Practical Guidelines for the Efficient Postbaking of Molded Phenolics

By Theodore N. Morrison Ph.D.
Plastics Engineering Co.
3518 Lakeshore Road
Sheboygan, Wisconsin

Presented at:

"Imagination & Implementation - Thermosets 2004"
Topical Conference (RETEC), Co-sponsored by the
Thermoset Division and the Chicago Section of the Society of Plastics Engineers
March 24-26, 2004 at the Wyndham Northwest Chicago in Itasca, Illinois

"Practical Guidelines for the Efficient Postbaking of Molded Phenolics"

By Theodore N. Morrison Ph.D.
Plastics Engineering Co.
3518 Lakeshore Road
Sheboygan, Wisconsin
More info. at: www.plenco.com

Introduction:

Postbaking is a manufacturing step where molded parts are heated in an oven after being removed from the die. Many compound molders make perfectly good parts and never need to postbake. For many applications, postbaking is not needed or even recommended, however, postbaking can have a profound effect on the physical properties of a phenolic part (1,2). For applications requiring high dimensional stability or resistance to high temperature, it is well worth the time and effort. It is, therefore, equally well worth the effort to try understanding what actually happens when we postbake.

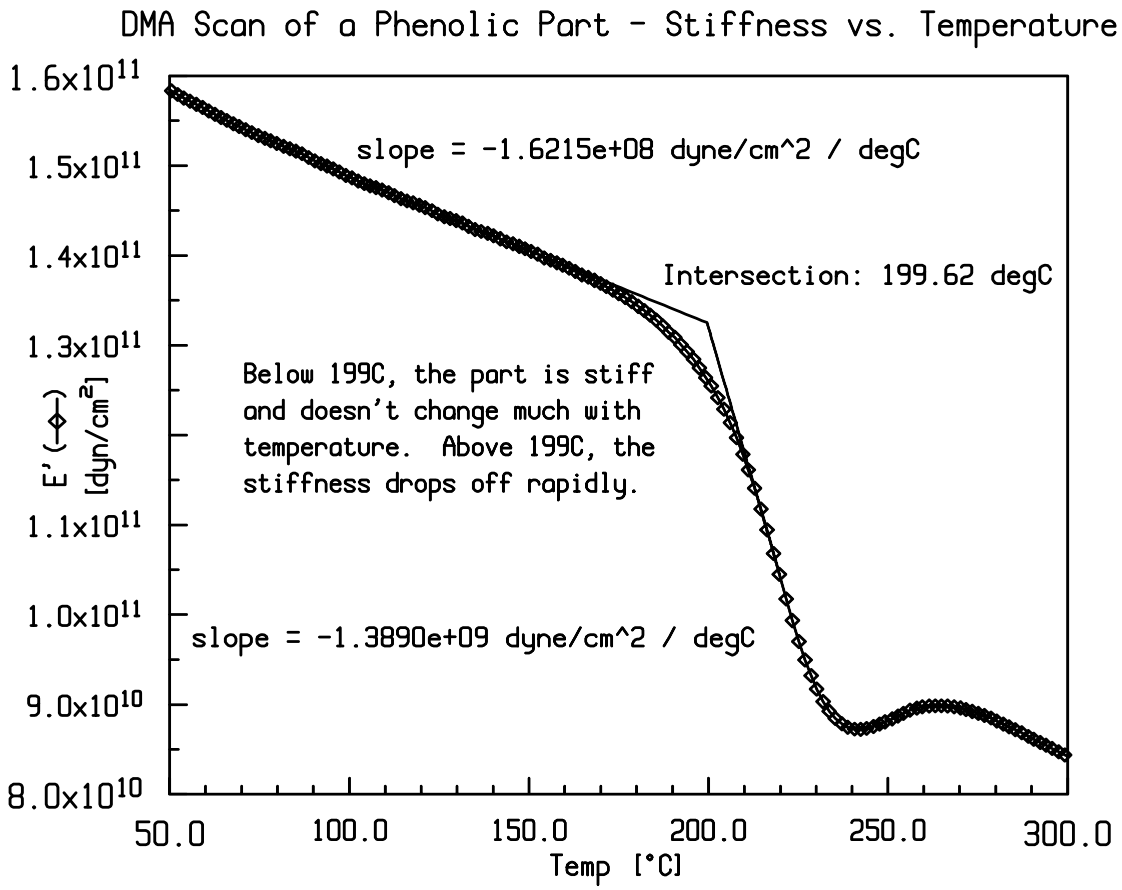
Though it is not the topic of this paper, outgassing is one of the most useful effects of postbaking. Most phenolic compounds are cured with hexamethylenetetramine (hexa), which produces ammonia as a byproduct of the curing reaction. Similar situations can occur with other thermosets where remnants of crosslinkers or curing agents might remain in molded parts. Ammonia removal is simply a diffusion process. Raising the temperature will increase the diffusion rate, but the effect is not linear. One of the most important factors in promoting rapid diffusion is maintaining a concentration gradient. This means it is important to have good ventilation in the oven. Another big factor is the gas permeability of the compound itself. Environmental and other situation specific parameters tend to dominate any predictions of the rate of outgassing. Optimization of this type of process is therefore best handled on a case by case basis.

This paper is concerned with the tremendous changes in physical properties that occur when phenolic compounds are postbaked. These changes are best characterized as the result of changes in the glass transition (T_G) of the resin. Fortunately, the change in the T_G is a chemical process, and follows a well-defined rate law. This makes it at least feasible, to derive a general rule for predicting the advance of the T_G based only on measurements of time and temperature.

The first step is to define what is meant by the T_G. A melt point is the temperature of transition from a crystalline solid, to a liquid. Materials that are not crystalline are called amorphous, and can never truly melt, because there are no crystals. A glass transition is what amorphous materials have instead of a melt point. The name derives from the temperature where solid amorphous glass suddenly begins to flow. The T_G is simply a temperature where the molecules transition from a state of less mobility to a state of more mobility. Phenolics are unusual among thermosets, in that they are never truly 100% cured (2). Instead, as the part is baked, the temperature of the "mobility transition" simply gets higher and higher. In reality, the TG is probably the best measure of the degree of cure of a phenolic.

Dynamic Mechanical Analysis (DMA) is a sensitive tool for studying the TG and its effect on physical properties. The DMA instrument measures the energy to flex the sample, called storage modulus (E′), and then measures how much of that energy is returned as springback. The energy that does not return is referred to as the loss modulus (E″) and is the amount of energy dissipated by molecular motion. A perfectly elastic sample would therefore return all of the energy, and have a loss modulus of zero. The ratio of loss modulus over storage modulus (E″/E′) is called tan(δ). This can be thought of as a measure of molecular mobility, scaled to the stiffness of the sample. Since it is a ratio of like measurements, the units cancel. This means it is often possible to collect valid tan(δ) data, even when non-standard part geometries prevent the calculation of true modulus values. The tan(δ) ranges from zero to one, with higher numbers indicating greater molecular mobility and lower numbers indicating less. Figure 1 shows a plot of storage modulus versus temperature from the Dynamic Mechanical Analysis (DMA) instrument.

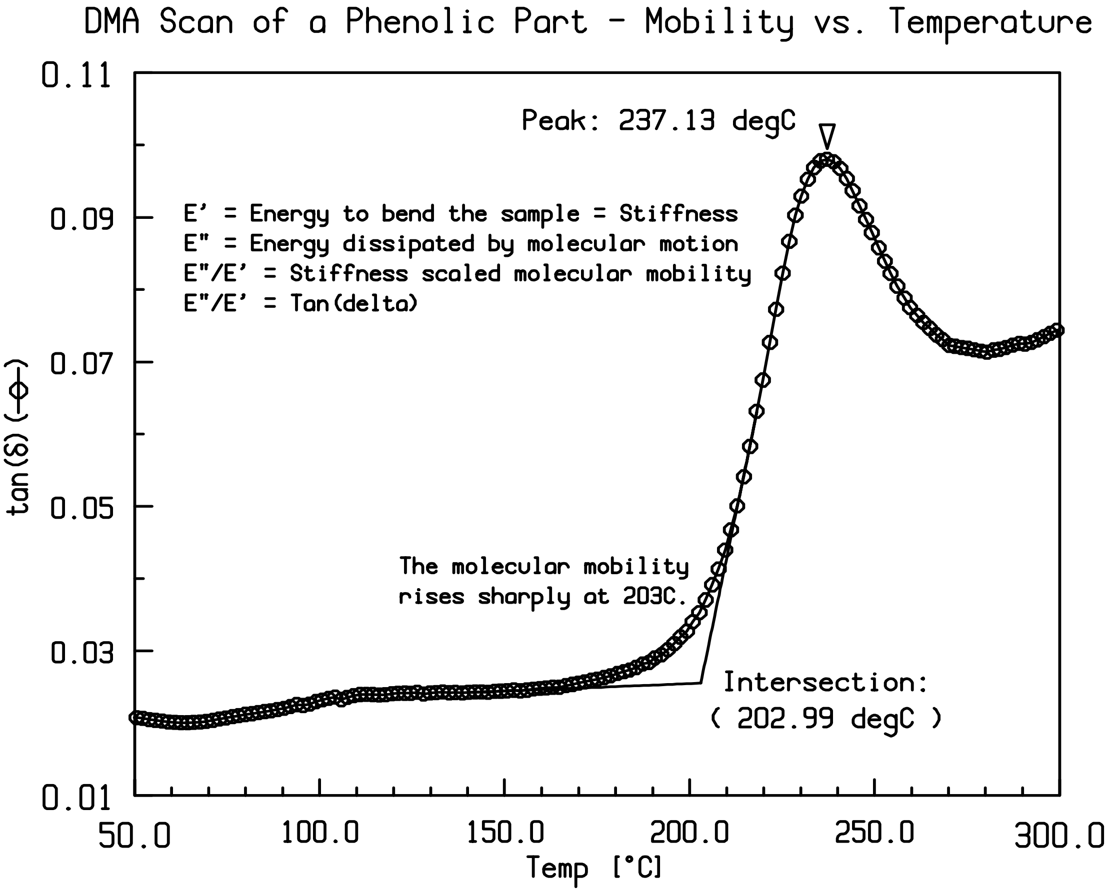
Figure 1:



The storage modulus (E′) on the Y-axis is a measure of stiffness. The graph shows that the stiffness drops at a steady pace as the temperature goes up, until approximately 199ºC. The sharp drop in stiffness that occurs when the temperature surpasses 199ºC is a direct result of an increase in molecular mobility. This is the glass transition.

Figure 2 shows the tan(δ) curve for the same sample as in figure 1.

Figure 2:



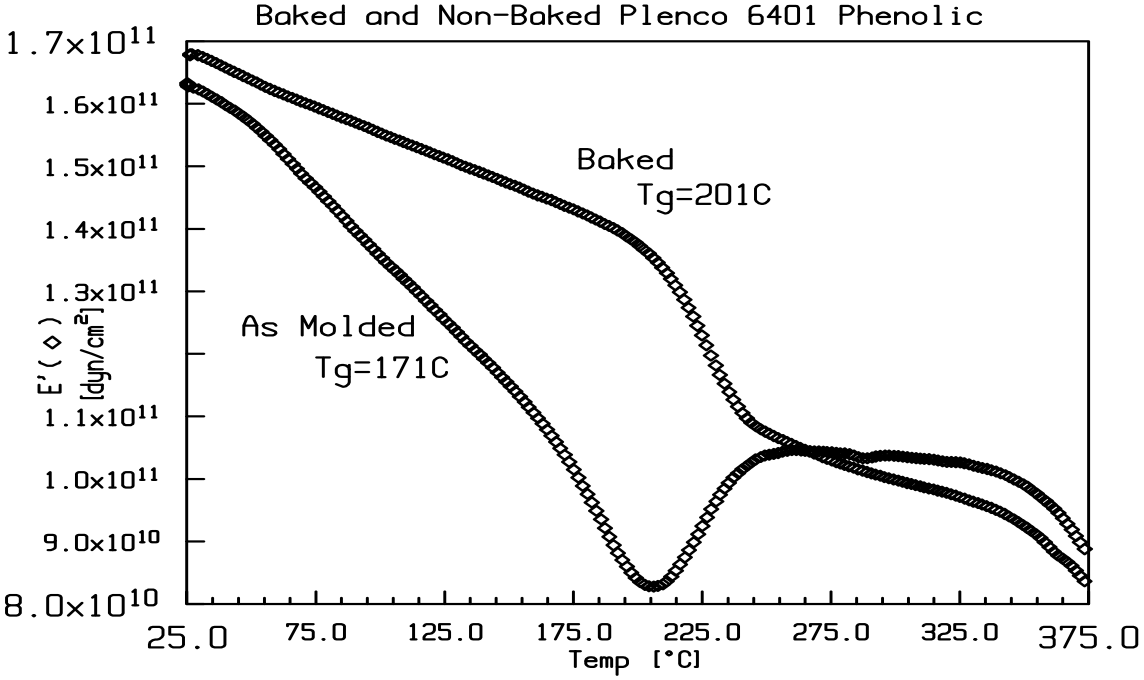
The tan(δ) starts out low, meaning that each time the sample is flexed, it springs back with nearly full force. Above 203°C, however, the tan(δ) rapidly rises, the energy of flexure is dissipated by molecular movement, and a visible creep occurs in the sample. The onset of the tan(δ) rise is another way of measuring the TG. The size (area) of the tan(δ) peak intuitively represents a measure of how much molecular mobility is available for the dissipation of energy.

Reasons for Postbaking Phenolics:

The response of phenolic compounds to postbaking is unusual, or possibly even unique. As mentioned, other thermosets are postbaked for outgassing and other reasons, but the effect on physical properties is far less pronounced. Epoxies are often postbaked, but this is usually done at temperatures above the initial TG of the part. This is quite different from phenolics, which can be effectively baked at temperatures below the initial TG. Likewise, BMC polyesters are sometimes baked, but this has more to do with outgassing and shrinkage, than with changes in crosslink density or TG. These observations are illustrated in Figures 3-5.

Figure 3 shows the DMA storage modulus curve for a baked and unbaked phenolic part.

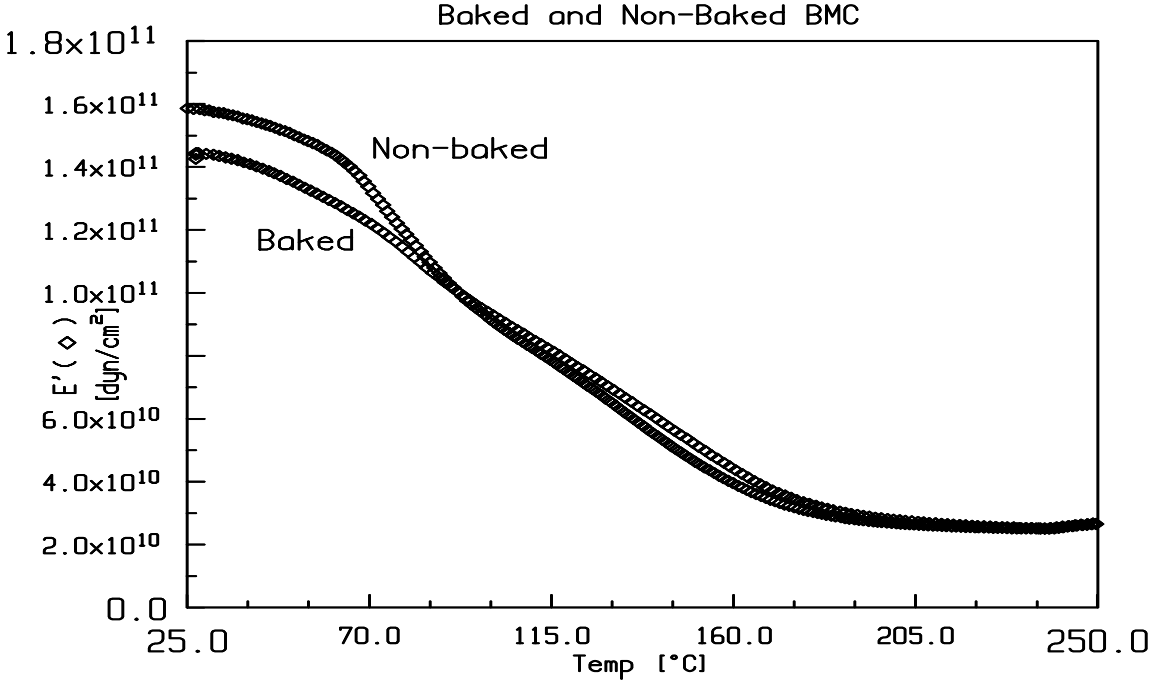
Figure 3:



A modest 4 hour bake at 160°C had a huge effect on the whole shape of the curve.

Figure 4 shows a similar comparison of a baked and non-baked BMC sample:

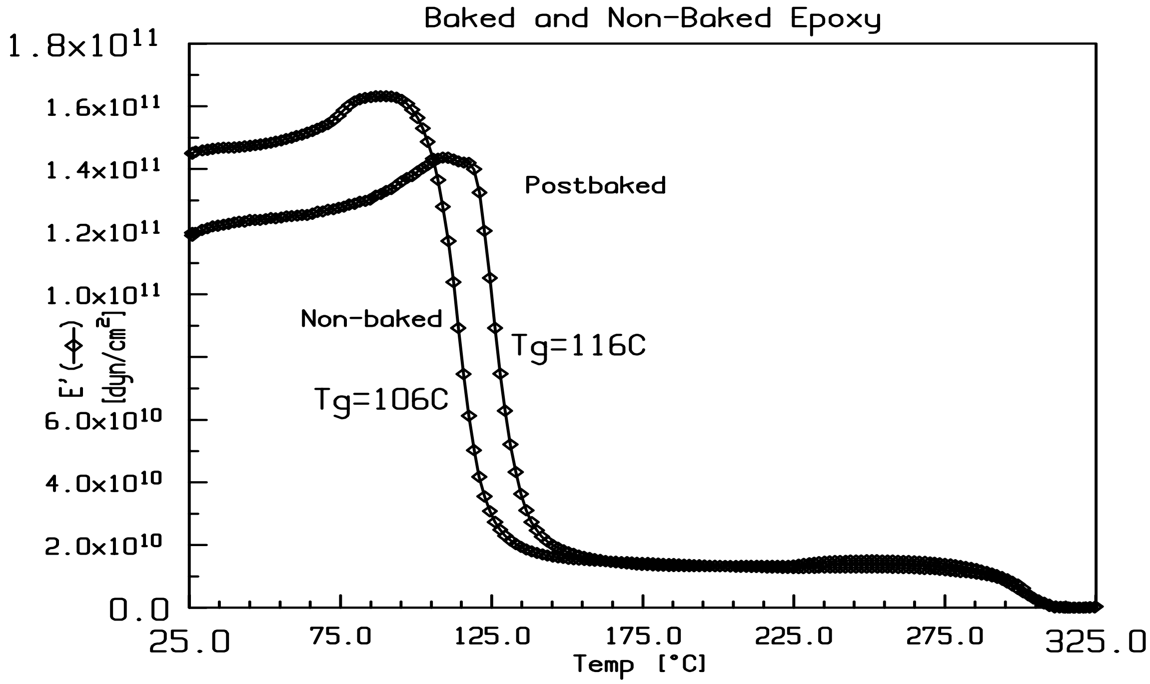
Figure 4:



The two scans are hard to distinguish from one another, but that is just the point. Post baking had some effect on these samples, but nothing approaching the magnitude of the phenolic.

Figure 5 shows a comparison of baked and non-baked epoxy:

Figure 5:



Postbaking has more of an effect on the epoxy than on the BMC, but the effect is still small compared to the phenolic. One interpretation of this data might be that other thermosets don't need to be baked, but phenolics do. A more accurate statement, however, is that there is a tremendous amount of unexpected potential in properly baked phenolics. In the right application, a postbaked phenolic has properties that are hard to match with other materials.

Broad Guidelines for Efficient Postbaking:

Because of the time, expense, and the sheer logistical nuisance of postbaking, it should first be determined whether it is necessary. The following reasons are often given for post baking:

Dimensional Stability – Thermal cycling causes non-baked parts to shrink. Post baking dramatically reduces this shrinkage, especially when the comparison is made at higher temperatures. Parts that are lapped to tight tolerances are often post baked prior to lapping.

Shrink to Fit – Shrinkage occurs during the post bake. Often the die dimensions must take into account the shrinkage resulting from the bake.

Retain Stiffness and Strength at elevated temperature – This is one of the most important and dramatic effects of post baking. Parts that will be used above 100ºC are often post baked.

Out gassing (ammonia) – Ammonia removal is especially important in switch housings. As previously discussed, this is a physical process best handled on an individual basis.

The print says to Postbake – This reason for baking may not be as frivolous as it appears. The phenolic molding industry is mature. Many applications are literally decades old, and everyone who knows why a given bake was chosen, is gone. Some caution must be exercised before changing a postbake protocol that has worked well for years.

Once the decision has been made to bake, it should be done according to the following guidelines:

1. **Spend as little Time as possible**
2. **Keep the Oven temperature below the Part's Glass Transition temperature (TG)**
3. **Bake the minimum amount that will get the job done**

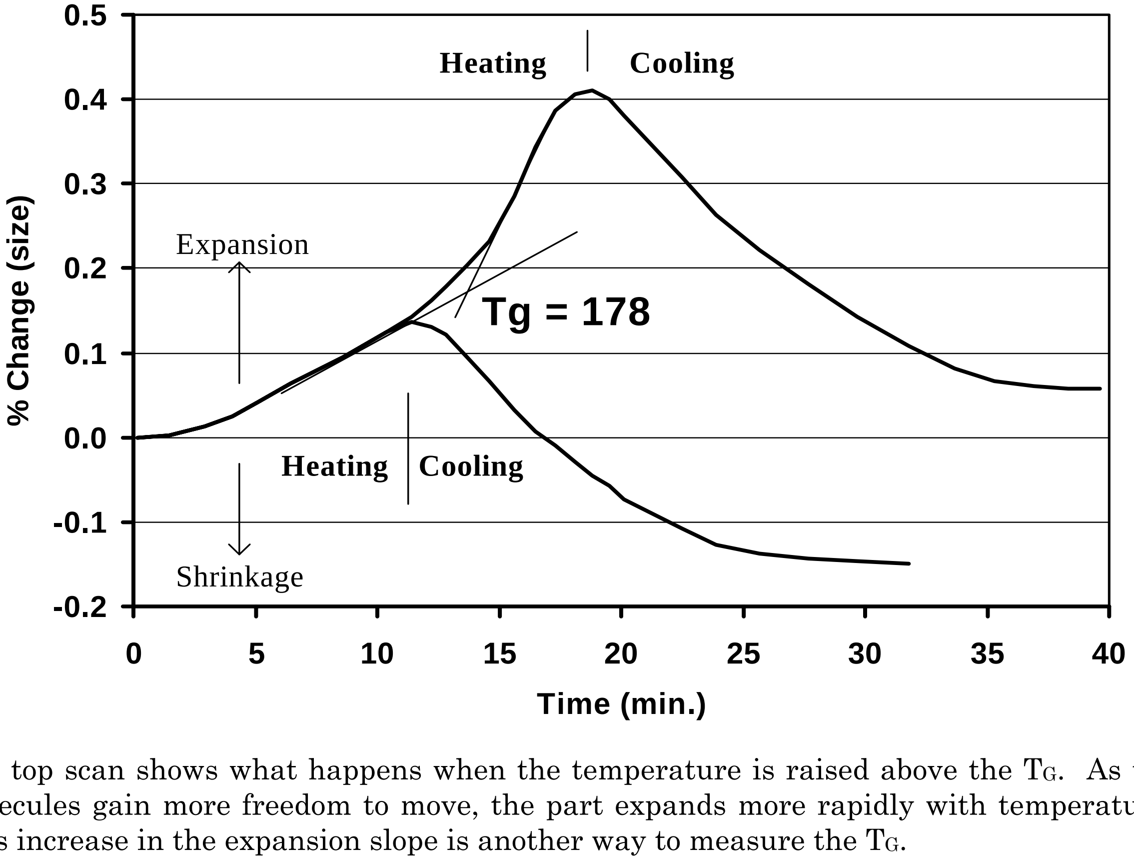
The first point is obvious; time is money. But, what does "as little time as possible" mean? To answer, requires some awareness of the other two guidelines.

The importance of staying below the TG can be illustrated with another instrument, the Thermo-Mechanical Analyzer (TMA). This instrument measures dimensional changes as the part is heated. As the temperature increases, the part expands. When it is cooled back down, it contracts.

Figure 6 shows two superimposed TMA scans of the same phenolic material.

Figure 6:

TMA Temperature Cycle of two Phenolic Samples (above and below the TG)



The top scan shows what happens when the temperature is raised above the TG. As the molecules gain more freedom to move, the part expands more rapidly with temperature. This increase in the expansion slope is another way to measure the TG.

The TMA scans illustrate a particularly interesting aspect of baking of phenolics. The cooling part of the top curve, where the sample was heated above the TG, shows that the temperature cycle caused the part to expand. Conversely, the sample in the bottom curve was heated and cooled before the TG was reached, and this heating cycle caused a net shrinkage.

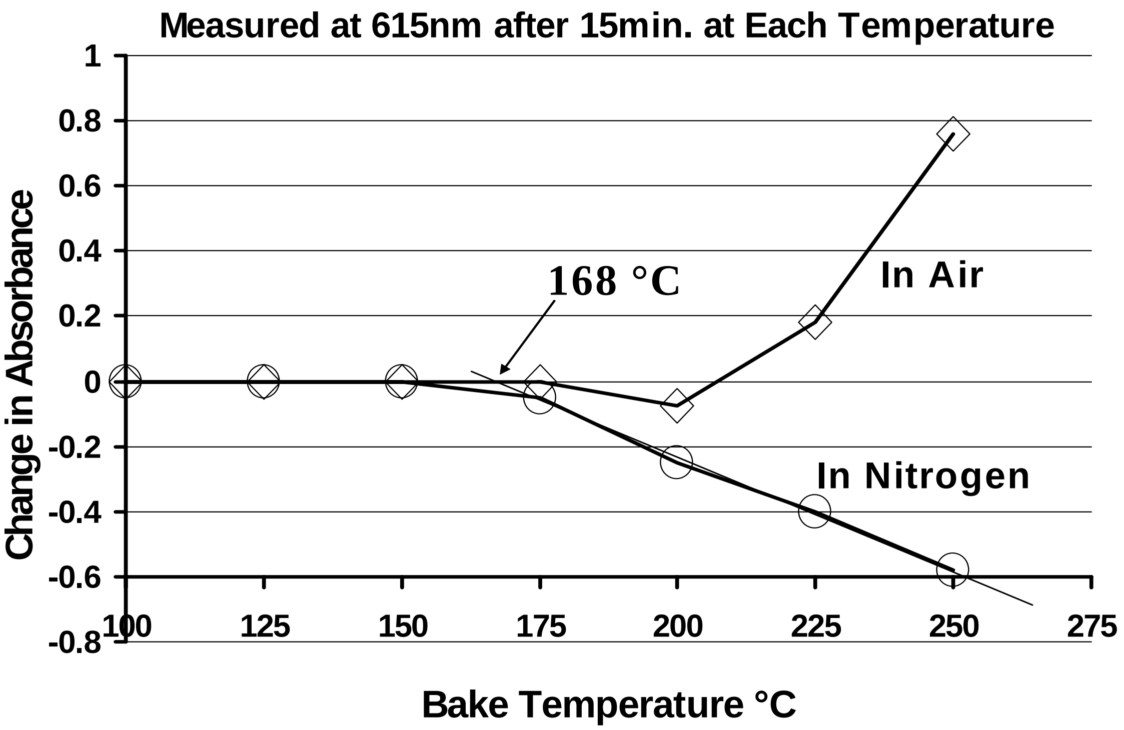
In our experience, when a phenolic is baked at a temperature below the TG, it will always shrink. This is expected, because the molecules are presumably relaxing, rearranging, crosslinking, and generally becoming more condensed. As the parts are baked, they are asymptotically approaching some final dimension. Different batches baked with the same program end up very close in final dimensions.

When a phenolic is baked above the TG, the final dimensions depend on how far above the TG it is baked, and for how long. The sample may shrink or expand. Different batches baked with the same program may have widely varying final dimensions. This is the first reason for the postbake guideline, that the oven temperatures never exceed the TG. The second reason is illustrated below.

Figure 7 shows plots of the clarity of individual unfilled phenolic resin samples that have been briefly exposed to high temperature.

Figure 7:

Light Absorbance of Baked Samples of Unfilled Phenolic Resin



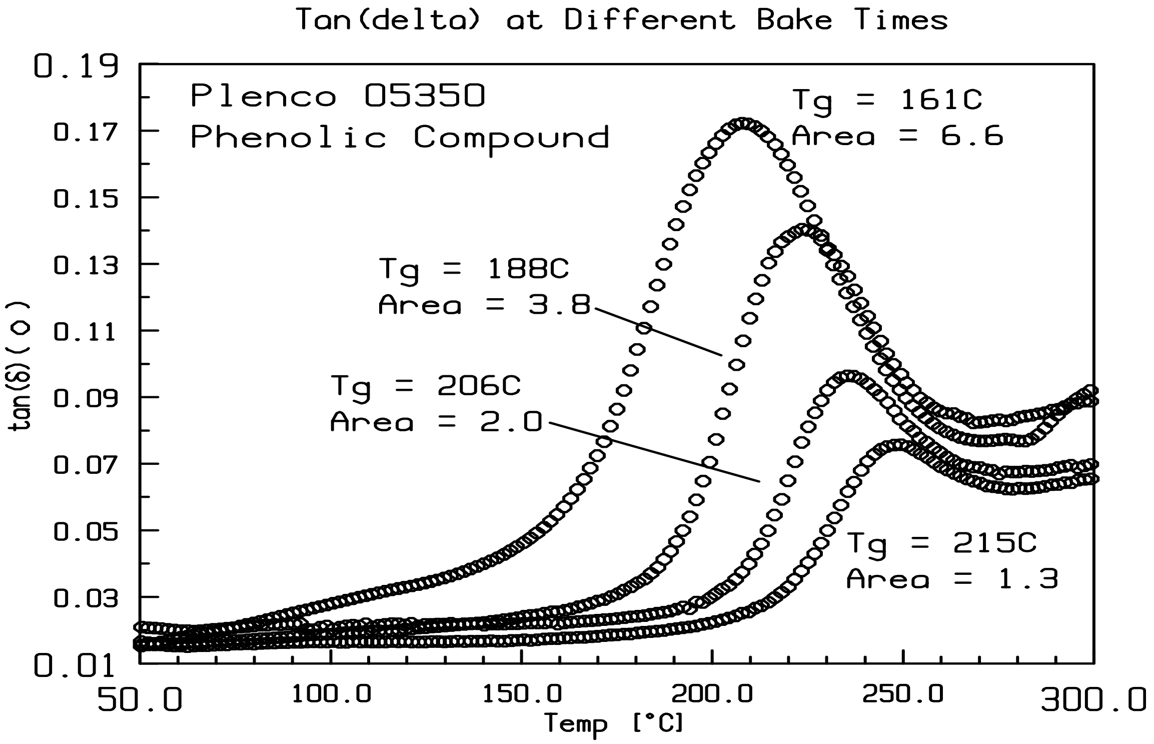
When the samples are first molded, they are a deep amber color. Fifteen minute exposures to successively higher temperatures had no effect on the light absorbance (color) until the TG was reached. Above the TG, if the part was baked in nitrogen, the color became lighter. After 15 minutes at 250ºC, the parts were a pale transparent yellow. When baked in air, the color deepened with each increase in temperature, until at 250ºC, the parts were nearly black. Each part was baked only once and only for fifteen minutes.

These rapid color reactions can be explained as follows: Below the TG, nothing much happens. Above the TG, the molecules have enough mobility for free radicals to form and to interact. In the absence of oxygen, the free radicals annihilate one another more rapidly than they are formed, and the part becomes less colored. When oxygen is present, it can attack the polymer and form new free radicals more rapidly than they can be eliminated. This causes the part to darken. In general, free radical reactions rip things apart. This experiment shows that there is little or no free radical activity when the temperature remains below the TG. While this would not be a good way to measure the TG in most circumstances, it does show that the chemistry of a phenolic compound changes when the TG is exceeded. The main conclusion is that even brief exposures above the TG can cause degradation of the polymer. The interpretations of Figures 6 and 7 provide ample reason for not raising the postbake oven above the TG of the part. This limitation is the main consideration in defining the meaning of "as little time as possible" in the first guideline.

The third guideline is to use the minimal postbake that will work in the application. This is related to the first guideline, to spend as little time as possible, but there is a deeper meaning:

Figure 8 shows the tan(δ) curves for phenolic samples that have been baked to successively higher TG values.

Figure 8:

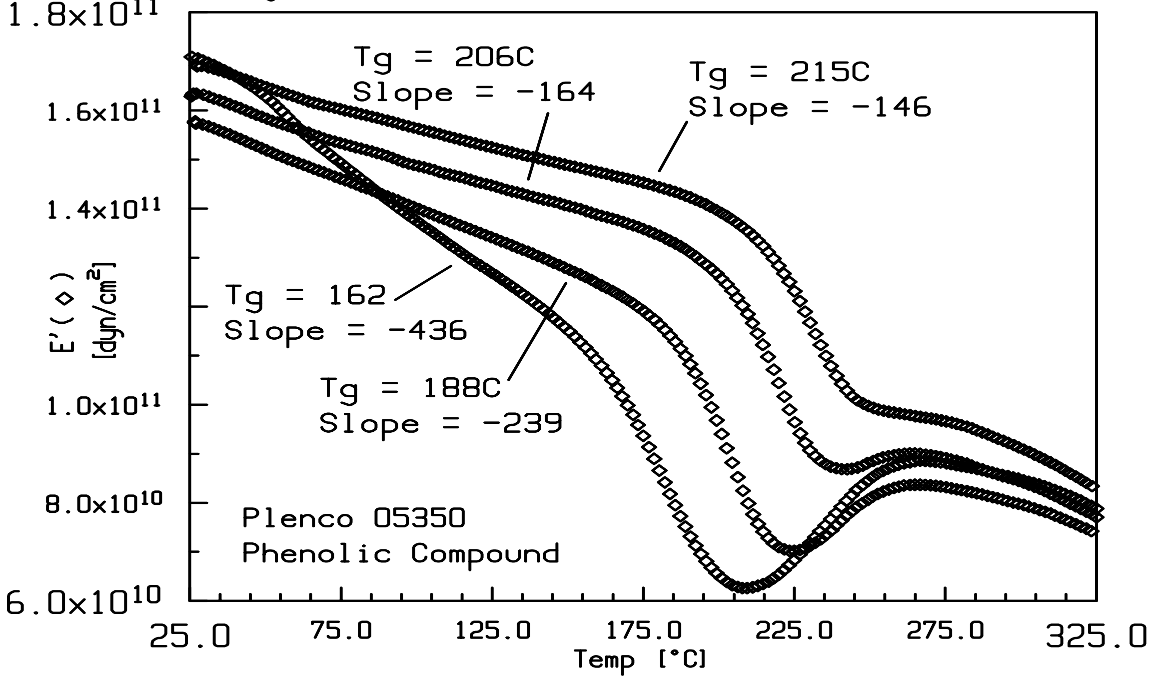


Clearly, as the TG is raised, something is consumed. The total available molecular mobility is reduced each time. In practical terms, as the TG is raised, the part becomes more brittle. Over baked parts may suffer from chipping, or cracking.

Figure 9 shows the storage modulus curves for the same samples:

Figure 9:

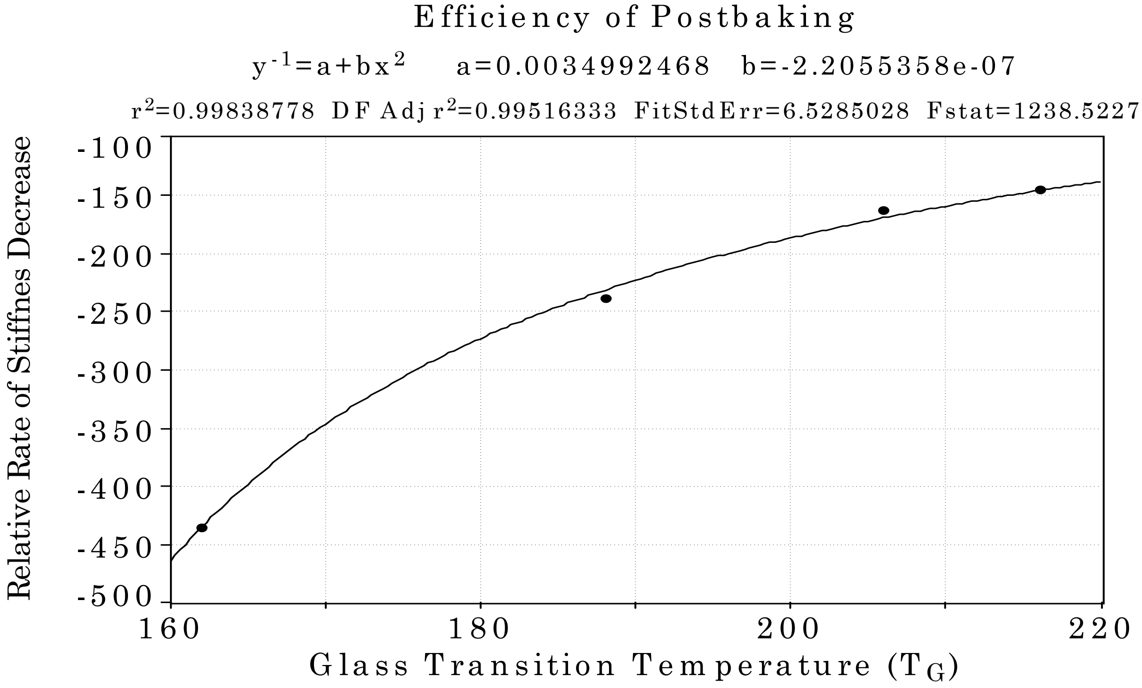
Storage Modulus {stiffness} at Different Bake Times



The steeper the slope, the faster the part loses stiffness as it is heated. As the TG is raised, the rate at which stiffness is lost decreases, but the greatest benefit occurs early in the bake. The data from figure 9 is replotted in Figure 10, to show how the change in slope becomes progressively less, as the TG is raised.

Figure 10:

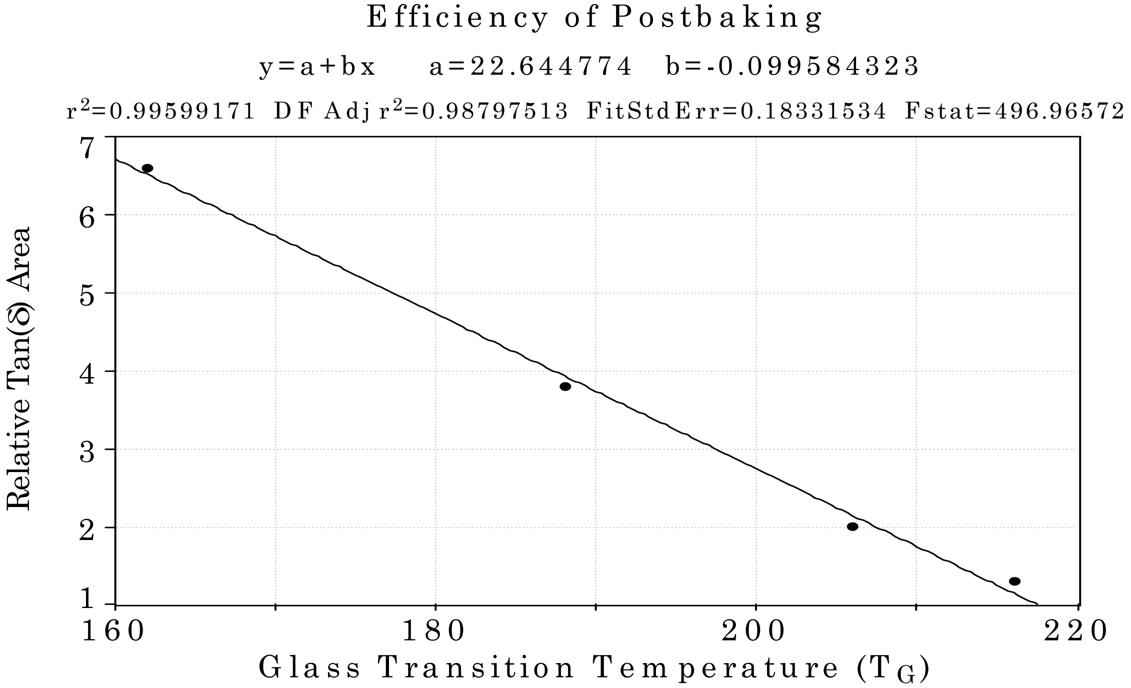
Diminishing Effect of Baking on the Rate of Stiffness Loss



While the beneficial effect that baking has on the stiffness slope diminishes, the loss in molecular mobility remains linear. The data from figure 8 is replotted in Figure 11, to show the decrease in tan(δ) area as the T_G is raised.

Figure 11

Constant Effect of Baking on Molecular Mobility Loss



Figures 8 – 11 show that there is a tradeoff between thermal stability and brittleness, and that the tradeoff is most advantageous early in the bake. Certainly, any given application may require a very high T_G, and level of thermal stability. In that case the increased brittleness can be handled by choosing the correct compound, and by incorporating radiuses in the part design to minimize stress.

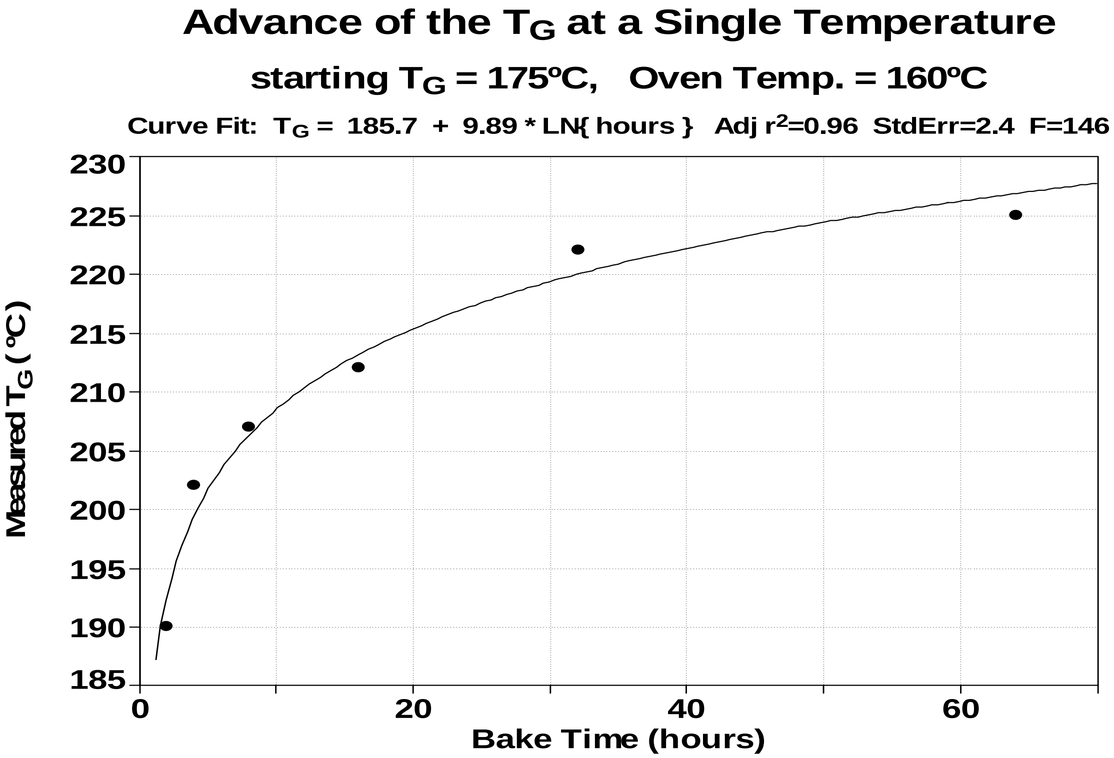
From all of the above observations, it is clear that the optimal postbake will raise the T_G just enough, but not too much, and will accomplish this in the minimum possible time, without the oven temperature ever exceeding the T_G of the part.

Optimizing the Postbake:

A number of approaches have been tried, to optimize the postbake. Sometimes parts are placed in cold ovens, and the heat-up rate is used as part of the bake. Sometimes multiple temperature ramps are used. Sometimes ovens are set only a little above the T_G, in the hope that it will do only a little damage. The simplest and safest solution, however, is to pick a suitably low oven temperature, and wait.

Figure 12 shows the measured T_G of parts baked at a single temperature for increasing lengths of time:

Figure 12:



The T_G increases with the log of time. If a high T_G is desired, a very long time might be required if only one oven temperature is used. To reach a T_G of 235ºC for example, the bake in Figure 6 would require 146 hours. Just 5 more degrees, to 240ºC, would require 242 hours. The first guideline would certainly cause us to seek a faster way.

In figure 12, the T_G starts out rising quickly. If the rate of advance of the T_G could be predicted, it would be possible to start the bake at a low temperature and wait until the T_G has safely passed some preset point. The oven temperature could then be raised to the preset point, which is now known to be below the current T_G, and the bake can begin anew. Successively stepping the temperature in this way effectively keeps the bake near the beginning part of the curve, where the T_G rise is rapid. The problem is one of finding a function in terms of the initial T_G, the oven temperature, and time, that will predict the new T_G. This problem was solved in 1992, by modeling the measured T_G values with the data from an orthogonal design of times, temperatures, and starting T_G values (3). The recently updated prediction model in ºC, is as follows:

Eq.1 $$T_G = 0.26 * T_{Ginit} + 0.74 * T_{oven} + 24.9 * \mathrm{Log}_{10}\{\mathrm{hours}\} + 23$$

Where: T_G = new T_G at the end of the bake (ºC)
$\mathrm{Log}_{10}\{\mathrm{hours}\}$ = log (base 10) of the bake time in hours
T_{oven} = oven temperature (ºC)
T_{Ginit} = initial T_G before the bake (ºC)

This model permits the simple design of multiple step programs as outlined above. Obviously, if a postbake can be broken down into multiple steps, the most efficient program would be composed of very small steps, essentially a ramp.

Optimized Ramp Postbake:

We have recently reexamined the postbake model. The goal was to broaden the range of starting conditions that are within the model, and to understand the effect of ramping the oven temperature.

Experimental:

All of the T_G measurements were taken from DMA scans on a Rheometrics RSA-II. The experimental designs were generated with “D.O.E. Fusion Pro” available from S-matrix Corp. The model phenolic compound was Plenco 05350. This is a predominately graphite filled compound used for ring seals. It was chosen for this study, because of the isotropic morphology, and inert chemistry of the graphite. This means there is a minimum of filler effects. In essence, 05350 has the cleanest DMA scans of any compound we have run. A select group of scans from other compound types were used to verify that the results are, indeed, general. The independent parameters in the design were: die temperature, oven start temperature, oven ramp rate, and final oven temperature. Start temperatures used in the design were constrained to be below the initial T_G of the part.

Observations:

To optimize the bake, there were some preliminary questions. The first item was to better define what is meant by “T_{Gstart}”. Most molders are not in a position to measure the T_G of their “as molded” parts. They need a reliable rule of thumb for estimating the T_{Gstart}, so they know where to start the oven. In the past, we have always said that the initial T_G is approximately the die temperature, but experience has taught that it is best to start the oven 10 – 15 C below the die temperature. To get a better rule of thumb, we molded samples over a range of die temperatures, and measured the T_G values. The results are shown in Figure 13:

Figure 13:

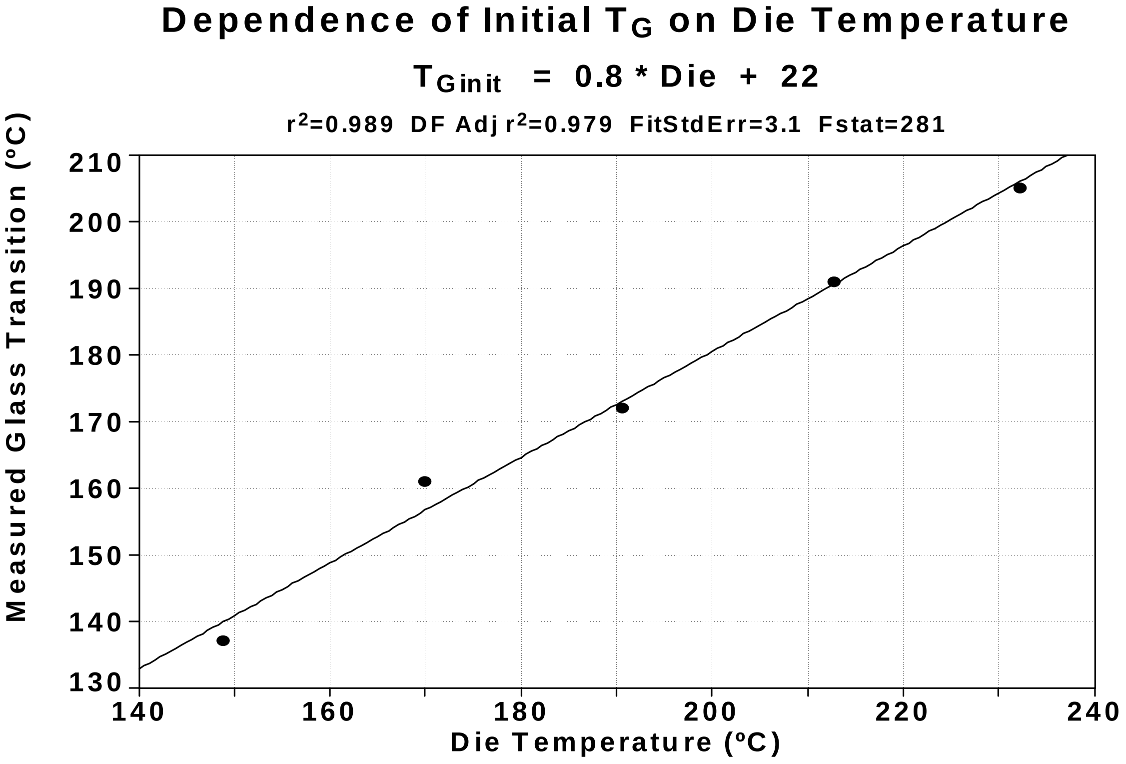


Figure 13 shows that there is not a direct 1:1 relationship between die temperature and T_{Ginit}, but it is first order and linear. A good estimate of the starting T_G is as follows:

Eq.2 $T_{Ginit} = 0.8 * \text{Die}^\circ\text{C} + 22$

Where: Die°C = temperature of the mold (°C)
T_{Ginit} = initial T_G of the molded part (°C)

Since many molding operations use the Fahrenheit scale, the following alternate forms may be useful:

Eq.3 $T_{Ginit} = 0.44 * \text{Die}^\circ\text{F} + 8$

Where: Die°F = temperature of the mold (°F)
T_{Ginit} = initial T_G of the molded part (°C)

Eq.4 $T_{GinitF} = 0.8 * \text{Die}^\circ\text{F} + 46$

Where: Die°F = temperature of the mold (°F)
T_{GinitF} = initial T_G of the molded part (°F)

For a typical molding temperature, such as 168°C (334°F) the predicted starting T_G is 156°C. This is just inside the 10 – 15 °C buffer that previously would have been recommended. When using the new guidelines, a buffer of 2 – 5 °C is probably sufficient to guarantee that the actual T_G is higher than the starting oven temperature.

The next preliminary question was how to set the maximum oven temperature ramp rate. If we ramp the DMA instrument at slower and slower rates, eventually, the oven rate should match the T_G rise rate. At this point, the tan(δ) peak should disappear, indicating that the T_G is staying ahead of the oven. Figure 14 shows the tan(δ) peaks for different temperature scan rates:

Figure 14

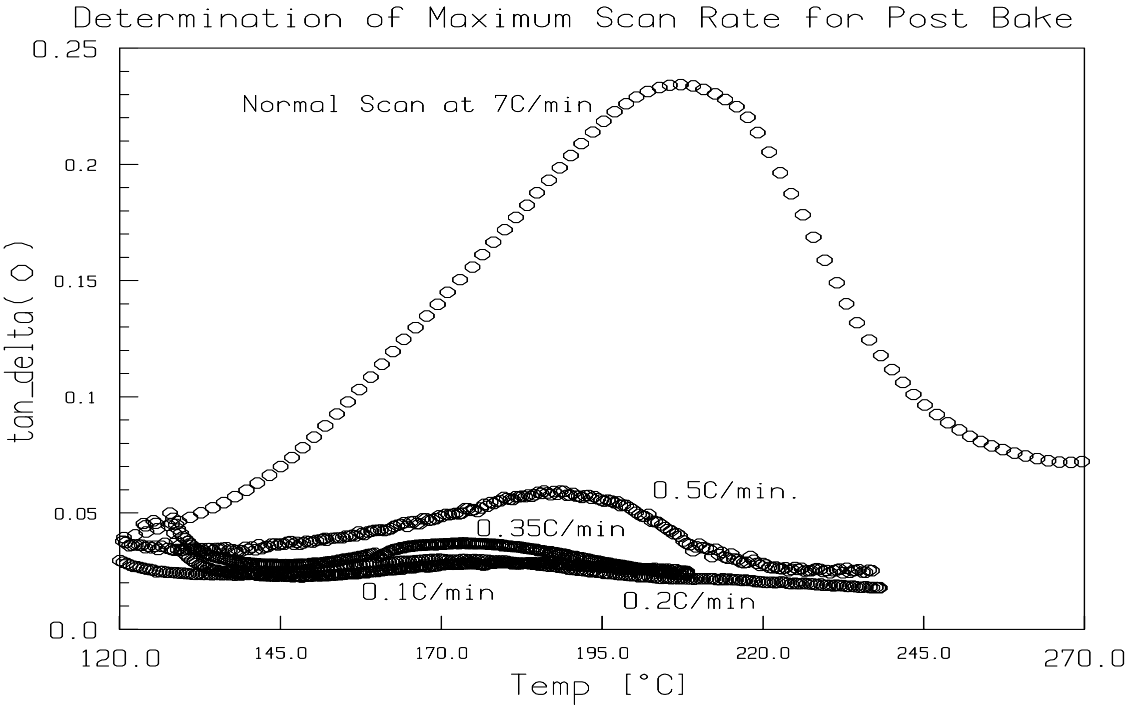
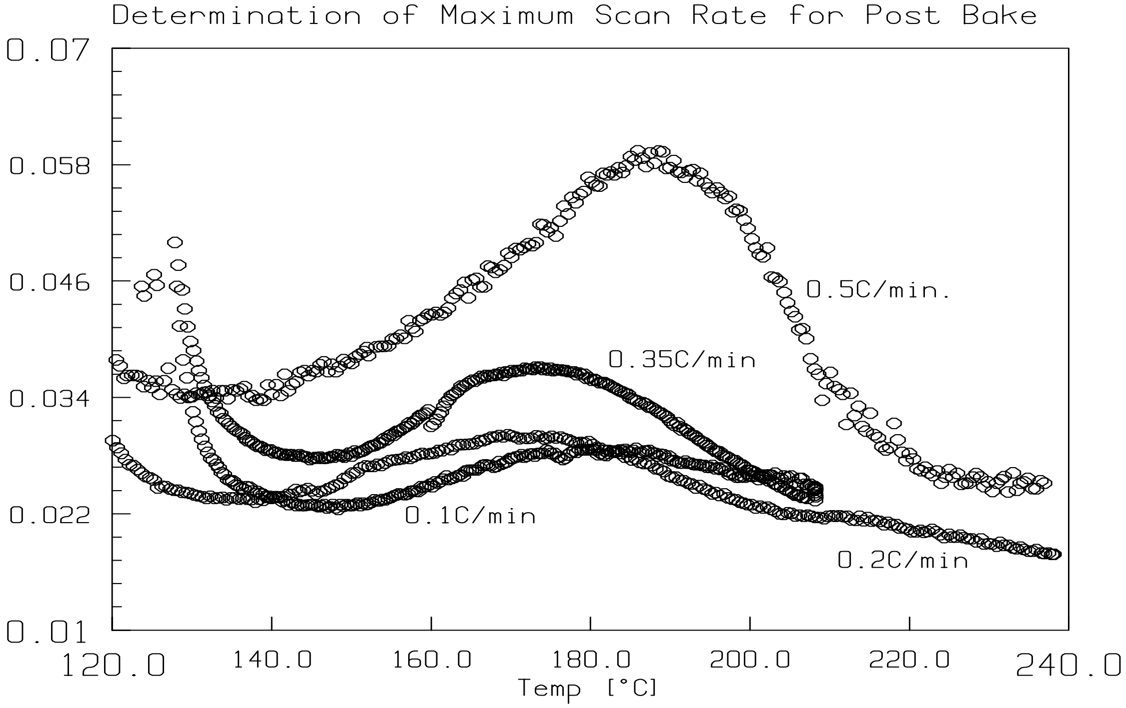


Figure 15 shows the same plot, but only the four slowest scan rates:

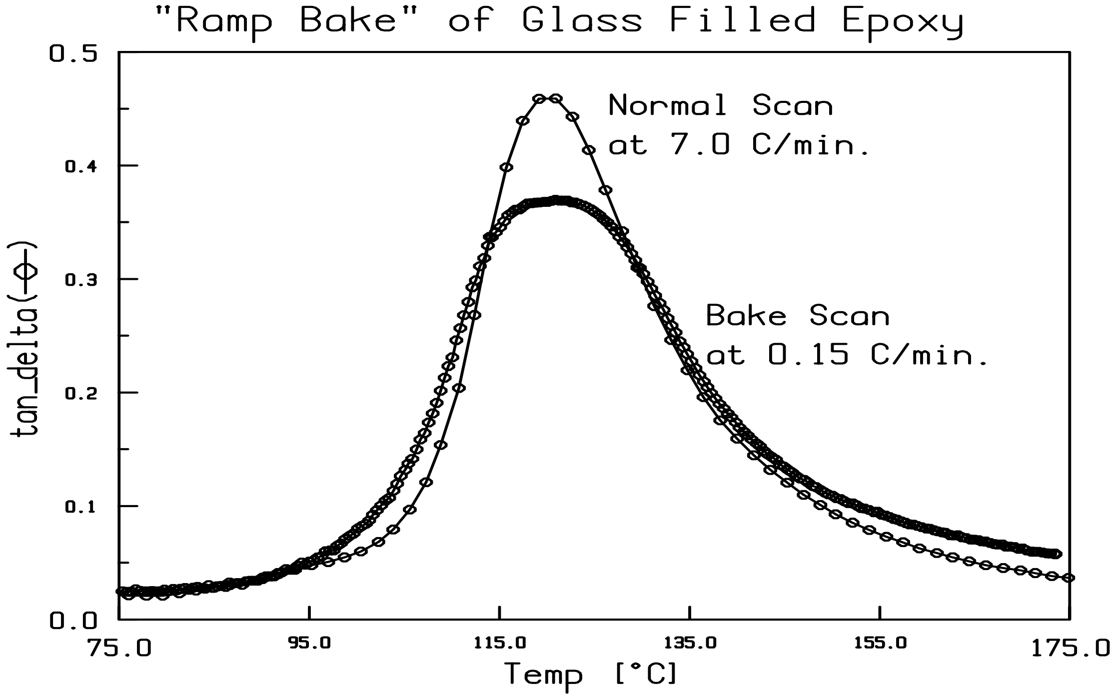
Figure 15:



Clearly, the 0.5ºC/min scan rate is still too fast. Slowing from 0.5ºC/min to 0.35ºC/min makes a huge difference, and the 0.2ºC/min scan is almost identical to the 0.1ºC/min scan. The fastest oven temperature ramp that can be used without exceeding the T_G of a phenolic is, therefore, between 0.35ºC/min and 0.2ºC/min. In practice, scan rates below 0.3ºC/min, or about 0.5ºF/min are fine.

Figure 16 illustrates again, how unique phenolics are with respect to post baking. The tan(δ) curves of an epoxy are shown at vastly different scan rates:

Figure 16:



The epoxy TG is virtually unaffected by scan rate. In effect, epoxies cannot be postbaked by scanning.

With the above information, an experimental design was prepared to determine the effect the following variables have on the TG:

1. **"As molded" TG (controlled with die temperature)**
2. **Starting oven temperature**
3. **Final oven temperature**
4. **Oven scan rate**
5. **Bake time**

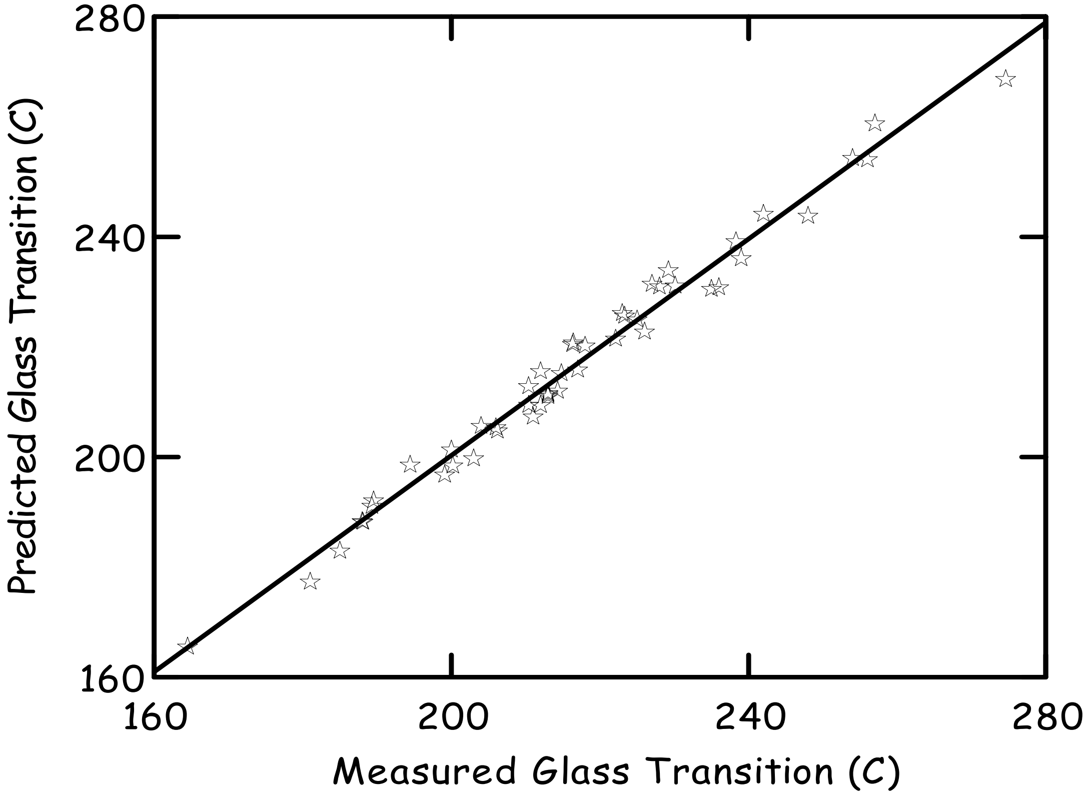
These five variables, plus the measured TG, would make a 6th dimensional surface. Fortunately, such a complicated model turned out not to be necessary. As long as the scan rate was kept below 20°C/hour (0.33°C/min) it didn't affect the result. This still left a 5th dimensional response surface. The unimportance of "scan rate" has some interesting implications. This means that a step bake can be treated as a scan bake, where the scan rate is zero, and the starting and final oven temperatures are equal. As a test of this approach, the original "step bake" data set was combined with the current "ramp bake" data, to derive a single general purpose postbake model. Although it is impossible to plot the response surface, it is useful to plot the measured versus predicted values. This is shown in Figure 17, along with the regression statistics:

Figure 17:

Correlation Plot for the Prediction of Glass Transition from Postbake Parameters

Tg = 0.285 * Tginit + 0.236 * OVstrt + 0.488 * OVstop + 21.5 * Log{Hr} + 22.3

n = 48; adj.R^2 = 0.982; S.E.E. = 2.96; F ratio = 626



The model in Figure 17 can be used for single step, multiple step, and ramp bakes. The only restrictions are that the oven start temperature is below the initial T_G, and all ramps are kept below 20°C/hour. The model is as follows:

Eq.5 $$T_{Gnew} = 0.285*T_{Ginit} + 0.236*Ov_{start} + 0.488*Ov_{stop} + 21.5*Log_{10}\{hours\} + 22.3$$

Where: T_{Gnew} = new T_G at the end of the bake (°C)
T_{Ginit} = starting T_G of the molded part (see **Eq.2**)
$Log_{10}\{hours\}$ = log (base 10) of the bake time in hours
Ov_{start} = oven start temperature (°C)
Ov_{stop} = oven stop temperature (°C)
Ov_{single} = if $Ov_{start} = Ov_{stop}$ then use $0.724*Ov_{single}$

Or with the log term in base 2:

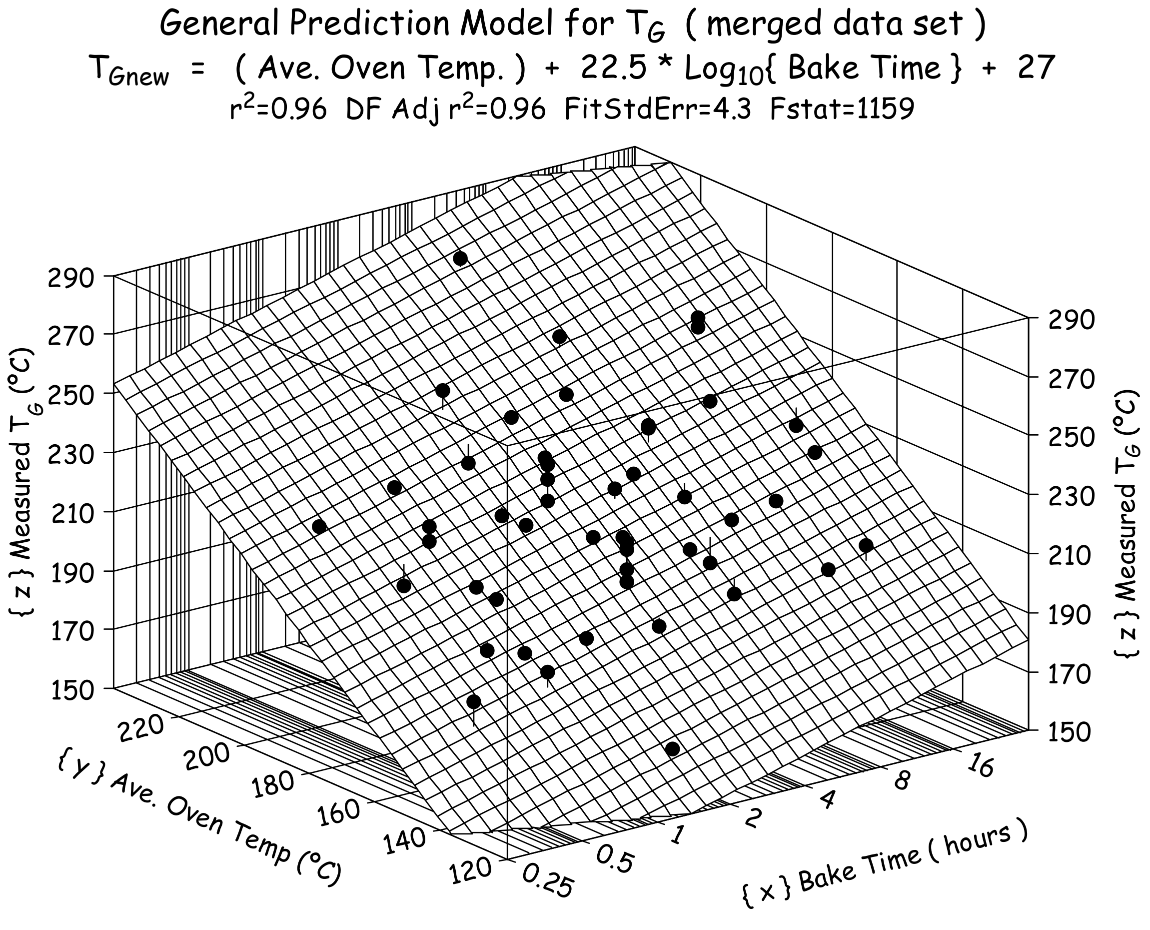
Eq.6 $$T_{Gnew} = 0.285*T_{Ginit} + 0.236*Ov_{start} + 0.488*Ov_{stop} + 6.5*Log_{2}\{hours\} + 22.3$$

Or with all temperatures in °F:

Eq.7 $$T_{Gnew} = 0.285*T_{Ginit} + 0.236*Ov_{start} + 0.488*Ov_{stop} + 38.7*Log_{10}\{hours\} + 39.9$$

As the overall purpose of this study is to derive easily applicable postbake guidelines, the least significant terms were dropped from the model. As it turns out, the data can be fit almost as well with only two variables: the average oven temperature, and the bake time, and furthermore, the coefficient for "average temperature" can be set to unity. Figure 18 shows the response surface for this simplified model:

Figure 18:



The degree of fit for both models is impressive. The standard deviation for the simplified model in Figure 18 is about 50% larger than for the more complete model in Figure 17. In either case, however, the precision of the model is similar to the repeatability of the T_G measurement itself, which is approximately ± 10°C.

The model in Figure 18 permits the statement of a simplified predictor equation for post baking as follows:

Eq.8 $\mathbf{T_{Gnew} = (\, Oven_{ave.}\,) + 22.5 * Log_{10}\{hours\} + 27}$

Where: T_{Gnew} = new T_G at the end of the bake (°C)
$\mathrm{Log}_{10}\{\mathrm{hours}\}$ = log (base 10) of the bake time in hours
$\mathrm{Oven}_{ave.}$ = Time averaged oven temperature (°C)

The same equation can be expressed with alternate units and log bases:

Eq.9 $\mathbf{T_{Gnew} = Oven_{ave.} + 9.8 * Ln\{hours\} + 27}$
Where: Ln{hours} = natural Log of the bake time in hours

Eq.10 $\mathbf{T_{Gnew} = Oven_{ave.} + 6.8 * Log_{2}\{hours\} + 27}$
Where: $\mathrm{Log}_2\{\mathrm{hours}\}$ = log (base 2) of the bake time in hours

Eq.11 $\mathbf{T_{GnewF} = Oven_{aveF.} + 40.6 * Log_{10}\{hours\} + 48}$
Where: all temperatures are in °F

Analysis and Application:

The model for predicting the T_G in **Eq.8** is surprisingly simple. One of the first tasks is to see how it compares to the original **Eq.1** model, and to the more rigorous **Eq.5** model. Consider the following example:

A part with an initial T_G of 160°C, is baked by scanning the oven temperature from 150°C to 210°C in 6 hours. This works out to 10°C/hour, which is well within the rate limits. The predicted T_G values are as follows:

T_{Ginit}= 160°C

150°C $\xrightarrow{\text{6hr}}$ 210°C

Eq.5 → $0.285*160 + 0.236*150 + 0.488*210 + 21.5*\mathrm{Log}_{10}\{6\} + 22.3 =$ 223°C

Eq.8 → $(150 + 210)/2 + 22.5*\mathrm{Log}_{10}\{6\} + 27 =$ 224°C

Both the detailed and the simplified models give the same answer for a single ramp.

Now consider the same temperature ramp, but broken into two identical parts. The first ramp is from 150°C to 180°C in 3 hours. The second half picks up immediately after the first, from 180°C to 210°C in 3 hours. The only thing different is that the calculation is done on each half separately. Physically, there is no difference between this bake and the previous bake, and the predicted T_G should, of course, be the same.

The T_G calculations are done as follows:

T_{Ginit}= 160°C

150°C $\xrightarrow{\text{3hr}}$ 180°C
180°C $\xrightarrow{\text{3hr}}$ 210°C

After the first ramp, **Eq.5** predicts a TG of 201°C and **Eq.8** predicts a TG of 203°C. The tricky part comes in calculating the TG for the second ramp. It would seem natural to use the calculated TG from the first stage as the starting TG for the second stage. When this is done, however, the **Eq.5** model predicts a TG of 234°C, instead of the 223°C that we know, from the previous example, is the right answer. Only when the original starting TG is used, is the correct answer of 123°C obtained. The simplified **Eq.8** model lacks a term for initial TG, and predicts the wrong answer of 233°C.

The detailed model in **Eq.5** works correctly for multiple ramp bakes when the original TG is carried along for each calculation. Intermediate TG values are not to be used for the TGinit term in the next ramp. The simplified model in **Eq.8** gives the right answer for both the long ramp and the short ramp, but should not be used to predict multiple ramp bakes. In practice, however, it is difficult to imagine what the purpose of a multiple ramp bake would be. The maximum oven scan rate, to avoid exceeding the TG, is approximately 15°C per minute. There is no particular advantage in scanning more slowly, so in most cases, this single ramp should be used, and the results are predicted perfectly well by **Eq.8**.

An interesting implication of the property discussed above, is that the TG is path dependant. Imagine two parts molded at different temperatures, so they had different initial TG values. If they are baked separately to the same TG, and then placed in a common oven and baked identically, they will have different final TG values because of their different initial TG values. This means that parts with the same TG may still not be at the same degree of cure. This is directly illustrated in Figures 19 and 20:

Figure 19:

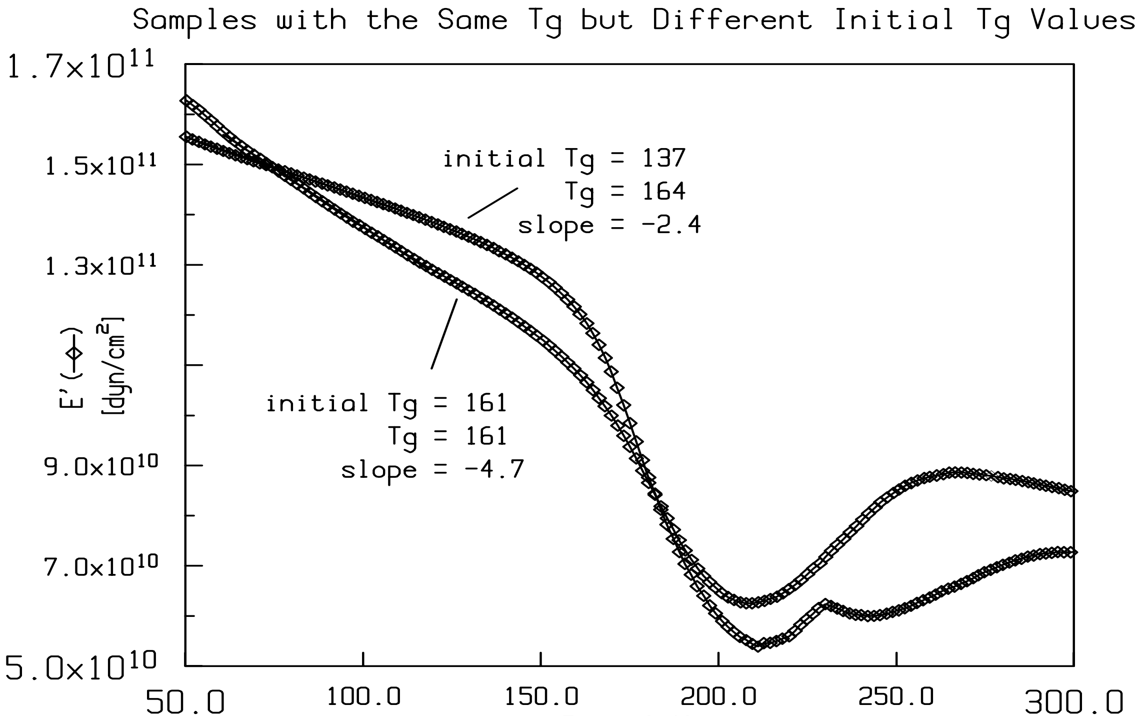


Figure 19 shows the stiffness curves of two samples that have been baked to the same TG, but were molded at different temperatures. The rate of stiffness loss is double for the sample that was baked less, even though the actual TG is the same.

The tan(δ) curves are shown in Figure 20:

Figure 20:

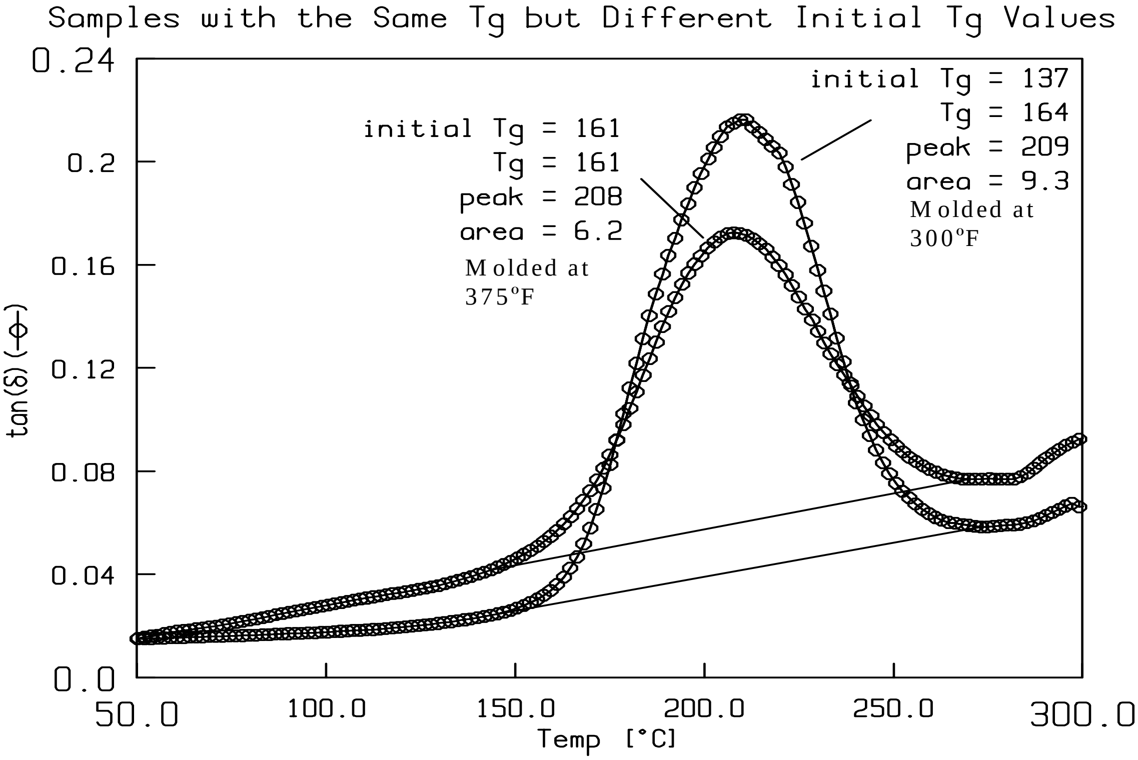


Figure 20 shows that the sample molded at the lower temperature, has a larger tan(δ) peak that the sample molded at a higher temperature, even though it is baked to the same T_G. While the T_G is one of the best measures of the degree of cure, a full description of cure is more complicated.

The previous examples used ramp bakes. A similar analysis can be done with step bakes. Consider a sample with an initial T_G of 160°C, baked 6 hours at 155°C. The T_G can be predicted as follows:

T_{Ginit} = 160°C

6 hours @ 155°C

Eq.1 → $0.26 * 160 + 0.74 * 155 + 24.9 * \text{Log}_{10}\{6\} + 23 =$ 199°C

Eq.5 → $0.285 * 160 + 0.724 * 155 + 21.5 * \text{Log}_{10}\{6\} + 22.3 =$ 197°C

Eq.8 → $155 + 22.5 * \text{Log}_{10}\{6\} + 27 =$ 200°C

All three models (original step model, rigorous ramp model, and simplified ramp model) work just fine for a single step bake.

Now, continuing the analogy with the earlier example, consider the same bake, but broken into two identical parts. The first part of the bake is at 155°C 3 hours, and the second part is also at 155°C for 3 more hours. Again, the only difference is that the calculation is done on each half separately. Physically, there is no difference between this bake and the previous 6 hour bake, and the predicted T_G should, of course, be the same.

The T_G calculations are done as follows:

T_{Ginit}= 160°C

3 hours @ 155°C

3 hours @ 155°C

After the first 3 hours, **Eq.1** predicts a T_G of 192°C, **Eq.5** predicts 190°C, and **Eq.8** predicts 193°C. If the original T_G is used in the second step, as was required with the ramp bake, there will be no difference from the first step. The second 3 hour will appear to have had no effect. This is clearly wrong. In the case of step bakes, the T_G result of the current step must be used as the starting T_G of the next step. When this is done, **Eq.1** correctly predicts a T_G of 200°C, and **Eq.5** predicts a T_G of 199°C. The simplified model lacks a term for the initial T_G, and therefore cannot give the correct answer.

The above rule should also apply when the temperature is actually raised for the second step. To directly demonstrate this, an actual sample, with T_{Ginit} = 158°C, was baked for 5 hours at 155°C and then 3 hours at 191°C. The **Eq.5** predicted T_G, with the original T_G used in each step, was 215°C. The predicted intermediate T_G after the 5 hours at 155°C was 194°C. Applying this value for the T_{Ginit} term in the second step resulted in a final predicted T_G of 226°C. The actual measured T_G of the postbaked sample was 224°C.

The detailed model in **Eq.5** works correctly for multiple step bakes when the T_G from the current step is fed into the calculation of the next step. The results are essentially identical to the older model in **Eq.1**. Because the **Eq.5** model is more versatile, it should be considered a replacement for the older model. The simplified model in **Eq.8** gives right answers for both long and the short bakes, but should not be used to predict multiple step bakes.

Conclusions:

Broad guidelines for postbaking, and reasons for following them, have been presented:

1. **Spend as little Time as possible**
2. **Keep the Oven temperature below the Part's Glass Transition temperature (T_G)**
3. **Bake the minimum amount that will get the job done**

From the above discussion it is now possible to fill in some of the details of how to accomplish these guidelines. Actual T_G measurements of production parts are seldom made. The required instrumentation is costly, slow, and requires extensive training. Because of the difficulty of measuring T_G values directly, all guidelines should be referenced to the die temperature.

The most efficient way to bake is a ramp bake. The starting temperature should be approximately 3°C below the initial T_G. This can be calculated from **Eq.2** and **Eq.4** as follows:

Eq.12 **Ramp Start (°C) = 0.8 * Die°C + 19**

Eq.13 **Ramp Start (°F) = 0.8 * Die°F + 41**

The ramp speed should be 15°C/hour or 30°F/hour. This information can be combined with **Eq.2** and **Eq.5** or **Eq.4** and **Eq.7**, to describe optimal temperature ramps for any desired T_G in terms of the Die temperature and the maximum Oven temperature:

Eq.14 $T_G = 0.417*Die°C + 0.488*Ov_{stop} + 21.5*Log_{10}\{(Ov_{stop} – 0.8*Die°C - 19)/15\} + 33$

Or with all temperatures in °F:

Eq.15 $T_G = 0.417*Die°F + 0.488*Ov_{stop} + 38.7*Log_{10}\{(Ov_{stop} – 0.8*Die°F - 41)/30\} + 63$

These equations are best viewed in graphical form. Figures 21 and 22 show contour plots of predicted T_G values, over a range of die temperatures and oven temperatures:

Figure 21:

Contour Plot of Predicted T_G (°C) for a 15°C/hour ramp {from Eq.14}

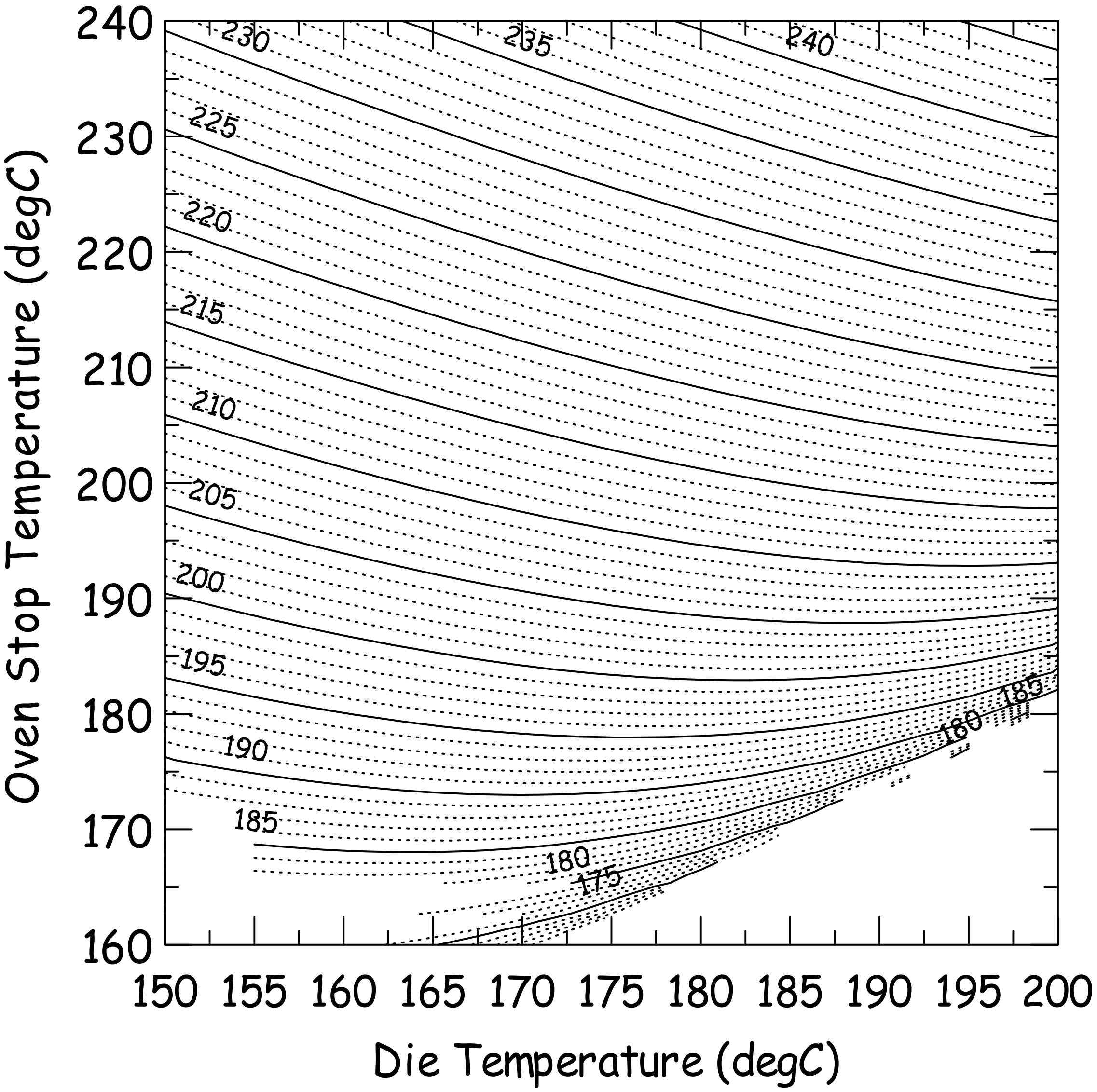
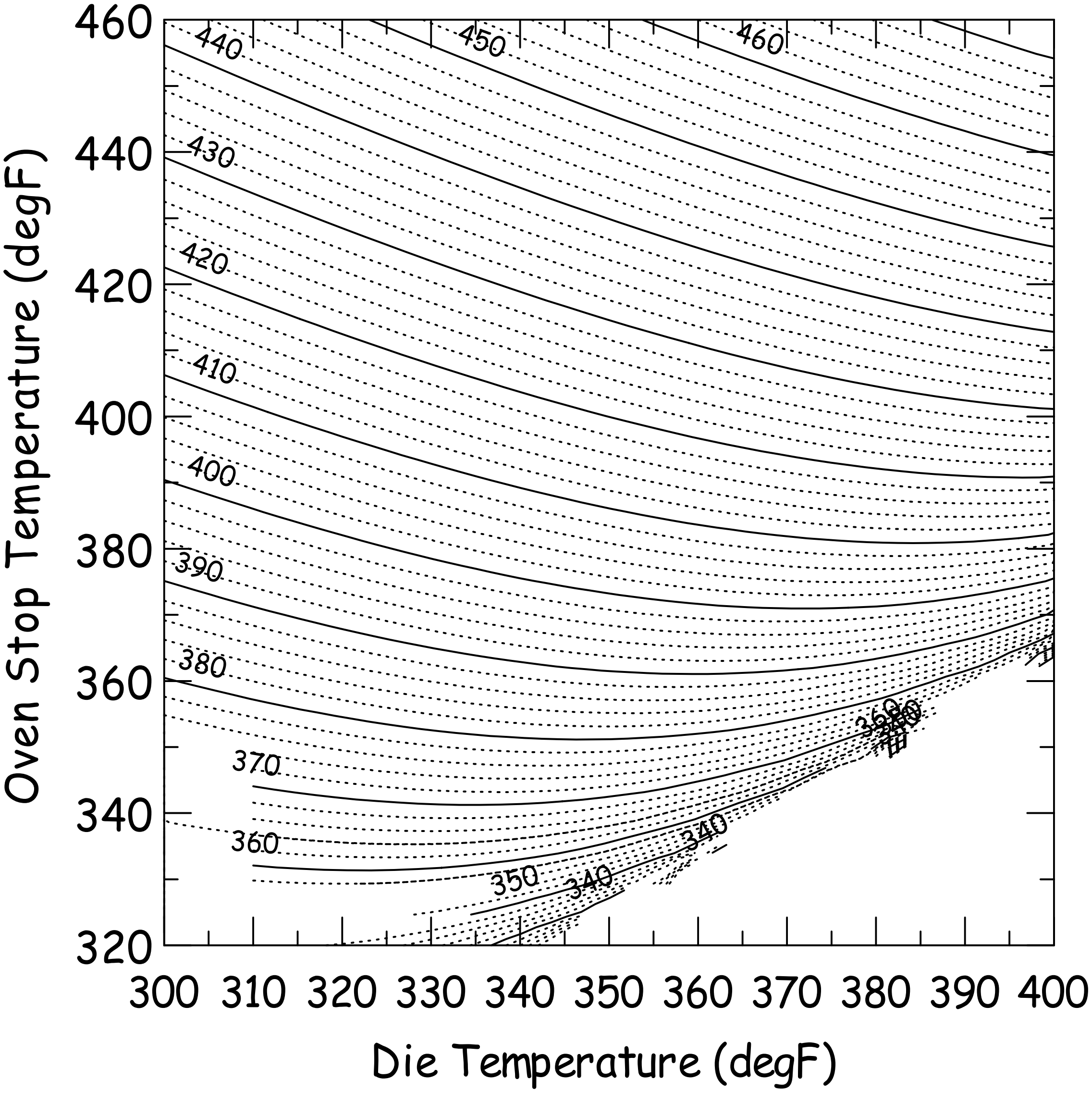


Figure 22:

Contour Plot of Predicted T_G (°F) for a 30°F/hour ramp {from Eq.15}



The above plots can be used to match parts molded at a particular die temperature, and with a desired T_G, to a maximum oven ramp temperature. The bake time is simply the maximum temperature minus the starting temperature (from **Eq.12** or **Eq.13**) divided by 15 (for °C) or by 30 (for °F).

In practice, it is usually not a good idea to exceed 200°C in air. This is the temperature where cellulose based fillers begin to decompose. To obtain a high T_G without exceeding 200°C, it is best to ramp to 195°C and hold until the desired T_G is reached. This hold time can be calculated by combining **Eq.14** with **Eq.5**.

This can yield a predictor of the T_G at different hold times at 195°C, after having ramped from 3°C below the die temperature to 195°C at 15°C/hour as shown in **Eq.15**:

Eq.16 $T_G = 0.119*\text{Die}^{\circ}\text{C} + 21.5*\text{Log}_{10}\{ \text{hours}*(176 - 0.8*\text{Die}^{\circ}\text{C})/15 \} + 200$

A similar predictor can be derived for the T_G at different hold times at 380°F, after having ramped from 5°F below the die temperature to 380°F at 30°F/hour as shown in **Eq.17**:

Eq.17 $T_G = 0.119*\text{Die}^{\circ}\text{F} + 38.7*\text{Log}_{10}\{ \text{hours}*(339 - 0.8*\text{Die}^{\circ}\text{F})/30 \} + 386$

These equations are best viewed in graphical form as shown in Figures 23 and 24:

Figure 23:

Contour Plot of Predicted T_G (°C) for Different Hold Times at 195°C, After Scanning to 195°C at 15°C/hour {from Eq.16}

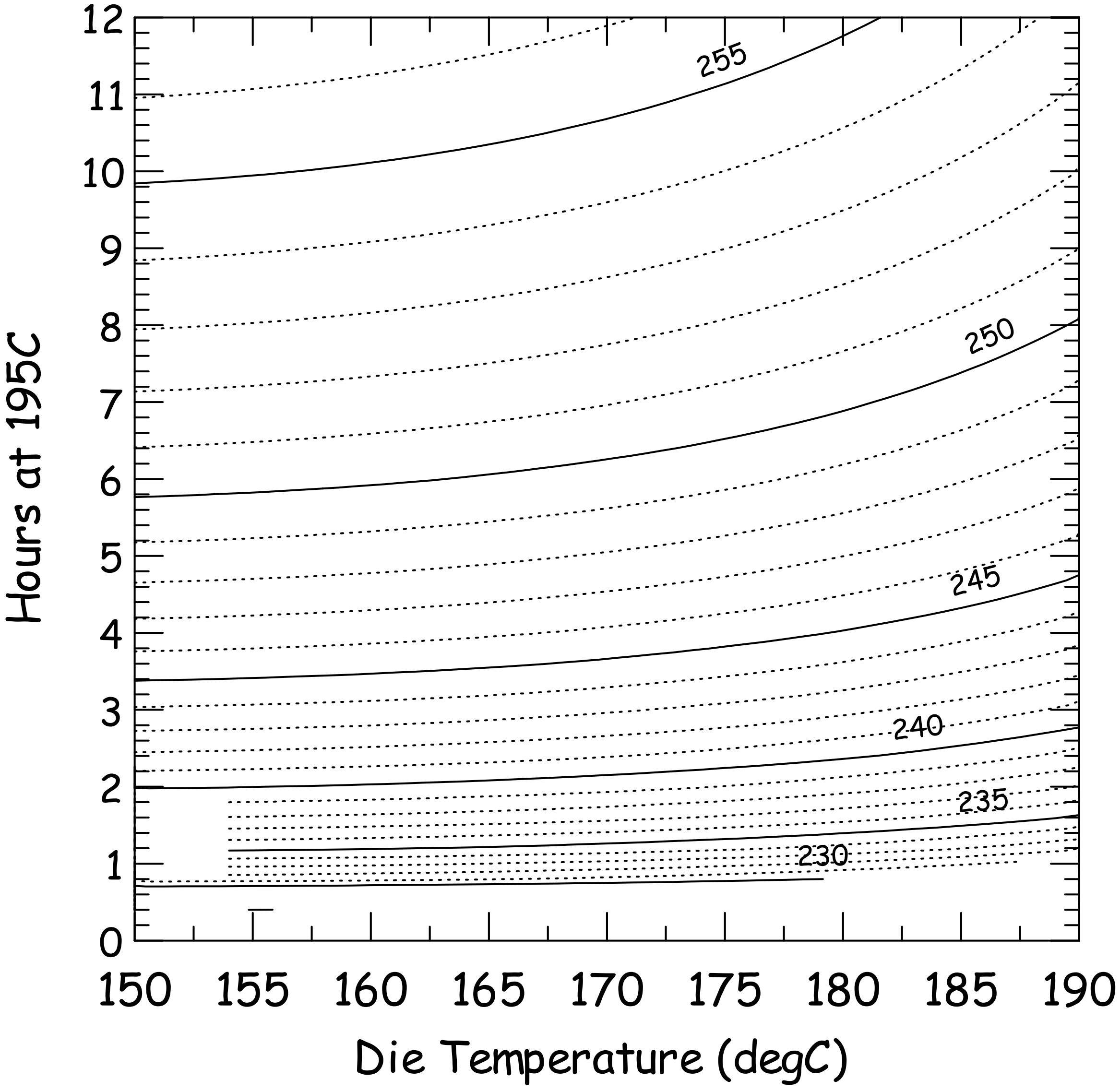
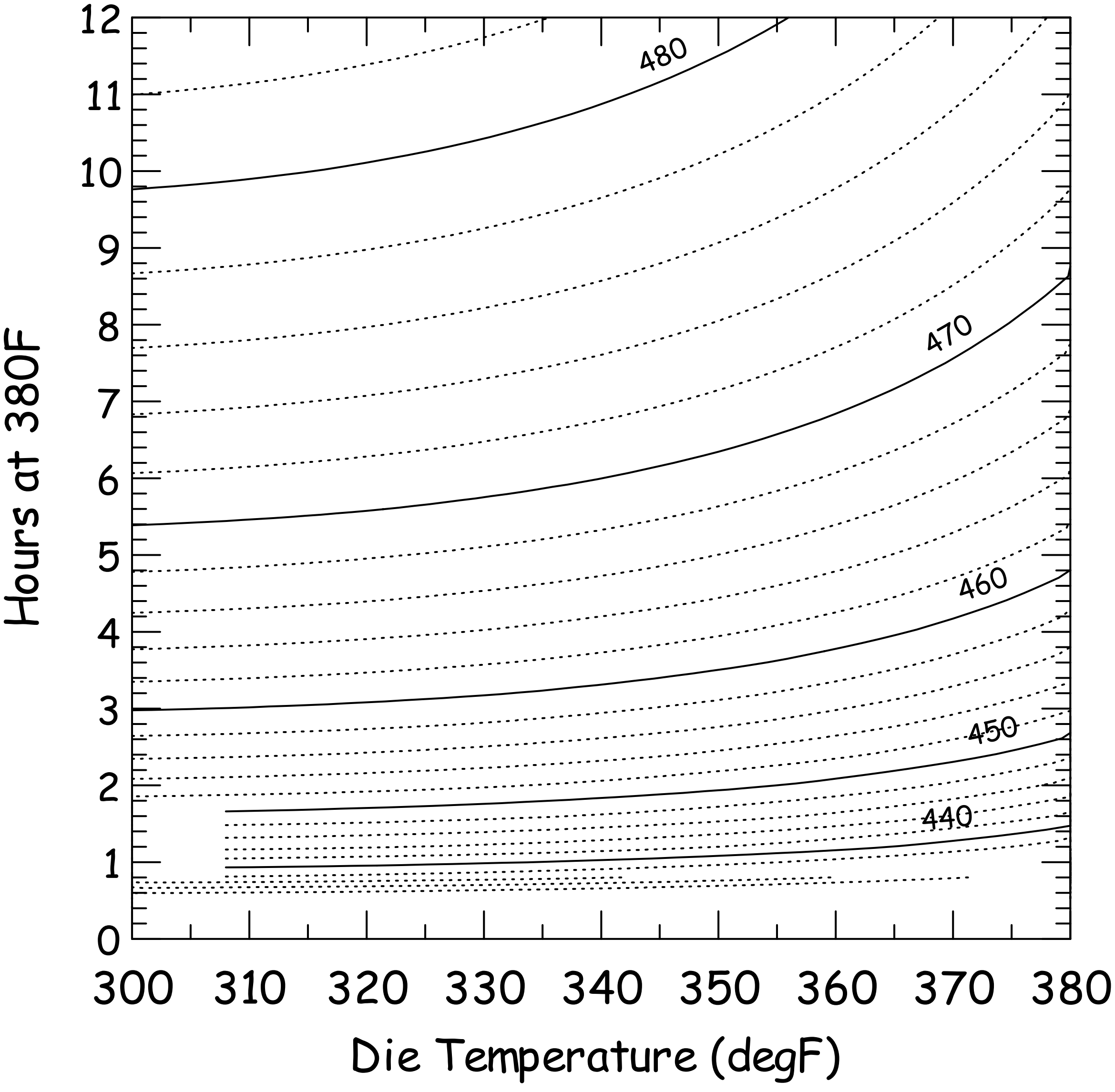


Figure 24:

Contour Plot of Predicted TG (°F) for Different Hold Times at 380°F, After Scanning to 380°F at 30°F/hour {from Eq.17}



By reading the charts in figures 21-24, it should be possible to quickly construct a near optimal postbake for any molded phenolic. There are some preliminary considerations. Before the bake, the oven should be ramped to the start temperature in such a way that there is no danger of thermal shock. 50°F/min is fine. This is much too fast to affect the TG. Naturally, care should be taken that the oven does not over-shoot the start temperature. Thermal shock is not always an issue. Some parts can be placed directly in a hot oven. This should be determined on an individual basis. As a postbake example, consider a part is molded at 340°F and a desired final TG of 235°C (455°F). From **Eq.13**, the oven should start at 313°F and be ramped to 380°F at 30°F/hour. This will take 2 ¼ hours. From figure 24, the temperature should then be held at 380°F for another 2 ¼ hours. The bake is completed in 4 ½ hours. Oven warm up and cool down may consume another hour.

Another use for the charts would be to estimate the final TG at the end of an existing post bake, and then determine whether the same endpoint could be reached in less time with a ramp bake. Imagine a part molded at 165ºC that is currently baked for 2 hours at 155C, and then 4 hours at 180C:

From **Eq.2:** $\mathbf{T_{Ginit} = 0.8 * Die^{o}C + 22}$
The initial T_G is 154ºC

From **Eq.5:** $\mathbf{T_{Gnew} = 0.285*T_{Ginit} + 0.236*Ov_{start} + 0.488*Ov_{stop} + 21.5*Log_{10}\{hours\} + 22.3}$

The current TG after the first step is: $\mathbf{0.285*154 + 0.724*155 + 21.5*Log_{10}\{2\} + 22.3 = 185^{o}C.}$
If this is used as the T_{Ginit} term for the 2nd step, the final T_G is predicted to be:
$\mathbf{0.285*185 + 0.724*180 + 21.5*Log10\{4\} + 22.3 = 218^{o}C}$
The final T_G after the current 2 step bake is 218ºC.

From **Eq.12**, a ramp bake should start at 151ºC. From the chart in figure 21, with a die temperature of 165ºC, we should get a final TG of 218ºC by ramping at 15ºC/hour to 215ºC. This should take 4 hours and 16 minutes. The same TG can be reached with a savings of 1 ¾ hours if ramp bake is used instead of a step bake.

References:

1. Louis L. Korb, Modern Plastics, April 1976
2. 'Studies of the Post Bake Process of Phenolic Resins',
   by Theodore N. Morrison and Phillip A. Waitkus,
   SPI Molding Division Technical Conference, 21st Century Phenolics, June, 1987.
3. 'A Multivariate Post Bake Study'
   by Theodore N. Morrison,
   SPE RETEC Irreplaceable Thermosets, March, 1992.