

Improving the Thermal Stability of Somos™ 6110 Photopolymer Patterns

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Abstract:

With the increased emphasis on functional testing and tooling applications using stereolithographic rapid prototyping (RP) techniques, the need for RP materials with improved thermal stability is becoming more pronounced. Glass transition temperature and Heat deflection temperature are two commonly used measures to determine the thermal stability of a polymeric material.

This paper shows the effect of different postcuring techniques on the heat deflection temperature (HDT) of DuPont Somos™ 6110 photopolymer. In addition, the benefits of using heat transfer mediums which provide neutral buoyancy and thus minimize thermal distortions are discussed.

Introduction:

The epoxy based stereolithographic photopolymers possess good dimensional and mechanical properties. The good dimensional properties are mainly attributed to the inherently low shrinkage during photocuring compared to the earlier acrylate based photopolymers. However, a major limiting factor of the first generation of epoxy photopolymers was their lower photo sensitivity. The recently introduced second generation epoxy resin **DuPont - Somos™ 6110** provides significant improvements in photo sensitivity, allowing increased throughput from the stereolithography (SL) systems. Somos™ 6110 is used in the Helium-Cadmium laser systems like SLA-250™ from 3D Systems Inc., USA and STEREOS DESKTOP™ from EOS Inc., Germany.

With the improvements in speed and physical properties possible from epoxy materials, the focus has now turned towards functional applications of the SL patterns. The SL patterns are now being widely used in a range of applications such as silicone rubber molding, injection molding as well as investment casting. With the ever increasing use in these tooling applications, the need for greater thermal stability of these patterns has become crucial.

This study focuses on methods aimed at improving the thermal stability of Somos™ 6110. The two main parameters that were looked into are the glass transition temperature (T_g) and the heat deflection temperature (HDT). These two parameters are related to the internal changes in the material.

Using the standard measuring techniques these two parameters were determined for the Somos™ 6110 epoxy photopolymer under various thermal postcure conditions. The relationships between these two parameters were studied with the objective of enhancing the HDT. Although no extensive quantitative data on the dimensional variations with thermal cure are available at this stage, a few preliminary results are presented.

Thermal Stability:

Two different temperature-dependent mechanisms exist in polymeric materials. The first mechanism is a reversible process representing the softening of a material with increasing temperature and is used to characterize the thermal stability. The second mechanism is the irreversible decomposition of the material due to heat. In this study we are primarily concerned about the first mechanism.

The thermal stability of polymeric materials can be expressed either by a temperature or time limit (at some specified temperature) up to which the material remains useful. A material is stable if no noticeable change occurs over any length of time or if any changes that occur are reversible. Typically, the point of thermal instability is observed by noting the onset of phase transitions that take place within the material. Two types of transitions are commonly observed on heating or cooling a plastic - a first order and a second order transition[1].

A first order phase transition is observed when the material properties change abruptly. A second order phase transition is much more gradual and can usually be related to the amorphous segments of the polymer. The most prominent of the several second order phase transitions is the glass transition. It is an intrinsic material property characterizing a reversible softening behavior. According to ASTM E1142, glass transition is defined as, "the reversible change in an amorphous material or in amorphous regions of partially crystalline material, from (or to) a viscous or rubber condition to (or from) a hard and relatively brittle condition". The glass transition temperature (T_g) is usually taken as the approximate midpoint of the temperature range over which the second order transition takes place.

Besides the occurrence of transitions, certain properties of the plastic are continuously changing with temperature. The vibration of the chain segments increases with temperature and this motion weakens the cohesive forces between the molecules. Decreased cohesion results in softening of the material (compromising its structural stability) and correspondingly affects the physical properties. On the basis of practical experience, criteria have been established which

determine the limit of structural stability under load and heat. One such criterion is the HDT. A brief review of T_g as well as HDT will be provided below which will help us better understand the experimental results.

Glass Transition Temperature:

Glass transition is an important parameter in deciding the applications of many crystalline and non-crystalline polymers. It represents the temperature ranges at which the polymer matrix transitions from the glassy state to the flexible state. Below the T_g, however, the unreacted groups may not be able to crosslink due to lack of matrix mobility. The polymer chain segments cannot move around -- they are frozen in place and the behavior of the material changes from ductile to brittle. Above the glass transition temperature there is enough mobility within the object matrix to allow segmental chain motion, and the chains can move more or less freely around. As the temperature increases this freedom continues to increase until the matrix approaches the "liquid" state (if the polymer is not crosslinked). Even lightly crosslinked (or thermoset) polymers will have a glass transition that involves the motion of the linear chain segments between the crosslinks. If the crosslink density becomes high enough the glass phase transition will disappear.

Some of the main molecular parameters influencing the T_g are [2]:

- Chain stiffness
- Internal plasticization and
- Intra molecular forces

The mobility of the polymer chains is primarily affected by the barrier to their rotation around the backbone carbon-carbon bonds within the polymer matrix. This in turn is determined by the size of the substituent groups on the carbon atoms. The larger the substituent or the more hindered the rotation because of multiple anchoring (Van der Waals forces between the side groups on the chain), the higher the T_g.

Inclusion of low molecular weight materials (as side chains on the carbon-carbon bonds) which generally have lower T_g, plasticizes the polymer. Therefore, the higher the concentration of low molecular weight side chains the lower the T_g of the material. The internal plasticization can either be due to inter-chain or intra-chain plasticization. Inter-chain plasticization is caused by small molecules that solvate and allow the polymer chains to move and become flexible. Water, for instance, can act as a plasticizer lowering the T_g. Intra-chain plasticization occurs when the primary chain of the polymer has long side chains (which act as plasticizers or chain softeners).

Crosslinking has the opposite effect of a decrease in molecular weight. Increasing crosslink density increases T_g correspondingly. Most of the highly crosslinked thermoset polymers are amorphous.

Several methods exist to experimentally determine the T_g . One of the most commonly used methods is differential scanning calorimetry (DSC). It is based on the power compensated null balance principle, in which the energy absorbed or liberated by the specimen is exactly compensated by adding or subtracting an equivalent energy to a heater located in the sample holder [3]. As the sample material passes through the glass transition upon heating, its (apparent) specific heat abruptly changes due to an increased motion in the material. In practice, specimens of thin flat disks of the material, usually less than 0.6 mm thick, are encapsulated inside an aluminum pan (0.08 mm thick) with a lid crimped in place to ensure uniform heat transfer. Platinum resistance heaters and thermometers are used in the DSC to carry out temperature and energy measurements. Another commonly used method for determining T_g is differential mechanical analysis (DMA). Values obtained using DMA are typically higher than those obtained using DSC [4]. In this study DSC was used.

Heat Deflection Temperature:

As mentioned before, the T_g is an intrinsic material property characterizing the reversible softening behavior of the material. Many techniques have been developed to determine, in a well-defined way, the maximum usable temperature of a material due to softening. Heat deflection temperature (HDT) measurement is one such practical technique.

The HDT is the temperature of the material at which a certain deformation is induced under flexural load of the test specimen. The test provides a measure of the thermo-mechanical stability of the material. A rectangular specimen 5" x 1/2" x 1/8" is placed on two supports 4" apart, immersed in a heat transfer medium (oil bath) with a load applied at its center to give a maximum fiber stress of 66 psi. Higher loads were not used because there is no advantage to using higher loads when measuring deflection temperature of the present-day plastics with present-day instruments¹. With the bar immersed and the load applied, the temperature is raised at a rate of 2 °C/min. The temperature at which a deflection of 0.010 inches occurs is noted as the HDT under flexural load of the material. The experimental testing reported in this study was done according to the ASTM D 648 standard.

Experimental Discussion:

The eventual physical properties are greatly influenced by the postcuring conditions used. The most common postcure techniques employed in curing green patterns are ultraviolet (UV) and thermal cure. The UV cure is intended to polymerize any uncured liquid trapped within the solid by irradiating the patterns

¹ASTM D 648 - 82 (Reapproved 1988) - Standard Test Method for Deflection Temperature of Plastics Under Flexural Load. Annual Book of ASTM Standards 1993. Section 8.

with broad-band UV light. Thermal cure, however, induces additional polymerization by increasing the mobility of the polymer chains allowing additional chemical reactions to occur. In this study several thermal postcuring techniques to improve the thermal properties were investigated.

With thermal postcuring techniques, concerns regarding dimensional distortions become important. At elevated temperatures due to the softening behavior of the material, distortions are likely to occur in unsupported regions under the influence of gravity. One way of reducing these thermally induced gravity distortions is to heat treat the specimens in a dense heat transfer medium like silicone oil. The silicone oil also acts as a uniform heat transfer medium. The silicone oil used in this study is a commercially available DOW CORNING® 550 fluid which has a specific gravity of 1.1.

Besides the gravity induced distortions mentioned above, thermal treatment can induce distortions due to swelling. Though this behavior has not been extensively investigated, a few preliminary experiments have been performed and the results are discussed later.

Another factor which can influence the dimensional stability as well as the glass transitions is the humidity. The Somos™ 6110 is designed to produce good dimensional characteristics at higher humidities. Studies are underway to study the effects of humidity on the glass transition and will be reported at a later date.

The experimental plan is essentially divided into three components. First, the T_g is determined using the DSC approach. Second, the HDT is determined using the ASTM D648 standard by thermally postcuring the specimens in air at various temperatures. Third, the HDT is determined by thermally postcuring the specimens in a silicone oil medium at various temperatures.

For the T_g determination, sample specimens 0.2 mm thick and 25 mm cross-section, were imaged in Somos™ 6110 using a SLA-250™. The imaged specimens were cleaned with tripropylene glycol monomethyl ether (TPM) and isopropyl alcohol to remove the residual uncured liquid polymer. Thermal postcuring was done in a programmable convection oven. The green parts are considered to be postcured at 25 °C (ambient temperature) while the UV parts are considered to be postcured at 40 °C (the UV chamber temperature). For the HDT determination, the specimens were made with dimensions as specified in the ASTM D 648 standard. The green HDT specimens were cleaned as mentioned above. Four HDT specimens were used at each postcure condition. The green T_g and HDT specimens were later postcured under conditions described in Table 1.

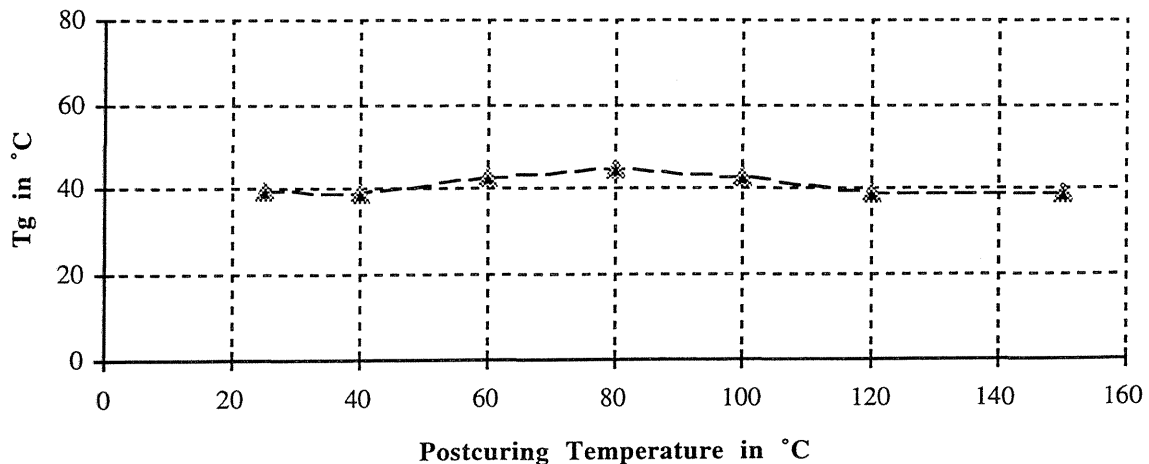
The T_g specimens were later measured for the glass transition using a DSC apparatus. The specimens were initially chilled below 0 °C before heating. A standard 10 °C/min. rate of temperature increase was used for all measurements with a maximum temperature of 100 °C. The results from the DSC measurements

are as shown in Figure 1. The T_g is measured as the inflection point in the glass transition phase curve on a temperature versus specific heat graph. The T_g of the material ranges from 39 °C and 44 °C. This seems to indicate that no significant changes in the phase transitions are taking place as a result of thermal postcuring. The variation of T_g with thermal postcuring in silicone oil has not been investigated. However, no significant differences may be observed.

Table 1: Postcuring Conditions for T_g Determination

#	Postcure Temp.	Description
1	25°C	Green patterns (ambient curing)
2	40°C	UV cured patterns (UV chamber temp.)
3	60°C	0.5hr ramp up; 1hr at 60°C; 0.5hr ramp down.
4	80°C	0.5hr ramp up; 1hr at 80°C; 0.5hr ramp down.
5	100°C	0.5hr ramp up; 1hr at 100°C; 0.5hr ramp down.
6	120°C	0.5hr ramp up; 1hr at 120°C; 0.5hr ramp down.
7	150°C	0.5hr ramp up; 1hr at 150°C; 0.5hr ramp down.

Figure 1: Influence of Postcure Conditions on T_g for Somos™ 6110



The heat deflection temperatures of the specimens postcured in air are shown in Figure 2. The HDT appears to improve with the postcure operations. Table 2 describes the postcure conditions of the specimens immersed in a silicone oil medium whose density was selected to provide neutral buoyancy for the part and thus reduce distortions during postcure. Four specimens were used at each postcure condition. The heat deflection temperature of the specimens postcured in silicone oil are shown in Figure 3. As shown in Figures 2 and 3, the HDT appears to improve

with the thermal postcuring. The HDT of the specimens postcured in silicone oil appears to be higher than the air postcured specimens. This may be because the specimens postcured in oil had a longer cure cycle and therefore were held at an elevated temperature for a longer duration. Longer and more gradual rate of increase in temperature appears to improve the HDT. However, the HDT appears to reach a peak at a postcuring temperature of 100 °C in silicone oil, while the trend in air postcured specimens appears to be more linear. This result needs to be further investigated.

Figure 2: Influence of Postcure Conditions on HDT for Somos™ 6110

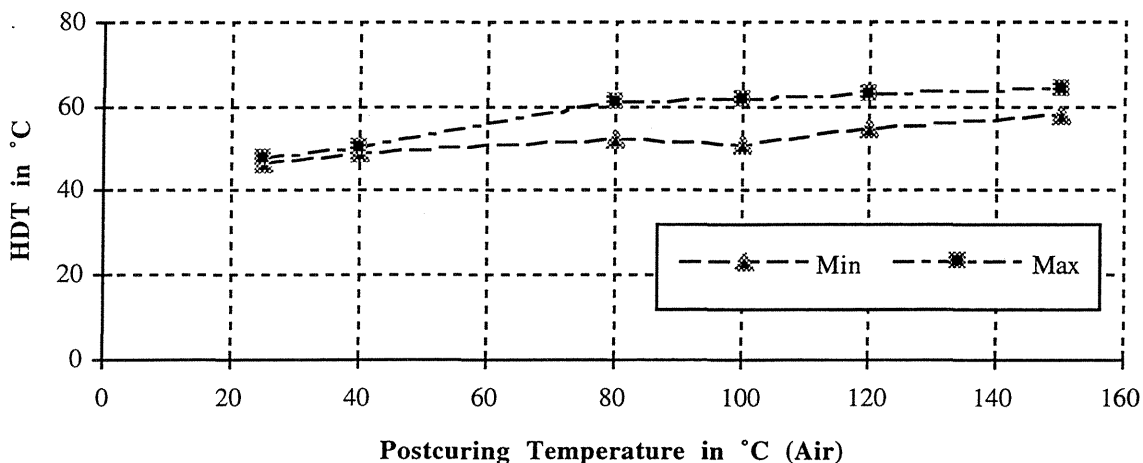


Table 2: Postcuring Conditions for HDT Determination in Silicone Oil

#	Postcure Temp.	Description
1	25°C	Green patterns (ambient curing)
2	40°C	UV cured patterns (UV chamber temp.)
3	60°C	2hr ramp up; 1hr at 60°C; 2hr ramp down.
4	80°C	2hr ramp up; 1hr at 80°C; 2hr ramp down.
5	100°C	2hr ramp up; 1hr at 100°C; 2hr ramp down.
6	120°C	2hr ramp up; 1hr at 120°C; 2hr ramp down.
7	150°C	2hr ramp up; 1hr at 150°C; 2hr ramp down.

In the thermal Postcuring of the SL patterns dimensional stability concerns are critical. Efforts are underway to fully characterize the nature of dimensional distortions induced during thermal postcuring. A few preliminary studies have been done to determine the changes in the dimensions of the specimens. Our results show that both UV as well as thermal postcuring increases the dimensions

by 0.1% to 0.13%. Though the thermal postcuring in silicone oil does seem to improve the dimensional increase, the specimens showed lesser gravity distortions. However, specimens which were conditioned in a desiccant chamber at 0% relative humidity for two days and thermally postcured showed a drop in the dimensional increase. Figure 4 illustrates this phenomena. This result seems to indicate that thermal postcuring in the absence of moisture helps maintain the dimensional stability.

Figure 3: Influence of Postcure Conditions on HDT for Somos™ 6110

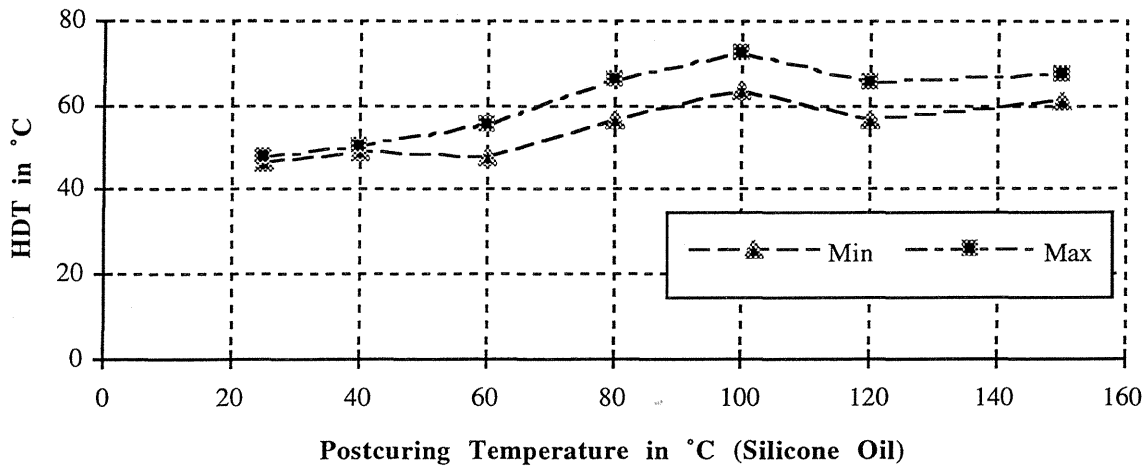
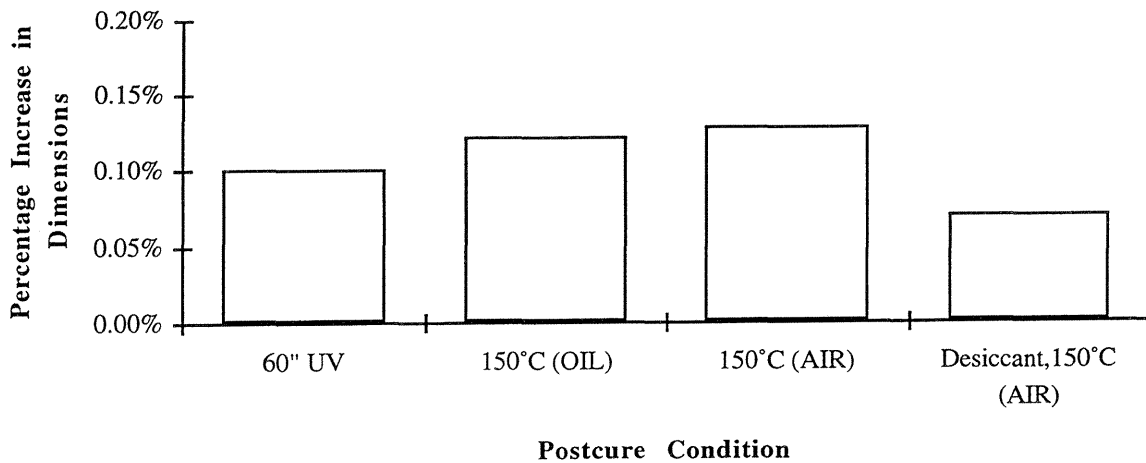


Figure 4: Increase in Length of HDT Specimens due to Postcuring of Somos™ 6110



Conclusions:

- The T_g does not vary significantly with thermal postcuring.
- The HDT, however, shows a increase of 15 to 25 °C under the same postcure conditions.
- The T_g is lower than the HDT of the material.
- Thermal postcuring in silicone oil improves the HDT over postcuring in air - perhaps due to extended time at temperature.
- Better dimensional stability can be achieved by conditioning the parts at 0% RH before thermal postcuring.

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Acknowledgements:

This presentation is a result of the efforts of many people in the Somos™ Materials Group. We would like to acknowledge the valuable assistance rendered to us by Mimi Keating and Al Colombo in the evaluation of the test specimens. We would like to thank Dr. Daniel Mickish and Dr. Glen Thommes for their continuous support and advice.

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