

Overcoming Vitrification of Polyester Solid Surface Resin for the Kitchen Environment using Postcure

by
Kenneth Lipovsky,
Reichhold, Inc

Abstract

Unsaturated polyesters were first developed over 20 years ago for the manufacture of solid surface kitchen surfaces. However, there were no scientific studies showing the optimum post cure temperature or time needed to get complete cure on solid surface polyester parts.

Kitchen sinks and countertops are exposed to extreme conditions compared to similar parts made for bathrooms. The higher demands of the kitchen make it imperative to insure parts develop maximum physical properties. This can only be accomplished by post cure but at what temperature and for how long?

Why Polyester Polymer?

Polyester resins by nature of its chemical composition are resistant to common household stains and chemicals. Polyester resins for the solid surface industry have low viscosities that can be easily blended with select fillers to create a matrix that can be cast into virtually any molded shape, then fabricated to create kitchen countertops and sinks in almost any color or aesthetics including simulated granite. These kitchen resist thermal shock and abuse from everyday use and can be manufactured by Cultured Marble shops using slightly modified equipment and fabricated with common wood working tools.

The Choices – Man-made or Natural

In the natural resource category we have: metal, soap stone, granite, slate, marble, limestone, and wood. Man made products include: tile, engineered stone, acrylics, melamine laminate, cultured marble, polyester concrete, plate glass and ceramic.

They can all be used for to make great countertops but fabrication of sinks is either impossible or must be made with special equipment not normally used by your typical cultured marble/solid surface manufacturing facility. Problems with countertops other than engineered stone, solid surface or cultured marble can in-

COMPOSITES 2006

clude: support of bacteria growth, acid etching, stains, watermarks, cracking, scratches and discoloration which must be repaired by a professional or replace with a more suitable product

Advantages of Polyester Solid Surface

Countertops and sinks can be integral units melding both as one piece. Countertops can be fabricated with virtual invisible seams with unlimited edge treatment and inlays. The selection of colors is unlimited including patterns, veined, stone and simulated granite looks.

Solid surface sinks and countertops can be fabricated and repaired with standard wood working equipment and in some cases by the home owner.

Introduction

In order to become the product of choice it is critical to make sure the part is completely cured. The only way to be sure is to post cure the parts. Recommendations were being made that post cure will happen over time or parts should be placed in an oven at temperatures from 150°F to 250°F for anywhere from 2 hours to 24 hours. Nothing conclusive was ever published for solid surface.

Postcure is elevating the composite's temperature after the room temperature cure to increase the amount of cross-linking of the polymer. The maximum cross-link density is when every carbon to carbon unsaturated group has been reacted and each end group of each chain is connected to another polyester chain. Short postcure times are made possible with ovens that elevate temperatures to the resin's Glass Transition Temperature (T_g) and higher. (For this study the T_g of the resin is 230°F/110°C).

Many of these assumptions came from earlier studies on marine laminating or Corrosion Resistant resins. However, solid surface resins are normally promoted to gel and cure at room temperatures with Methyl Ethyl Ketone Peroxide without the use of powerful and yellow promoters like Dimethylaniline, Diethylaniline or Dimethylparatoluidine common in open molding operations.

Other studies centered on high temperature cure systems used in closed molding operations that contain no promoter but rely on high temperature initiators like Tertiary Butyl Perbenzoate, Benzoyl Peroxide, Tertiary Butyl Peroxide, Cyclohexanone Peroxide and Cumene Hydroperoxide. In addition to these initiators the molding temperature is usually above the T_g of the resins

Determination of Complete Cure

There are different ways to determine if a part is completely cured. They include: residual styrene monomer, residual exotherm of the part, ultimate physical properties and glass transition temperature (T_g). The glass transition temperature shows the maximum crosslink density or ultimate cure.

In this paper Physical Properties" will performed on actual polyester solid surface parts since we are evaluating the fit for use of solid surface polyester resins in the kitchen and bath environment.

Definition of Solid Surface

Solid surface is a densified, void-free product. It can be either a homogeneous single-colored product or simulated granite. Air is removed from the resin / filler matrix during manufacturing, which makes it a solid surface product by definition. If the product contains any air at all, it cannot be claimed to be "solid surface." The final parts can be cut, shaped and fabricated after manufacturing.

Solid surface is a mixture of polyester resin, alumina trihydrate, pigments or granules and initiator. The resin is the "adhesive" or "bonding agent" of the composite which is UV (ultra-violet) stabilized to minimize yellowing from exposure to UV rays. The resin is low in viscosity containing air release and wetout agents for good filler wetout, good flow and high filler acceptability. The resin used for solid surface is both stain and chemical resistant. and can contain special additives for rapid cure.

Polyester Chemistry for Solid Surface Resins

Polyester resin is formed by reacting a polybasic acid and a glycol (antifreeze), The polymer is then blended with a reactive diluent like styrene and promoters to give the necessary performance characteristics for a particular application. In our case kitchen countertops and sinks.

Crosslinking begins by free radical polymerization with the introduction of an initiator. In room temperature cure systems Cobalt carboxylates are used to promote the polymerization of monomers and begin the cross-linking of the polyester resin.

The selection process for building a polyester solid surface resin begins by examining what properties are important to the final product. In the case of countertops and kitchen sinks, we carefully look at all the fundamental building blocks used in this process.

After careful screening using lab experiments and producing actual solid surface parts for testing, the

selection process made it clear that neopentyl glycol and isophthalic acid yields the best performance compared to orthophthalic acid-based resins.

Glycols

Propylene Glycol - This glycol is branched with one pendant methyl group. It provides good corrosion resistance and structural properties making it acceptable for countertops and sinks.

Neopentyl Glycol - This is the glycol of choice for solid surface. It is branched with two pendant methyl groups producing a resin that has both good corrosion and weather resistance.

Dibasic Acids

Orthophthalic Acid - The most commonly used acid, but yields a resin with comparatively low heat and chemical resistance properties.

Isophthalic Acid - Has both high heat and chemical resistance compared to Orthophthalic Acid base resins necessary for kitchen sink manufacturing. Orthophthalic is received as a liquid in the anhydride form (dry from water) and converted to an acid in the presence of water. This takes place in our reactor under heat. The acids groups are in the Meta position which makes a good chain but not the best.

Maleic Anhydride - This is the reactive part of the resin that connects to the monomer (styrene) to form a thermoset polyester. It is used in every polyester solid surface resins.

The Reaction

Acid and glycol react under heat to form polyester resin and water. Between the acid and glycol molecules is the ester linkage which is the weakest part of the polymer link. A large molecule such as isophthalic and neopentyl glycol offer the best protection from attack from stains and/or hot water necessary in kitchen and bath operations.

When the reaction is complete, the resin is pumped into a monomer such as styrene where is cooled and modified with additives for stability, gel and cure properties.

Neopentyl Glycol /Isophthalic vs. Propylene Glycol/Orthophthalic Acid

PG/Orthophthalic based resins are used mostly behind a protective gel coat to produce parts such as: flat stock, window sills, statues and decorative parts. NPG/ISO resins can do the same job of the PG/Ortho resins and are preferred for solid surface applications, especially sinks, because of their higher heat deflection temperatures (HDT), better chemical and water resistance, which make them superior for thermal shock while minimizing blushing due to continuous exposure to water. See figure 1 & 2.

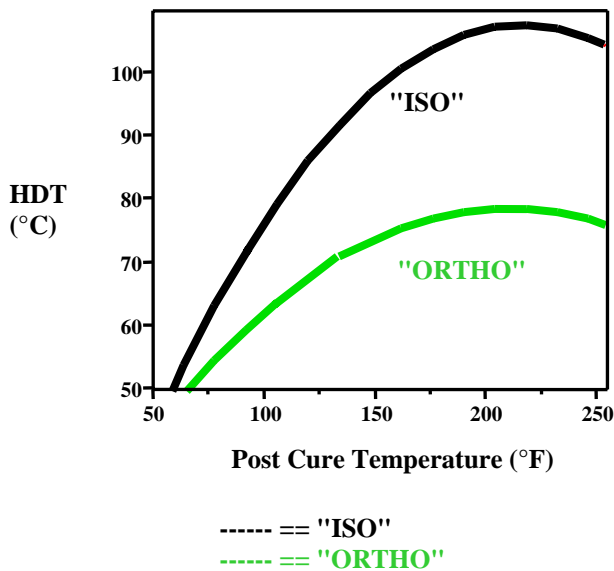


Figure 1

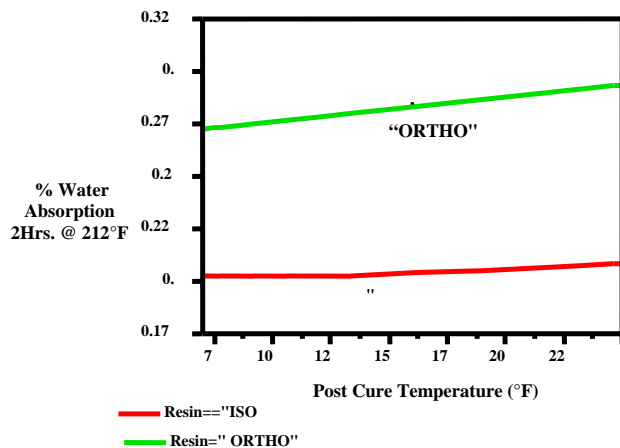


Figure 2

Water Absorption 2 hours @ 100C/212 F

.Analysis of the data confirms that the HDT is significantly lower with the Orthophthalic based resin (~176°F/80°C) as compared to the Isophthalic Acid

based resin (>212°F/100C). Knowing that the temperature of boiling water is 212°F/100C, (spaghetti water etc) having an HDT lower than 212°F/100C opens the opportunity for a premature failure.

The water absorption of the Orthophthalic Acid based resin compared to the Isophthalic Acid based resin reinforces the concerns in the kitchen. Even post curing the Orthophthalic Acid based resin up to 25 hours at 250°F didn't help the water absorption properties. High water absorption may explain blushing and thermal shock failure. PG/Orthophthalic Acid resins Orthophthalic Acid based resin should definitely not be considered for the harsh environment of the kitchen sink. However, both Iso and Ortho resins showed improved properties after being post cured.

Thermal Shock Testing (ANSI Z124.6, 70/190°F-21/88°C)

A series of sinks were manufactured with both and Orthophthalic/Pg resin and a NPG/Isophthalic resin then tested for ANSI Z124.6 thermal shock resistance. The sinks made with the Orthophthalic Acid based resin failed after 25 cycles while the NPG/ISO exceeded the 250 cycles without any type of failure.

Solid Surface Composition

Resin: Solid surface resins are specially formulated to produce non-gelcoated parts that can accept 50-65% filler which cures sufficiently to yield a good final product.

Filler: The most widely used filler is alumina trihydrate (ATH). The filler adds stiffness, dimensional stability, translucency, flame and smoke resistance. ATH filler ensures ease of fabrication and gives better physical properties to solid surface compared to calcium carbonate fillers.

Pigments: Background colors are generated using pigments specifically designed for polyester resins.

Granules: Solid surface panels ground up to specific particle sizes form granules. Using multiple colors, they are blended to produce granite or stone look.

Initiator: Also know as "catalyst" is the component instrumental in making the resin transform from a liquid to a solid state. Common initiators are methyl ethyl ketone peroxide or MEKP / acetylacetone peroxide (co-catalyst) for faster curing.

Recipe

The amount of resin used in solid surface is dependent on the particle size of the filler. The finer the particles, the higher the resin demand. The initiator, on the other hand, is resin dependent in addition to the ambient temperature of the matrix and manufacturing facility. The selection is made simple with the availability of summer and winter resins. For this experiment the recipe used is as follows using a batch mixer under vacuum:

- Resin 40%
- Filler 60%
- Initiator 2.00%

Manufacturing Methods

There are three methods used to produce solid surface. The most common is the batch process followed by continuous then compression molding (compression molding is a specialized process not used by your typical solid surface shop).

Batch Process

In the batch process method, resin and pigments are thoroughly blended together. Filler is then added (whether it is ATH or granite chips) and then mixed under vacuum for 5 - 10 minutes, (depending on the efficiency of the equipment) until the matrix is free of dry filler or agglomerates. The most efficient mixing takes place under vacuum, but the temperature of the matrix can increase significantly while mixing under vacuum. The reactivity will double if matrix is allowed to increase 10°C.

Release the vacuum then open the mixer. Scrape any dry powder off the blade back into the mixer, then mix again for an additional 5-10 minutes under vacuum. Release the vacuum, open the mixer, scrape the blade, and then add the initiator. Close the mixer and mix under vacuum for another five minutes. Release the vacuum and open the mixer.

Remove the mixer blade without scraping it (to prevent residual dry filler from dropping into the mix). Transfer the mixing pot (using proper safety equipment) to the pouring area. Start the vibration machine and pour the matrix into the mold, spreading the matrix evenly. Continue to vibrate for one minute after the matrix is level. The vibration removes air incorporated during the pouring step, but *excessive vibration causes settling, warpage, and poor stain resistance.*

After the matrix hardens, de-mold the part, and then place it in an oven to post cure.
COMPOSITES 2006

Continuous Operation

For continuous mixing, a computerized, automated vacuum mixer is used. It can produce 7-100 Kg/min (15-220) pounds/minute depending on the equipment. There can be multiple filler hoppers from 2-12 to handle aluminum trihydrate (ATH) and granite fillers. Each unit has its own initiator, solvent & pigment delivery systems.

Most have a heat exchanger to warm the matrix which helps guarantee consistency. It can also pull vacuum to remove the air from the matrix. The initiator, resin and filler are mixed by an auger to be deposited directly on the mold.

Post Curing Solid Surface made from Polyesters

When the solid surface parts are gelled and can be moved it is important to insure they are completely cured to meet the demands of the ANSI/ICPA-SS1-2001 and ISSFA standards. There are too many reasons complete cure of polyester can be compromised in production. The problems that contribute to undercure include: moisture, contamination, ambient conditions, improper MEKP levels, poor mixing, wrong filler, wrong pigments or the wrong initiator was used.

The parts should be post cured after gelling to maximize its full cure. But at what temperature and for how long? As mentioned before, Solid surface resins do not use the powerful promoters common in open molding operations due to their effect on color. Irregardless, a study performed under Dr. Laurence Loh's direction confirmed that even highly promoted resins must be post cured to attain maximum physical properties.

Complete Cure at Room Temperature 5

The objective of this study was to dispel the myth that an unsaturated polyester will naturally reach its maximum crosslink density over time at ambient temperatures. The method to determine complete cure in this study was measuring the T_g with a DMA (Dynamic Mechanical Analysis).

Castings were prepared using MEKP and a marine resin promoted with Cobalt 12% with the addition of DMA and DEA co-promoters. Clear castings were prepared at 0.125 inch thickness between two glass plates and allowed to gel and cure at room temperature.

The resin that was used in this study had a T_g of 76°C/169° F with parts being evaluated at 7 days, 1 month and 1 year. The castings had a T_g of only

45°C/115°F after one week 48°C/118°F after 1 month and remained at 48°C/118°F after 1 year when stored at 23°C/73°F. The study contradicts the belief that thermo-set polyesters will complete its cure over time at ambient conditions.

Solid Surface Resins for the Kitchen Environment Post Cure Study

This study was performed to determine the ideal post cure conditions for solid surface parts. A design of experiments (DOE) was generated to evaluate solid surface parts made with a NPG/Isophthalic acid base resin (T_g=108°C/226°F) and the effect of post cure range from 0-25 hours between 70°/250°F-21/121°C.

The physical properties for this study were selected to provide empirical data rather than pass/fail values. The conclusion had to be accurate, demanding test criteria that insured objective results with minimum human error, using reliable equipment that would give us measurable data having a high degree of confidence of 95% or better.

Design of Experiments (DOE)

A Design of Experiments or DOE is an organized method to determine the relationship between different factors in a process and how they affect the output of that process. In our case we are looking at the effect of two factors, “Temperature and Time” and how they affect the responses of specific physical properties. The DOE uses mathematical statistics to make a thorough measurement of the factors and their interactions.

The program used in this study was “ECHIP” (Experiments in a Chip). We selected the variables with a bold numerical range to overcome any statistical errors. Echip has a built in algorithmic design capability to remedy any infeasible variable combinations.

Variable	Range
Temperature C/F	70-250
Time, hours	3-25

The low temperature selected was the ambient temperature of the test lab. The high temperature of 121°C/250°F was selected because of the equipment capabilities in the solid surface industry and because the temperature is well above the T_g of the resin,

The post cure time range was chosen to compare no post cure for any time period to a manufacturing facility that leaves their parts in the oven overnight or worse case scenario of 25 hours. The time could also help predict any polymer degradation that may take place for a given temperature. This can be important when
COMPOSITES 2006

stove tops are installed in the countertop or boiling water is poured into a kitchen sink. “Echip” generated a design experiment, with 16 trials, 5 replicates, linear with a center point being 71°C/160°F.

Responses

HDT and water absorption were presumed to be the most critical tests for the kitchen environment but it was important to extend the testing to a broader range. The tests we selected for this evaluation were HDT (deflection temperature), Barcol hardness, Flexural Modulus (stiffness), Tensile Modulus (toughness), Compressive Strength (psi), Water Absorption (24 hrs. at room temperature) and QUV-B for 500 hours (evaluated for Delta E). For this study anything under 95% confidence level was not considered as being significant.

Heat Deflection Temperature (HDT) ASTM D 648

The HDT is the temperature the casting yields under 264 psi and compares the relative heat resistance of the plastic. This property is important to predict any problems associated with heat from boiling water poured into the kitchen sink, hot utensils placed on countertops and heat from a countertop stove. See Figure 3.

Test Results:

- The highest HDT value observed was 226°F (108°C).
- Higher temperatures at shorter times is more significant than longer post cure times at lower temperature.
- Low post cure temperatures or no post cure resulted in failing to attain ultimate HDT.
- HDT decreased after extending the post cure time past the T_g for extended time period.

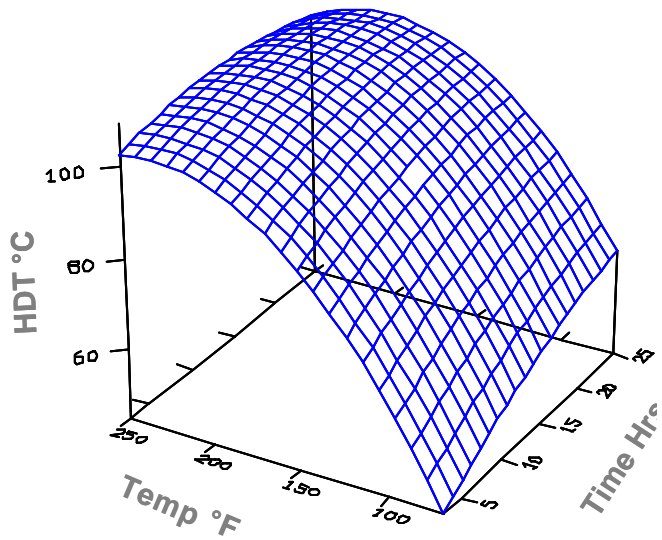


Figure 3 HDT – Post Cure Temperature vs. Time
Water Absorption

Parts are submerged in water for 24 hours at 25°C. The parts are weighed to calculate the % water absorption as weight gain. This test predicts any unexpected and undesirable moisture absorption that can predict problems associated with staining and thermal shock failure. Since the solid surface parts were manufactured under vacuum resulting in no voids, the water absorption for all test specimens was very low. It is only when the graph scale is magnified do you see an improvement in water resistance with post cure.

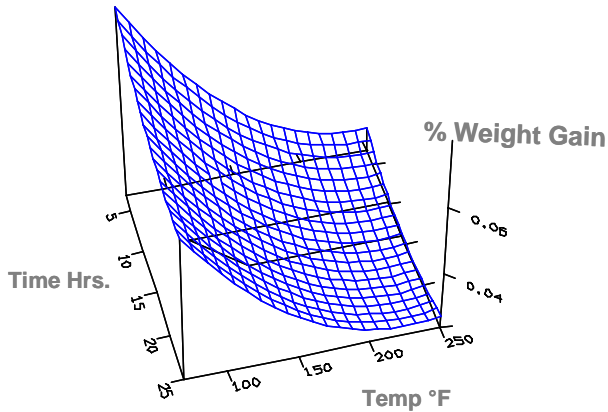


Figure 4 Water Absorption – Post Cure Temperature vs. Time

HDT and the water absorption tests help predict how a kitchen sink would hold up to the thermal shock of hot water and excessive heat of a countertop stove.

Barcol Hardness (ASTM D 2583 -79)

Barcol hardness is a value that selects a specific value for how vulnerable the product is resistant to penetration by a foreign agent. The Barcol GYZJ-934-COMPOSITES 2006

1) gauge is the tool for measuring hardness. It has a spring loaded indenter which gives an instant dial reading. Similar to the previous example the rate of hardness improved with higher post cure temperatures.

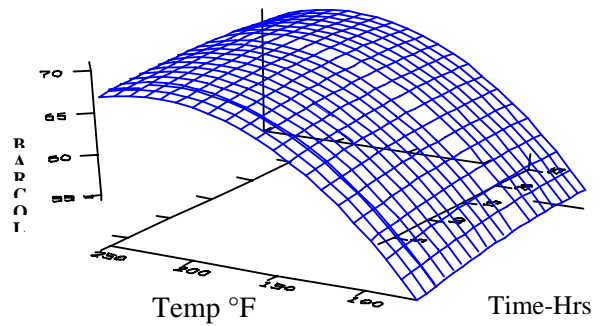


Figure 5 Barcol Hardness – Post Cure Temperature vs. Time

Tensile Modulus ASTM D 638 (x10⁵ psi)

Tensile modulus is the measurement of the lateral strain to the axial strain. It is also referred to as Young's Modulus. Simply described as the stress in tension or stretching.

The graph shows an improvement in physicals immediately after being exposed to the high temperatures for short times. However, when held for a long time at the high post cure temperature there is a great decrease in elasticity.

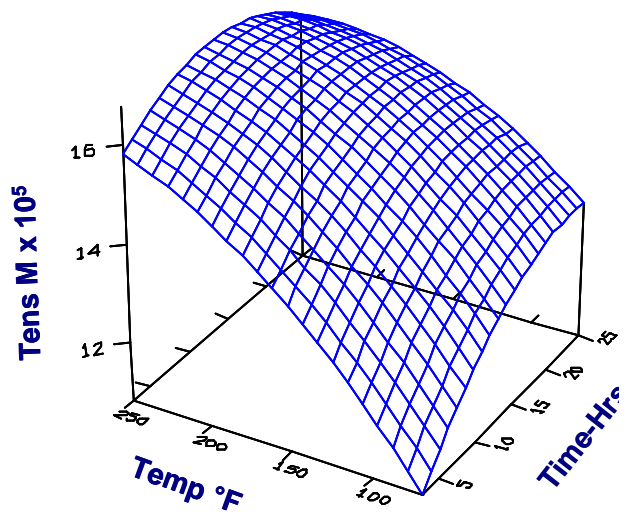


Figure 6 Tensile Modulus– Post Cure Temperature vs. Time

Flexural Modulus ASTM D 790

Flexural modulus measures the stiffness of the part also known as the "Elastic limit of stress/strain". The measurements were taken on a Instron Series IX Automated Materials Testing System.

The graph below shows that there is an immediate improvement in physical properties with post cure. The flexural modulus begins to degrade after being exposed to 121°/250°F for over 16 hours.

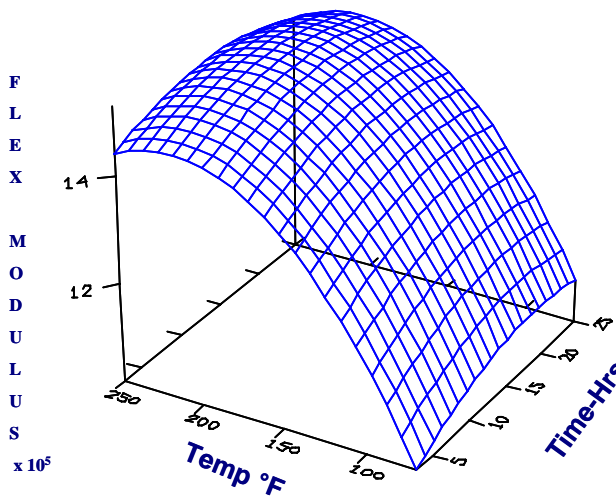


Figure 7 Flexural Modulus - Post Cure Temperature vs. Time

Color Fastness QUV-B Tested for 500 Hours

The QUV-B Chamber accelerates degradation of the part with the use of a lamp that has the wavelength of sunlight. Colorfastness failures are a major reason for not passing the ANSI/ICPA-SS-2001 standards.

The results confirm the need for post curing to pass this test. However, the graph does not show the color contribution of exposure to high temperatures for long periods of time.

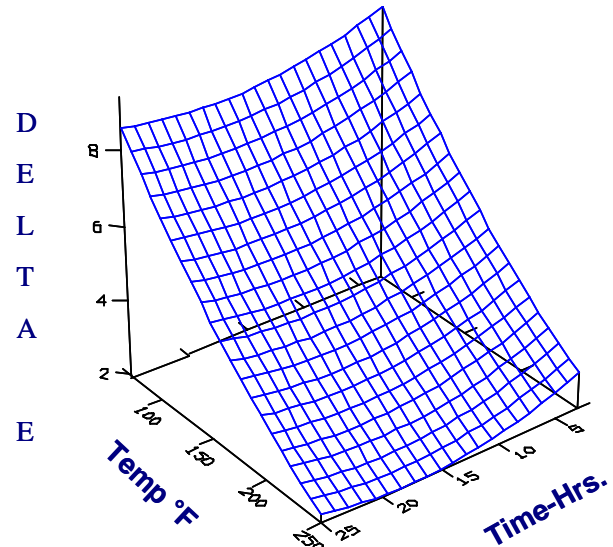


Figure 8 Delta e color change – Post Cure Temperature vs. Time

Quality of Solid Surface

The most critical part of solid surface manufacturing is "product quality." To ensure quality, both the International Cast Polymer Alliance (ICPA) of the Association of Composites Manufacturers (ACMA, formerly CFA) and the International Solid Surface Fabricators Association (ISSFA) have established quality standards. These standards ensure that quality products are being produced and installed with skilled workmanship and that the final appearance is acceptable for all parts used in all architectural applications.

In order to meet these tasks we have to rely on either Manufacturers or Independent laboratories with proper equipment to perform the tests that apply to our application and generate reliable results with minimum variability.

Industry standards for the Kitchen & Bath Arena include:

- ASTM – American National Standards Institute, Inc.
- NEMA – National Electrical Manufacturers of America
- IAPMO – International Association of Plumbing and Mechanical Officials
- ISSFA-2-01 (2002)
- ANSI/ICPA-SS1-2001

Conclusion

1. Parts stored at ambient temperatures will not completely cure over time.
2. The higher the post cure temperature, the higher the physical properties up to a point.
3. The maximum cross link density is achieved when every carbon-carbon unsaturated bonds have reacted with the cross-linker and the end groups of each cross-linking molecule are attached to different polyester chains.
4. To reach maximum cross-link density during postcure, an unsaturated polyester resin should be heated to or slightly above its T_g .
5. Time plays almost no role in post cure, except exceptional long times at high temperatures will cause the polymer to degrade.
6. When the parts were heated above $121^{\circ}\text{C}/250^{\circ}\text{F}$ (which was above the glass transition temperature (T_g) of the resin) for extended periods of time we saw a decrease in physicals.
7. It is imperative to make sure the entire part is heated evenly and confirm how long it takes. This amount of time will determine how long the part should be post cured.
8. Solid Surface parts stored at ambient conditions for extended time periods then post cured showed significant improved in all physical properties

REFERENCES

1. International Cast Polymer Alliance of the Composites Fabricators Association" (ICPA/ACMA)
2. International Solid Surface Fabricators Association" (ISSFA)
3. Echip Inc. 7460 Lancaster Pike, Suite 6, Hockessin, DE 19707.)
4. The Chemistry & Manufacturing Basics of Solid Surface, Kenneth Lipovsky, published in the Polymer Connection 2004
5. Reichhold Corporate Research Center Sterling Forest NY, Dr Laurence Loh VP Director of Research

Glossary of Terms

ICPA=International Cast Polymer Alliance

ISSFA=International Solid Surface Fabricators Association

DOE = Design of Experiments

DSC =Differential Scanning Calorimetry

T_g =Glass Transition Temperature

Authors Biography:

Kenneth Lipovsky, CCT-I, CP, M; Applications Specialist-Cast Polymer Reichhold Inc. RTP NC

Ken Lipovsky started in the composites industry in 1972 and has been with Reichhold, Inc. since 1980. A native of New Jersey, he currently resides in Durham, NC. Before this latest position Ken was the Technical Service Support for the Composites Distribution Team providing technical service for Reichhold's US Plants and the Cast Polymer Team.

Prior to Reichhold, he worked with Composite Technology Division of the DeLorean Motor Company, LOF Plastics in Detroit Michigan, and Marco Chemicals in Linden NJ & Jacksonville AR.

Ken has written articles and papers on solid surface and many cast polymers applications. He has presented and taught in various countries including Mexico, Africa and South America.

Ken is a certified CCT instructor for Cast Polymers, Solid Surface, Open Molding and Marine courses. Ken supports customers for Bowling Ball, Body Patch, Button, Clay Pipe, Clear Casting, Furniture, Surfboard, Cultured Marble, Solid surface, Engineered Stone, Polymer concrete, and gel coat applications.