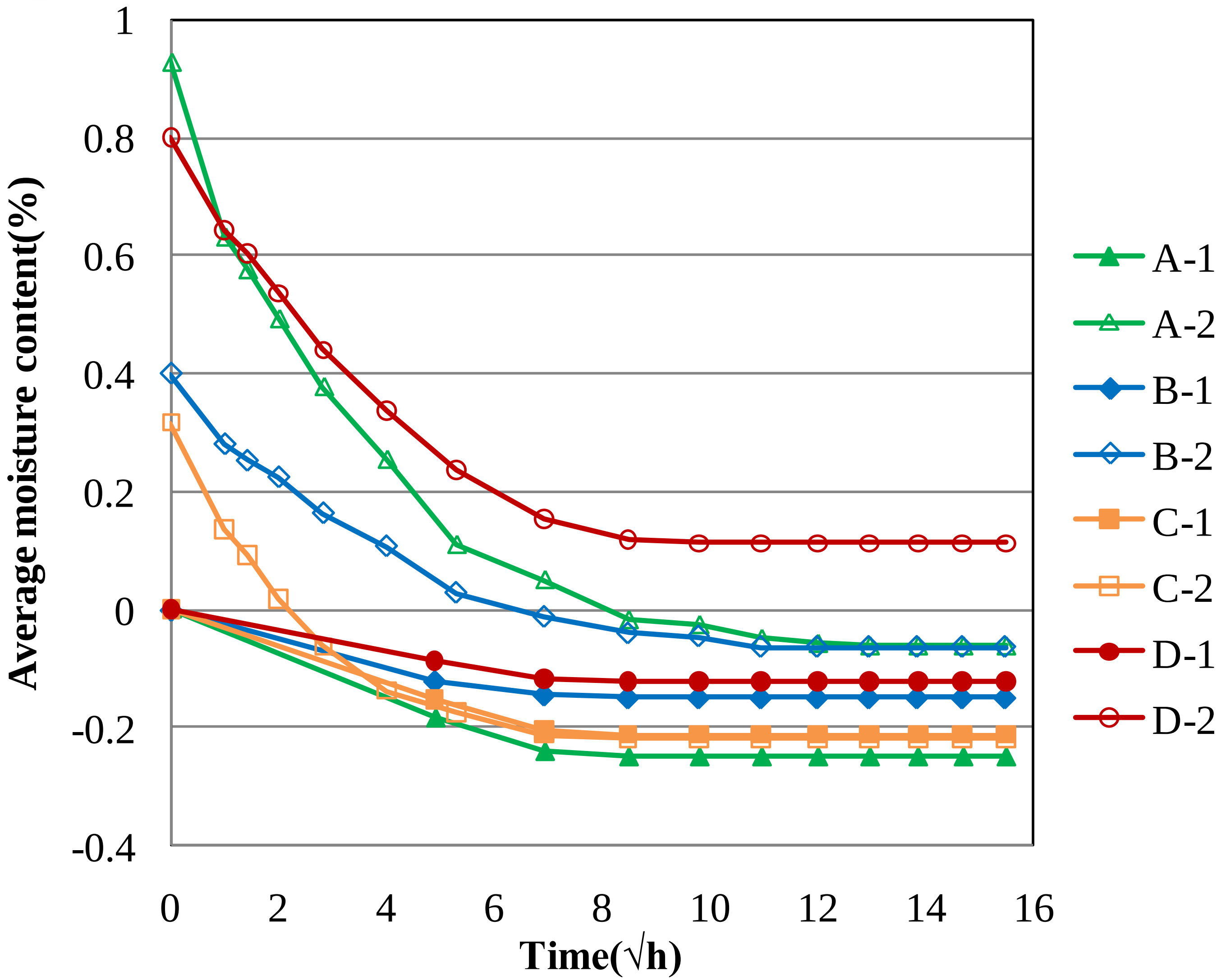






Specimens were gold coated

Moisture Desorption Experiment



Moisture desorption experiments were baked at 105ºC on two kinds of specimens:

1.baked from room storage condition.

2.baked after moisture absorption in 85/85 for 2112 hours.

Upon bake, test coupons did not release all moisture absorbed during 85° /85%RH exposure.

Moisture absorbed in Laminate

- The water molecules absorbed into epoxy can be classified into two types [1, 2]:
  - ‘‘bound’’ water which is trapped at polar sites that is usually bonded to hydroxyl groups in the epoxy network;
  - ‘‘free’’ water which is clustered in the free volume or voids inside the epoxy.

[1] Zhao, H.; and Li, Robert K.Y., “Effect of water absorption on the mechanical and dielectric properties of nano-alumina filled epoxy nanocomposites”, Composites. Part A, Applied science and manufacturing, v 39, n 4, pp: 602-611, 2008.

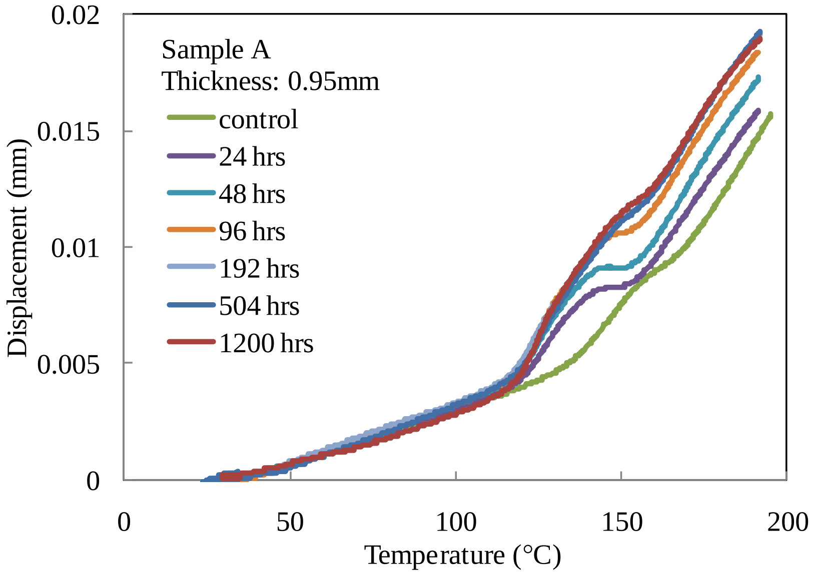
[2] Maggana, C.; and Pissis, P., “Water sorption and diffusion studies in an epoxy resin system”, Journal of polymer science. Part A, Polymer chemistry, v37, n 11, pp: 1165-1182, 1999.

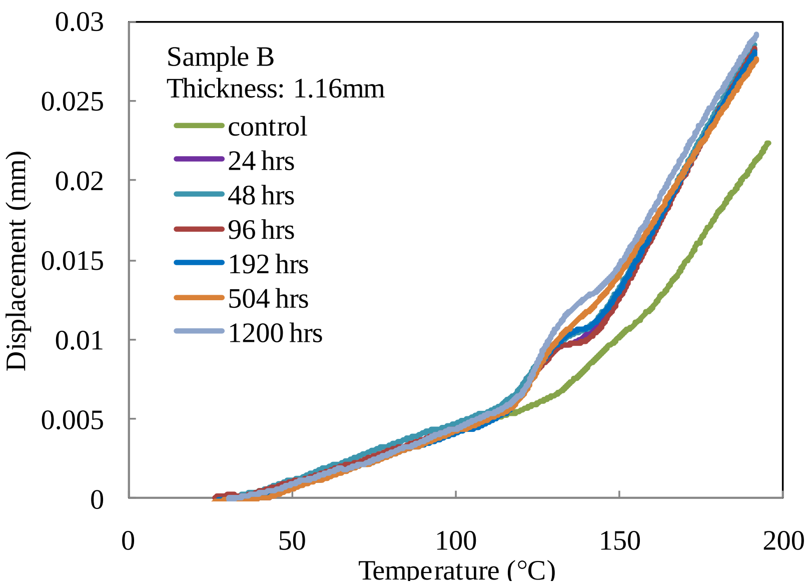
CTE (Z) Results

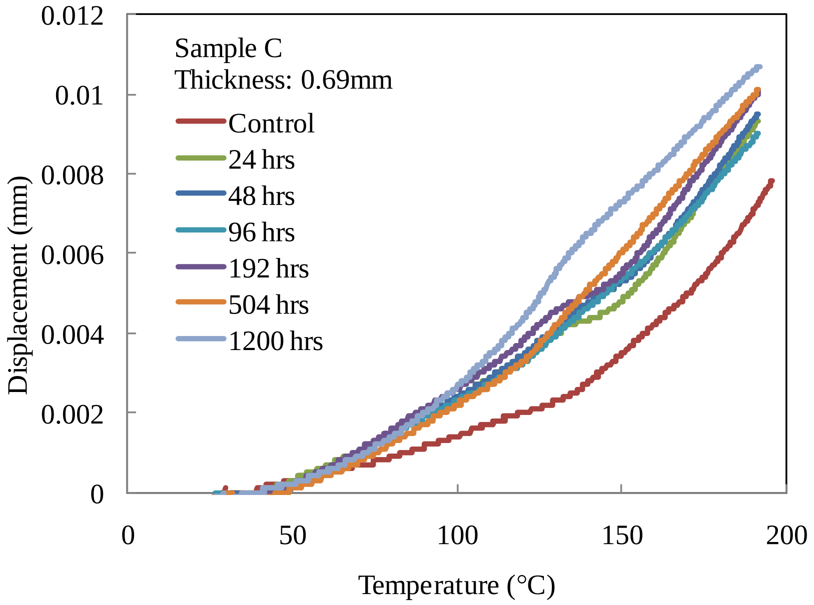
Sample	A		B		C		D	
	Below T_g	Above T_g	Below T_g	Above T_g	Below T_g	Above T_g	Below T_g	Above T_g
datasheet	30-50	200-230	55-70	270-300	40-55	170-250	35-45	180-240
b-72 hrs	45	257	54	313	49	210	76	398
b-48 hrs	58	280	57	309	46	206	78	389
b-24r hrs	47	256	55	312	48	189	76	390
control	44	219	54	270	46	153	63	358
a24-b2hrs	47	217	61	309	55	160	72	373
a48-b2hrs	56	231	59	315	66	153	84	364
a96-b2hrs	60	242	61	318	53	145	83	344
a192-b2hrs	48	220	60	299	60	143	85	340
a504-b2hrs	63	230	54	280	61	144	93	380
a1200-b2hrs	48	213	60	294	60	115	92	333

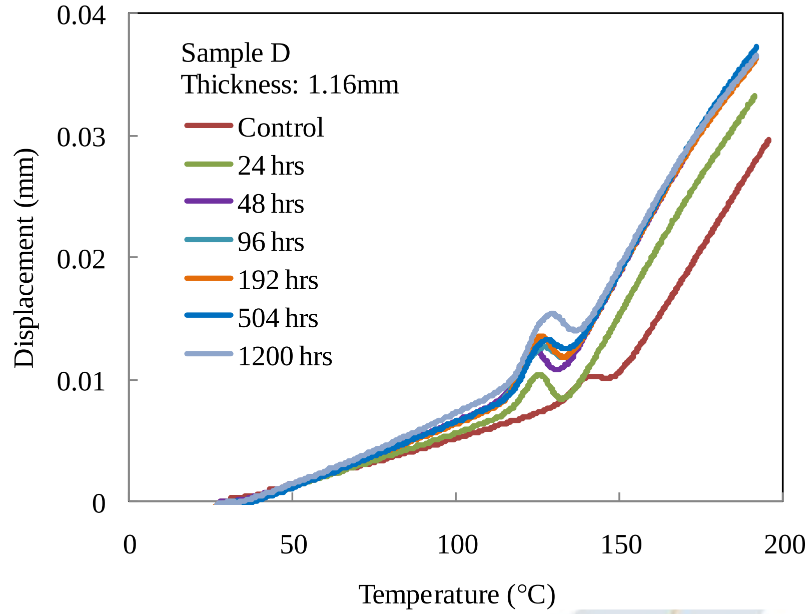
Each datapoint is average of 3 samples

Z-CTE Results of 85/85 Samples

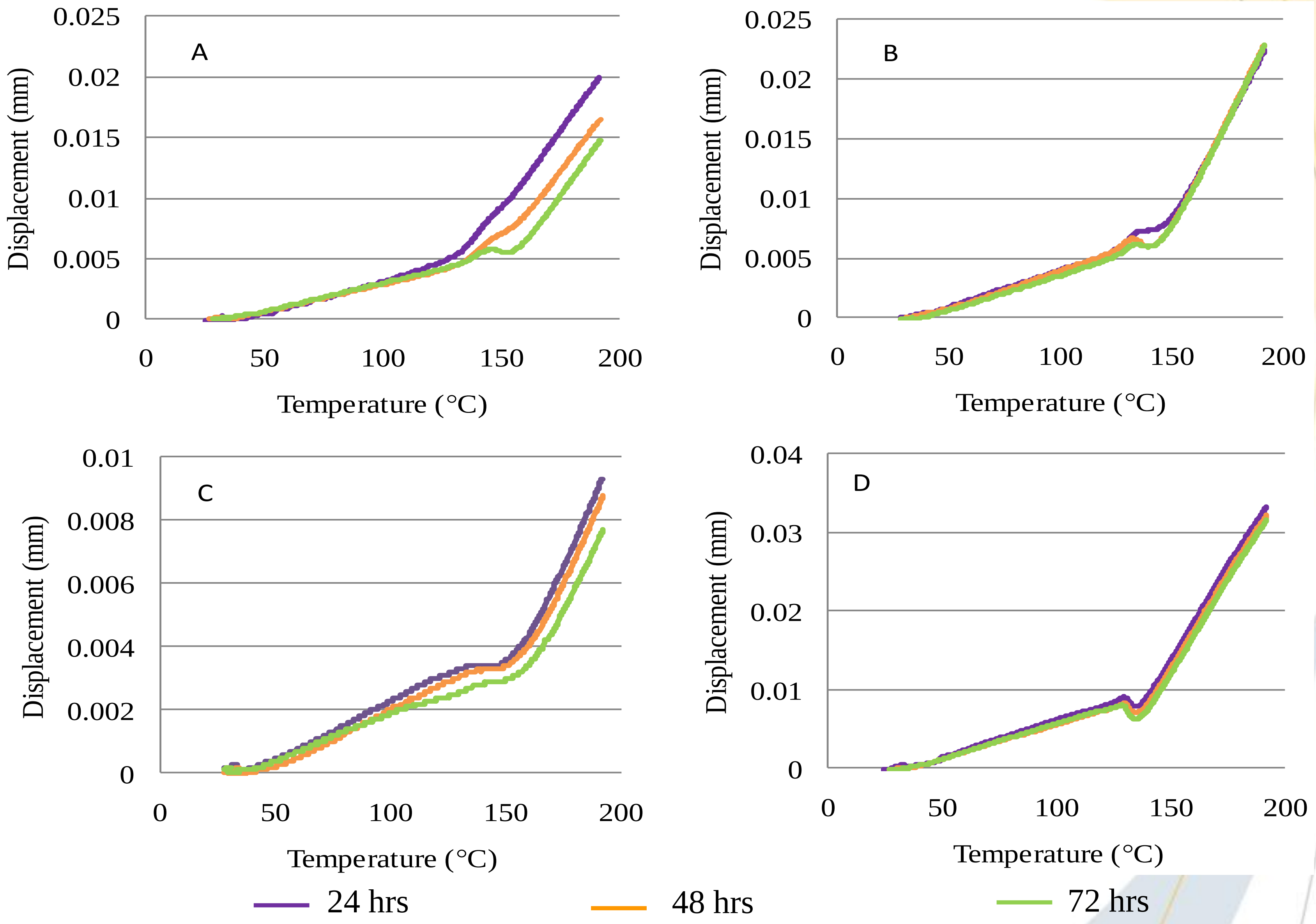








Z-CTE Results of Baking Samples

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CTE (Z) Results

Sample	A		B		C		D	
	Below T_g	Above T_g	Below T_g	Above T_g	Below T_g	Above T_g	Below T_g	Above T_g
datasheet	30-50	200-230	55-70	270-300	40-55	170-250	35-45	180-240
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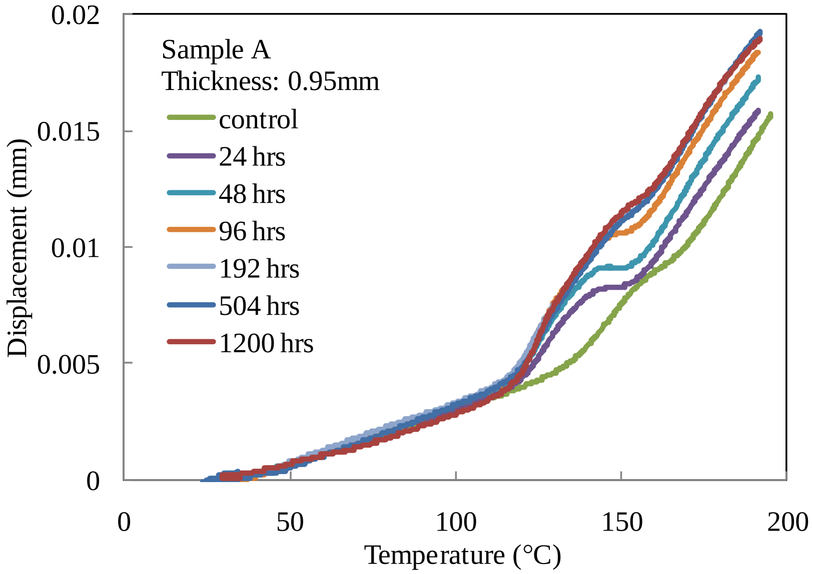
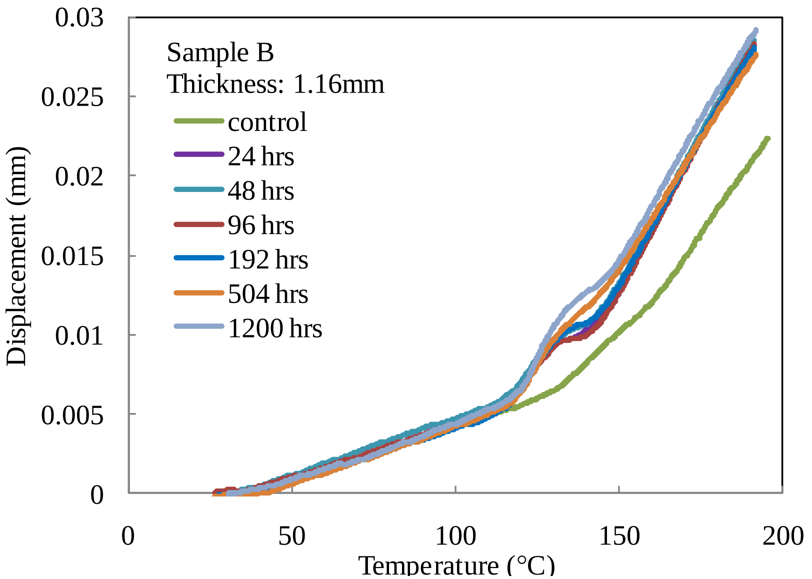
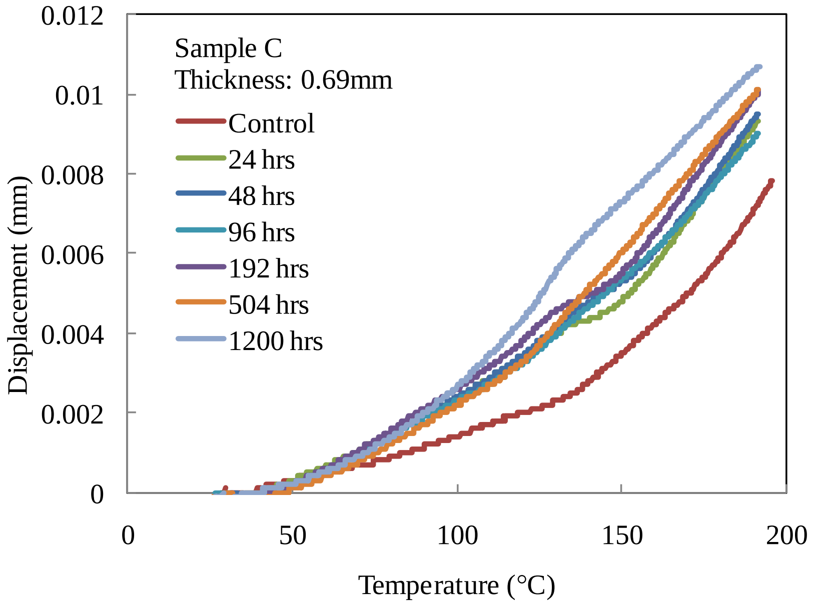
a1200-b2hrs	48	213	60	294	60	115	92	333

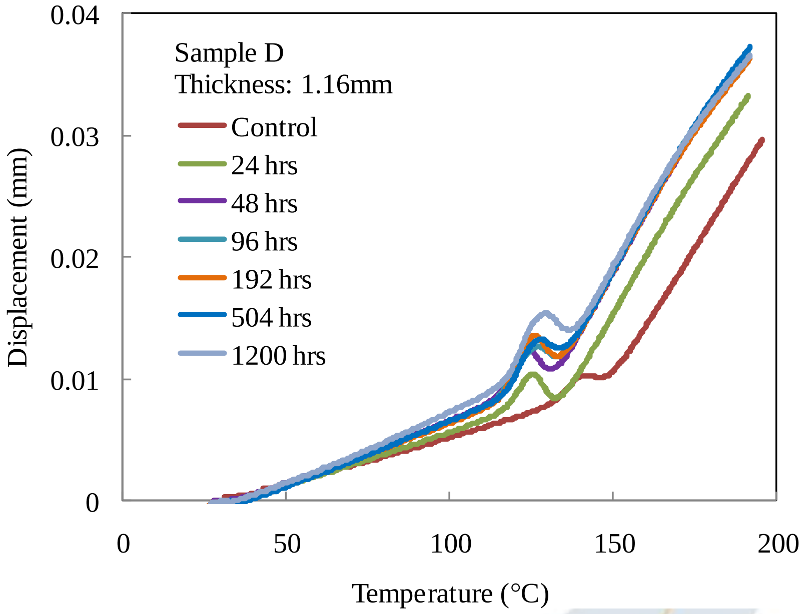
Each datapoint is average of 3 samples

Z-CTE Results of 85/85 Samples









Z-CTE Results of Baking Samples