Influence of Post Curing Conditions on the Mechanical Properties of Stereolithographic Photopolymers

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Abstract:

Post cure methods have always been a critical issue for most of the currently used stereolithography photopolymers. Different post cure conditions can be used to enhance the mechanical and physical properties of the stereolithography models. To better understand the influence of post cure conditions on these material properties, an experimental study evaluating various post cure conditions has been conducted. Ultra-violet, thermal and ultra-sound post curing techniques are investigated and a comparative study is made for one epoxy based photopolymer - Somos™ 6100. Similar results should be attainable for other epoxy based photopolymers.

Introduction:

The post curing stage still remains a critical element in the processing of models built using stereolithography. The eventual mechanical properties as well as the physical properties are greatly influenced by the post curing conditions used. Thermal and the ultra-violet post curing techniques have been in use for quite some time now. In this study a third approach involving ultra-sound post cure has been investigated. Initial results show that the ultra-sound post cure is better than the UV post cure. However, since the physical properties are very much dependent on the photopolymer material, no generalizations to other materials can be made. The photopolymer used in this study is an epoxy based resin called Somos™ 6100. Epoxy based photopolymers in general have substantially better mechanical properties than acrylate photopolymers. Further improvements in the properties of the epoxy based green parts is achievable by a proper choice of the post curing conditions.

To a large extent the most common post cure techniques employed in curing green parts are UV and thermal cure. UV cure is intended to directly polymerize any uncured liquid trapped with the solid by irradiating the part with broad-band ultra-violet light. Parts subjected to additional UV exposure show an increased concentration of acid initiators resulting in additional polymerization. On the other hand thermal cure induces additional polymerization in the green part by increasing the mobility of the polymer chains through higher temperatures. Yet another approach which can induce additional polymerization in a green part is ultra-sound curing where the degree of cross-linking is increased through a combination of vibrational and some thermal post cure. The polymerized chains of epoxy molecules within the object matrix still contain some active groups and movement of the chain segments induced by ultra-sound vibrations and rise in temperature bring together unreacted groups causing additional monomer conversion and

cross-linking. In general, in the epoxy based materials, the photopolymer cure is initiated by the laser exposure. This laser curing will theoretically continue in time until the glass transition temperature(Tg) is reached. Above the glass transition temperature there is enough mobility within the object matrix to allow the acid molecules to initiate polymerization and for the unreacted groups to find each other and cross-link. Below the glass transition temperature, however, the unreacted groups may not be able to cross-link due to lack of matrix mobility. Post cure techniques that elevate the object temperature above the Tg should produce better mechanical properties. Table 1 presents a summary of the average values of various mechanical properties under different curing conditions. Table 2 shows the best and worst performance for the various post cure techniques.

#	*Post cure condition*	*Tmod (MPa)*	*Tstr (MPa)*	*Elon (%)*	*Fstr (MPa)*	*Fmod (MPa)*	*Shore D*	*Izod (Ft-lb/in)*	*HDT (C)*
1	60 min thermal post cure @ 80 °C	2645	68	5.3	105.0	2803	82	0.88	59.6
2	60 min thermal post cure@ 130°C	2172	68	5.5	**105.4***	2872	82	0.91	**69.1***
3	60 min thermal post cure @ 150°C	3180	69	9.7	105.7	**2922***	83	0.88	67.5
4	60 min ultra-sound post curing @ 80°C	2949	66	5.5	101.2	2811	82	0.77	60.3
5	60 min UV post cure in a PCA Oven	2585	61	5.3	94.1	2736	84	0.69	51.2
6	30 min ultra-sound + 30 min thermal post cure @ 80°C	**3722***	66	5.5	103.9	2884	83	0.69	52.8
7†	30 min ultra-sound + 30 min thermal post cure @ 130°C	3418	68	6.7	103.7	2890	84	NA	61.3
8	30 min ultra-sound + 30 min UV post cure in a PCA Oven	3692	65	4.7	100.0	2815	84	0.77	49.5
9	30 min UV post cure + 30 min thermal post cure @ 100°C	3179	66	8.1	100.0	2726	84	0.90	66.8
10†	30 min thermal post cure @ 100°C + 30 min UV post cure	3328	**70***	**10.3**	NA	NA	**85***	**0.95***	59.5

(*=Max value; NA= Not available; †=best overall)

Table 1: Average Mechanical Properties from Different Post Cure Conditions.

Experimental Conditions:

Ten different sets of post curing conditions involving varying degrees of ultra-violet, thermal and ultra-sound post cure have been investigated. The number of samples in each set was five. The UV post cure was done in a 3D systems, Inc. PCA-250 using 10 Philips TLK-40W / 05 bulbs. The thermal post cure was done using a BLUE-M programmable convection oven. In the ultra-sound post curing, a standard test condition was used throughout the study.

All the test samples in the ultra-sound post cure were subjected to the vibrational cure (using a Branson™ 220 ultra-sound cleaner operating at a frequency of 25 kHz) in a bath of silicone oil held at 80°C. All sample parts were post cured one hour following the completion of the part build. Parts were built without supports on a sheet of Mylar® glued to the platform, thus minimizing post processing. They were imaged by an Ar+ laser operating at 351+364 nm using an overlapped X-hatch with a 2 mil hatch spacing and 5 mil beam diameter. The parts were tested within one week of post curing. ASTM procedures were followed for all tests.

Discussion of Material Properties:

One of the initial results from this study is that the different post curing approaches, namely photo, thermal and mechanical post curing, have their relative merits and demerits in inducing better mechanical properties to the resulting parts. Though this study cannot claim to be comprehensive it nevertheless provides some valuable insights into understanding the influence of different post curing conditions for an epoxy based photopolymer. The following discussion explains the different mechanical properties and compares the relative merits of the various post curing methods studied. The different sets of post curing conditions represent typical ranges of thermal and UV post cure conditions generally used in the industry. It is observed that different curing conditions affect the various mechanical properties in differently. Table 2 lists the material property and the best and worst curing conditions based on the maximum and minimum values obtained as illustrated in the accompanying charts.

#	Material Property	Highest Max. Value Meas. (Longest Bar)	Lowest Max. Value Meas. (Shortest Bar)
1	Tensile Modulus	30 min ultra-sound + 30 min thermal post cure at 130°C	60 min thermal post cure at 80°C
2	Tensile Strength	30 min thermal post cure at 100°C + min UV post cure	60 min UV post cure.
3	Tensile Elongation	30 min thermal post cure at 100°C + min UV post cure	60 min thermal post cure at 80°C
4	Flexural Strength	60 min thermal post cure at 80°C	60 min UV post cure.
5	Flexural Modulus	30 min ultra-sound + 30 min thermal post cure at 130°C	60 min UV post cure.
6	Izod Strength	30 min thermal post cure at 100°C + min UV cure	60 min UV post cure.
7	Heat Deflection	60 min thermal post cure at 130°C	60 min UV post cure.
8	Shore Hardness	30 min ultra-sound + 30 min thermal post cure at 130°C	60 min thermal post cure at 80°C or 130°C

Table 2: Best and Worst Curing conditions for the various mechanical properties.

While the influence on some of the mechanical properties (e.g., tensile modulus, heat deflection temperature) was considerable, not much variation has been observed in the others (e.g., flexural modulus). It is observed that the ultra-sound curing in combination with thermal

curing offers improved mechanical properties. In general, a combination of cure techniques is preferred over a single technique. The most common technique, 60 min UV post cure, frequently produces the lowest maximum properties.

Tensile Properties:

In the evaluation of tensile properties, the three properties of interest are the modulus of elasticity, tensile strength and the percent elongation. *Stress-strain characteristics for plastics almost always show a linear region at low stresses, and a straight line drawn tangent to this portion of the curve permits calculation of an elastic modulus.*[1] This modulus is defined as the ratio of stress to the corresponding strain below the proportionality limit of a material. The modulus of elasticity (**tensile modulus**) is calculated by extending the linear portion of the load-extension curve and dividing the difference in stress corresponding to any segment on this straight line by the corresponding difference in strain. Many polymeric materials are visco-elastic in their stress-strain behavior and display significant non-linearity and strain-rate sensitivity. For materials where no proportionality is evident, the **secant modulus** is calculated. Secant modulus is calculated at a designated strain (typically 1% or 5%) and is obtained by dividing the corresponding stress by the designated strain.

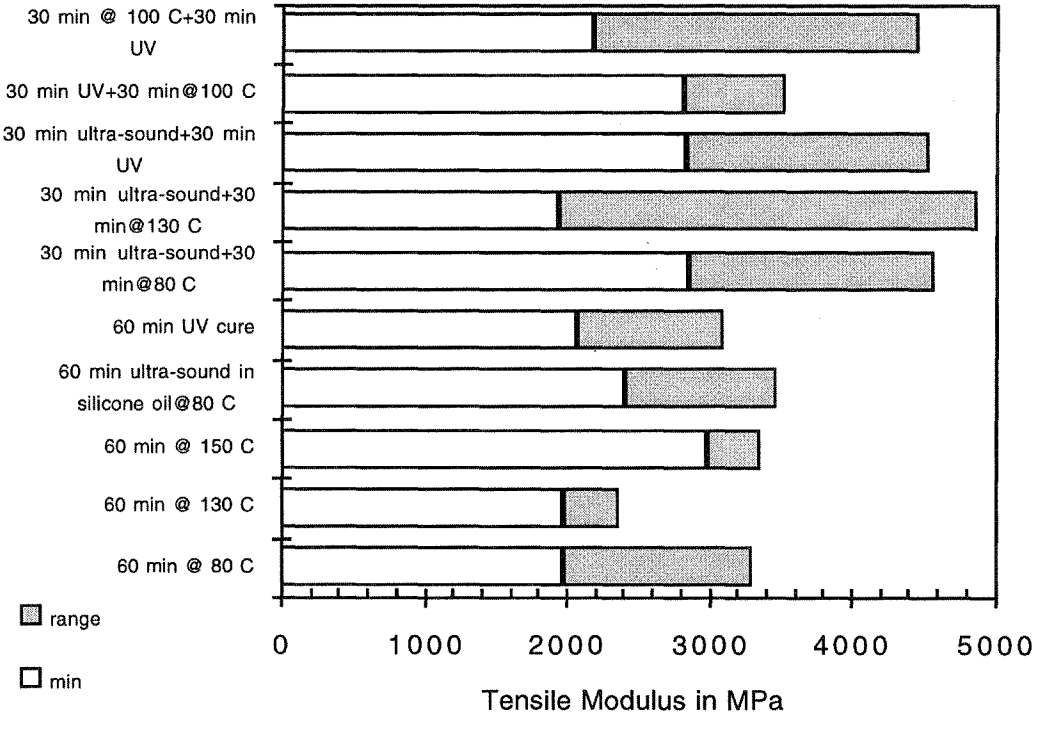

Figure 1: Tensile Modulus per ASTM D 638

All test results reported here were measured at pull rates of 0.2 in/min. Specimens were type M1 with a 1 cm square cross-section. Figure 1 shows the ranges of values for the various

[1]ASTM D 638 - Standard Test Method for Tensile Properties of Plastics. Annual Book of ASTM Standards 1993. Section 8.

post cure conditions. The ultra-sound approach seems to provide improved modulus values because of the higher mobility induced into the polymeric chains which allows the various unreacted chains to move closer and join together. The induced mobility followed by additional polymerization in a high temperature medium makes the material stronger. Another interesting result observed from the table below is that thermal cure followed by the UV cure yields better results as opposed to UV cure followed by the thermal cure under similar circumstances. This relationship seemed to hold for several other properties as well.

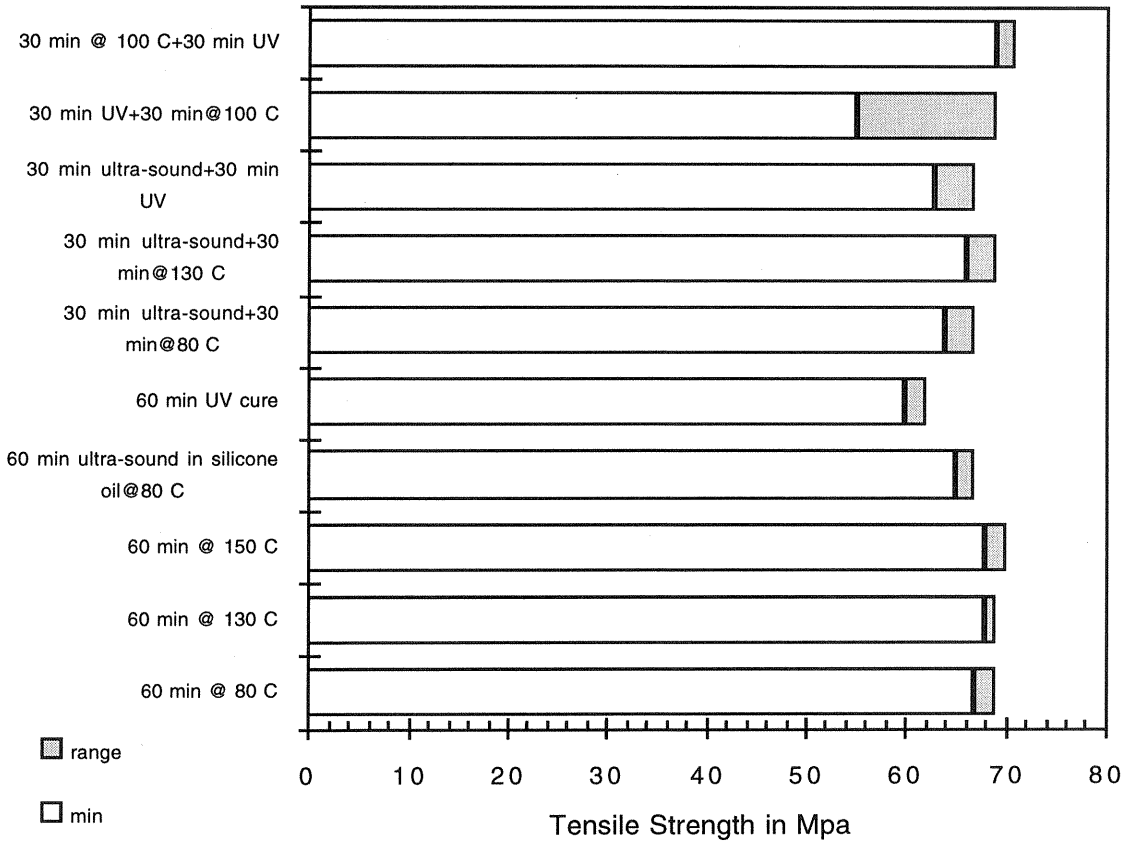

Figure 2: Tensile Strength per ASTM D 638

The **tensile strength** is the maximum tensile stress sustained by the specimen during a tension test. It is calculated by dividing the maximum load by the cross-sectional area of the specimen. Not much variation is observed in the tensile strength values. Though considerable variation is observed in the modulus, the small variations in the tensile strength of the samples suggests that the specimens are subjected to different levels of induced strain. Figure 2 shows that the ranges of variation of the tensile strengths in almost all the different post curing conditions are quite narrow suggesting that the material attains the optimal tensile strength during the building stage itself. Interestingly, the most widely used technique, UV only post cure, produced the lowest values.

The **elongation** of the test specimen as a percent of the gage length is evaluated to determine elongation behavior of the specimen under load. It is obtained by dividing the change

in gage length at the moment the applicable load is reached, by the original length. The result is expressed as a percentage. The experimental testing reported here was done according to the ASTM D 638 standard. Figure 3 shows the percent elongation under different conditions. It is seen that the percent elongations are lower under ultra-sound curing combined with thermal cure. Highest elongation values are obtained by curing the parts at 100°C for 30 minutes followed by a 30 min UV cure. In general it is observed that the vibrational cure lowers the elongation values while the thermal cure increases these values.

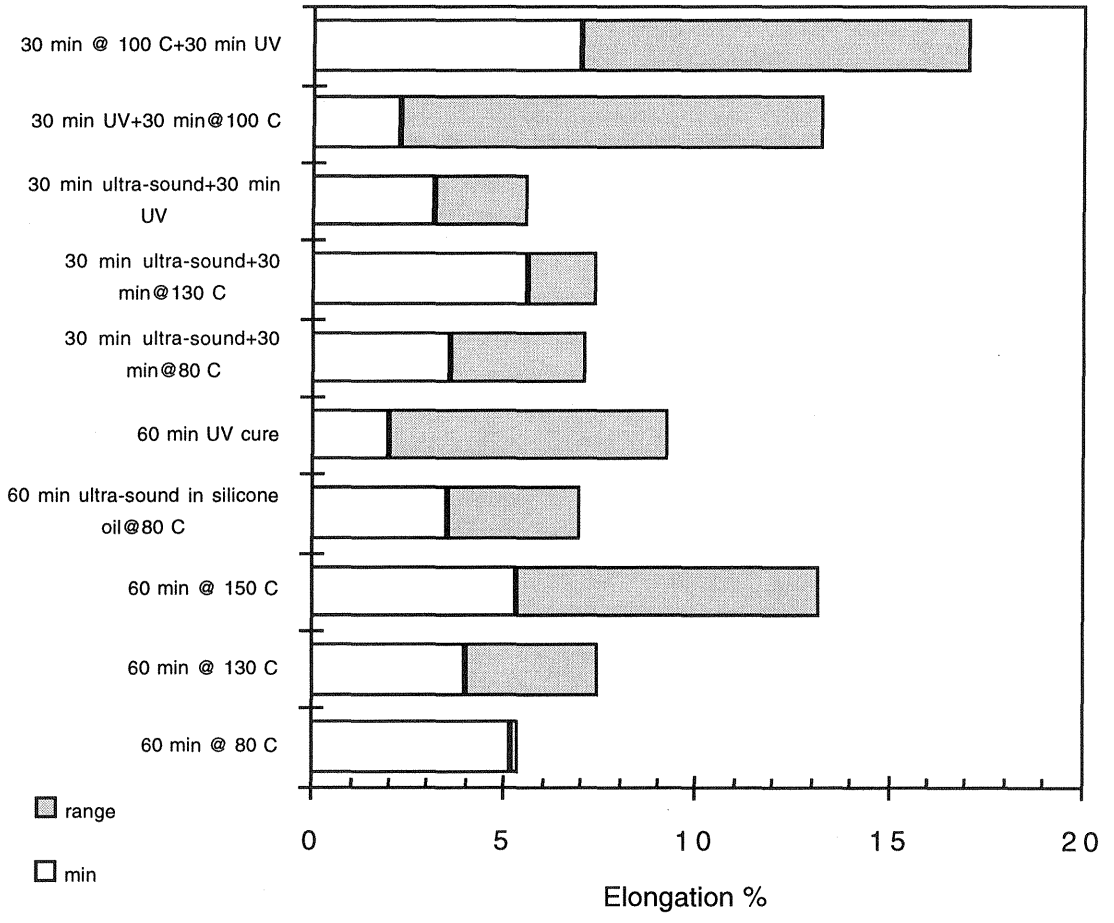

Figure 3: Tensile Elongation per ASTM D 638

Flexural Properties:

The two main flexural properties of interest in the evaluation of photopolymer materials are flexural modulus and flexural strength. These properties are evaluated using a three point loading system: center loading on a simply supported beam. When a simply supported beam of homogenous elastic material is tested in flexure the maximum stress is induced in the outer fibers at the midspan. This stress is designated as the **flexural strength** of the material at the moment of break. In case the test piece does not fail, the corresponding flexural strength at yield is evaluated. For materials that do not break at the maximum fiber strain (5% for ASTM D 790), there exists a point on the load-deflection curve at which an increase in the deflection

occurs without a corresponding increase in load. This point is used to calculate flexural strength at yield. In either case, whether in failure or in yield, the flexural strength is calculated.

As shown in Figure 4, not much variation is observed in the flexural strength. Interestingly, parts post cured just under UV showed slightly lower values than parts cured under conditions involving UV cure as well as thermal cure or UV cure as well as ultra-sound cure. This suggests that the increased mobility in the polymer chains resulting from either the thermal or vibrational cure helps improve the flexural strength. Both thermal and vibrational curing approaches yield similar results.

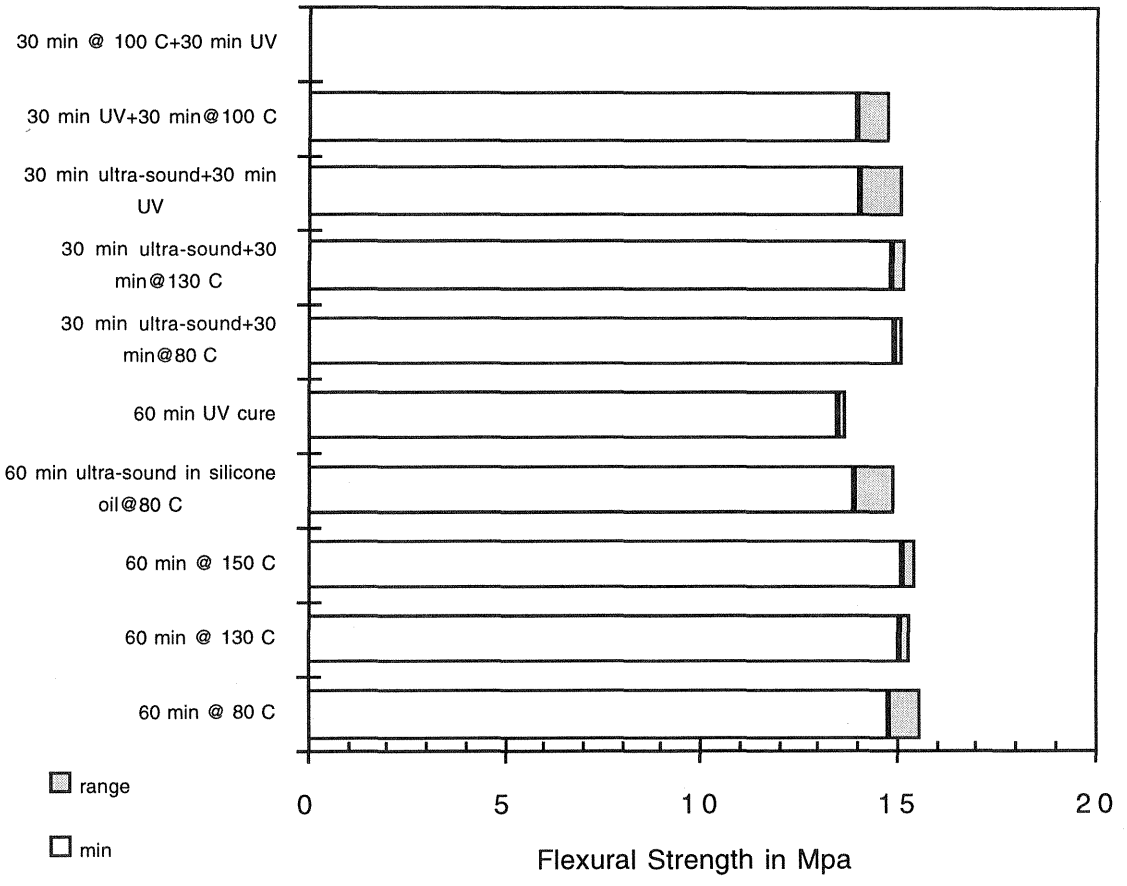

Figure 4: Flexural Strength per ASTM D 790

Flexural modulus is the ratio of the stress to the corresponding strain within the elastic limit. In case no apparent proportionality is observed, the flexural secant modulus is calculated. It is the slope of the straight line that joins the origin and a selected point on the actual stress-strain curve. The experimental testing reported here was done according to the ASTM D 790 standard.

Figure 5 shows the flexural modulus values for the ten different cure conditions. All curing conditions yielded more or less similar ranges of flexural properties, suggesting that the nature of

the post cure is not influential in varying these properties. Results for the parts cured at 100°C for 30 minutes followed by a 30 min UV cure are not available. In general, the thermal and vibrational cures do not significantly enhance the flexural strength of the samples. The slightly improved values obtained using the thermal and vibrational cures as opposed to just the UV radiation cure suggests that the polymer chain mobility which results due to the additional energy supplied using these techniques is responsible for inducing additional cure.

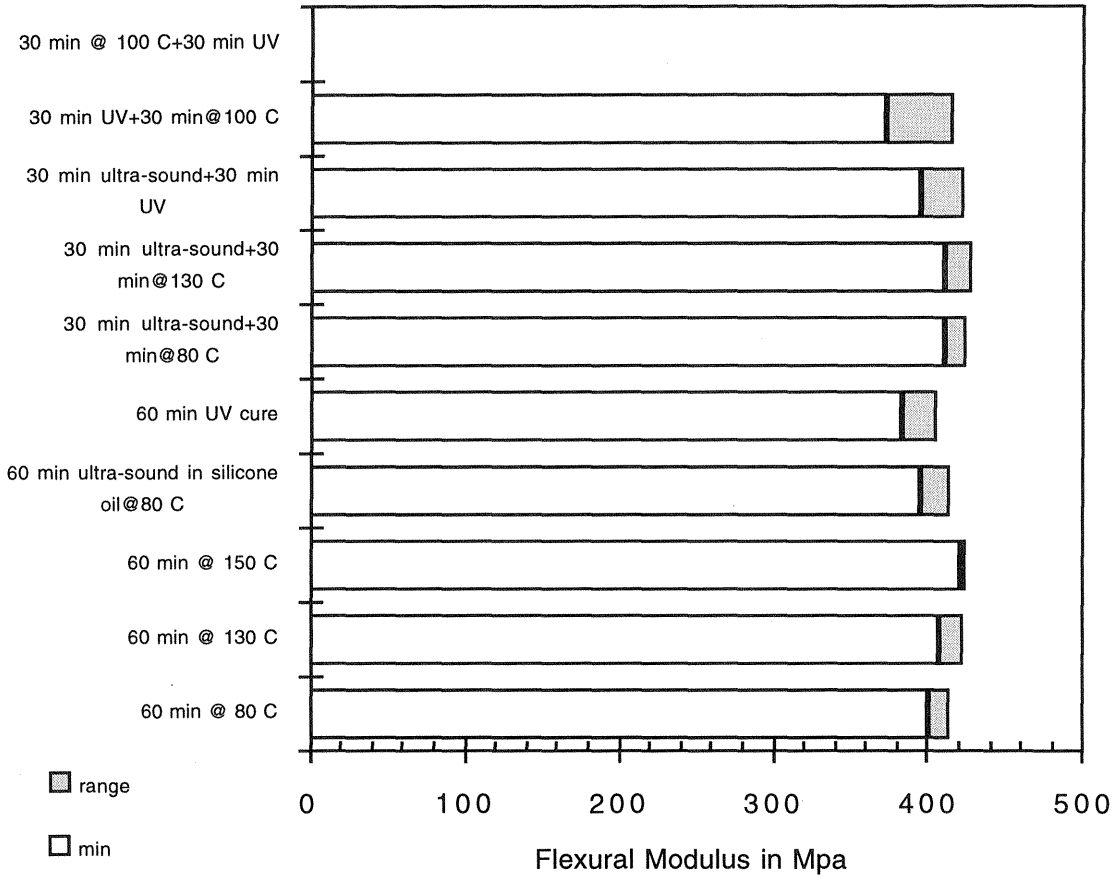

Figure 5: Flexural Modulus per ASTM D 790

Hardness Properties:

In this test a very hard indenter is pressed under a load into the surface of the material. For the photopolymer materials the most commonly used measure is shore hardness (Shore D). Here the indenter is a steel pencil in the form of a rounded cone. With a prescribed force exerted by a spring, the pencil is pressed into the material and the indentation depth is measured on a scale ranging from 0 to 100. Shore (durometer) hardness is a measure of the **indentation hardness** of the material and is inversely proportional to the penetration. The indentation hardness is dependent on the elastic modulus and the visco-elastic behavior of the material. However, the property only allows an empirical estimation of the hardness since there exists no simple relationship between the shore hardness and any fundamental material property. Type D

Shore durometer is typically used for reporting the hardness of photopolymer materials. The experimental testing reported here was done according to the ASTM D 2240 standard. Figure 6 reports the shore D values. The maximum values of hardness are obtained under a 30 minute ultra-sound cure followed by a 30 minute thermal cure at 130°C. However, most of the values fall in the range of 80 to 84 on the shore D scale, suggesting that post cure has a small effect on hardness.

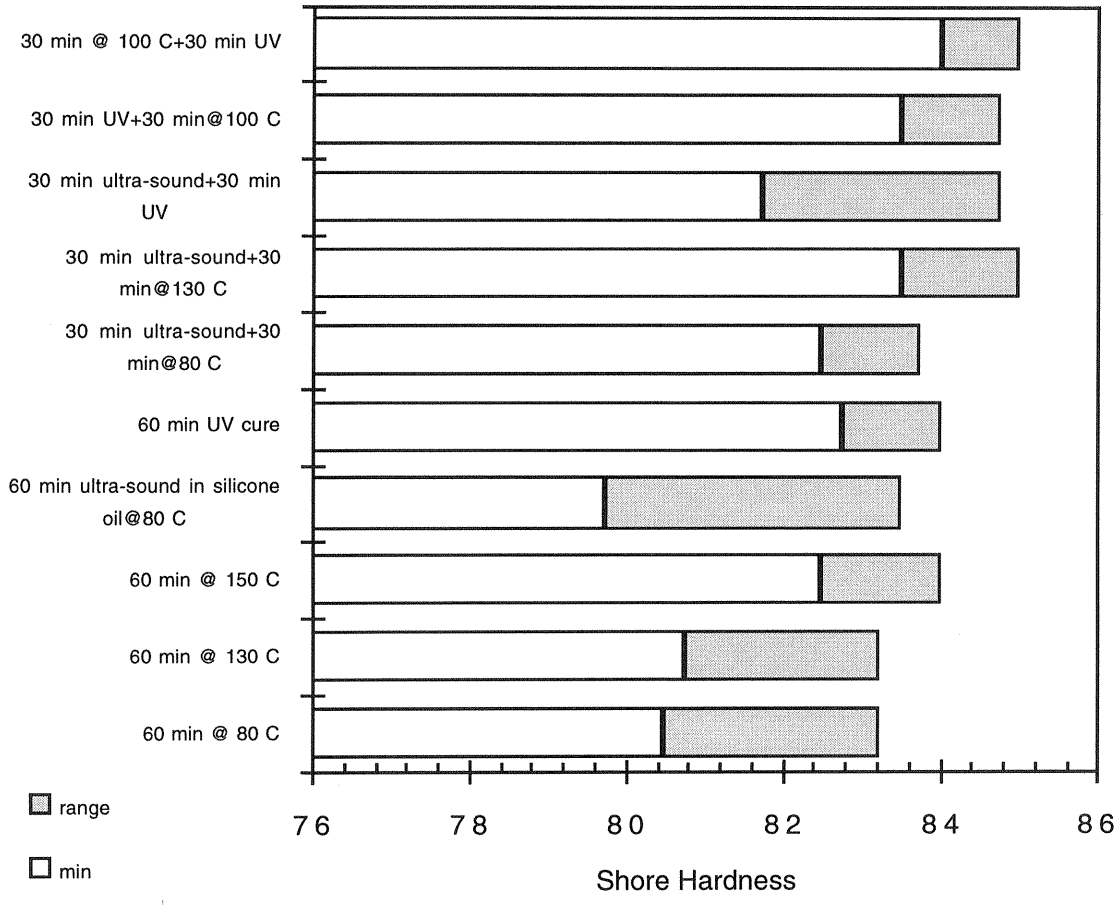

Figure 6: Shore 'D' Hardness per ASTM D 2240

Impact Strength

Impact strength of the material is a measure of the resistance to breakage by flexural shock. The typical method for evaluating the impact strength is the Izod type test in which a notched specimen is held as a vertical cantilever beam and is broken by a single swing of a pendulum with the line of initial contact at a fixed distance from the specimen clamp. (Some vendors have reported results for un-notched specimens or have not specified whether the specimens were notched. This data should only be compared to the data for notched specimens.) The experimental testing reported here was carried out according to the ASTM D 256 standard. Figure 7 shows the impact strength results. The results from the samples cured for 30 minutes in a ultra-sound chamber followed by a thermal cure for 30 minutes in an oven at 130°C are not

available. In general, thermal cure gives better impact strength compared to vibrational or radiational cures. However, as can be seen from the figure below, considerable variations are observed within in each data set.

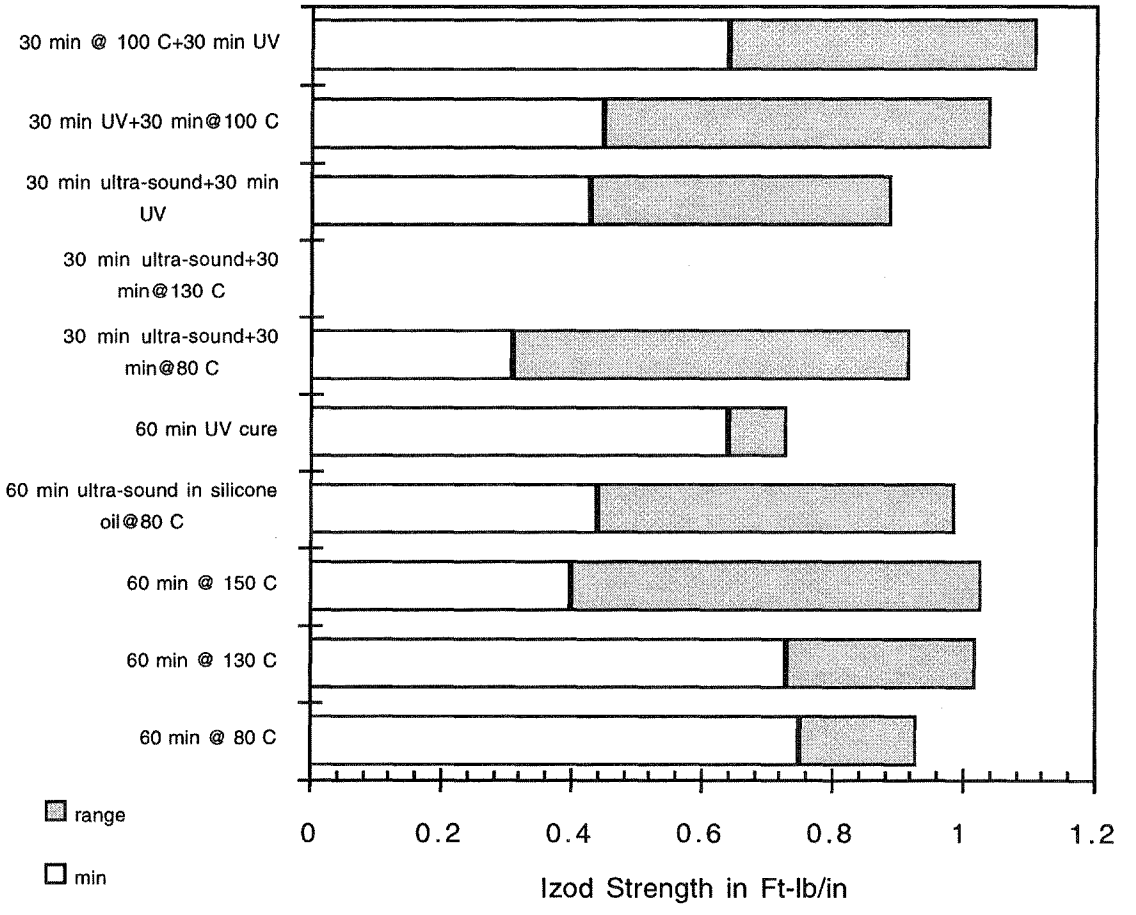

Figure 7: Izod Impact (Notched) Strength per ASTM D 256

Heat Deflection Temperature:

This test provides for the determination of 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 is tested as a simple beam while immersed in a heat transfer medium 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 instruments[2]. With the bar immersed and the load applied, the temperature is raised at 2° C/min. The temperature at which a deflection of 0.010 inches occurs is noted as the **heat deflection temperature** under flexural load of the material. The experimental testing reported

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

here was done according to the ASTM D 648 standard. Figure 8 shows the results of the heat deflection study under different post curing conditions. Thermal cure is more effective than the vibrational or radiational cures . Thermally induced distortions due to the effects of gravity in the samples can be minimized by placing the samples in a dense medium like silicone oil.

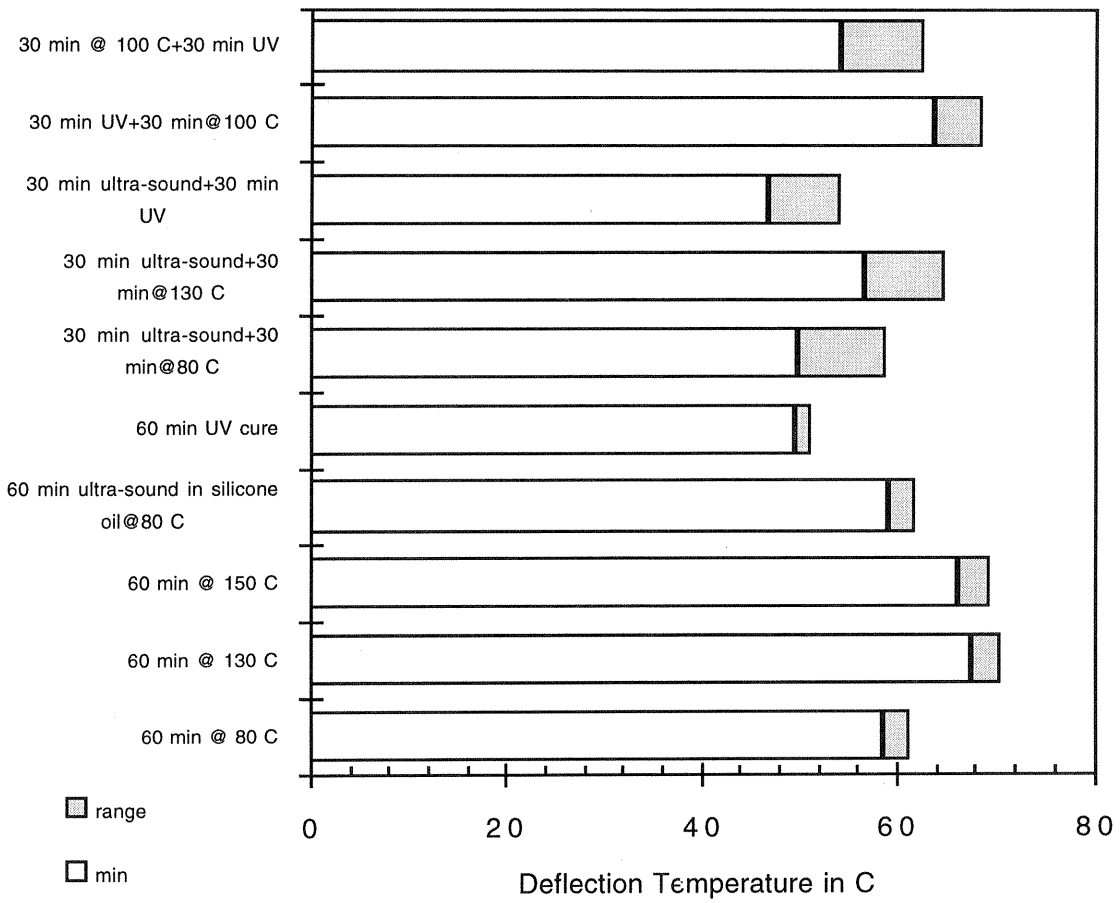

Figure 8: Heat Deflection Temperature per ASTM D 648

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