Design for Controlled Thermal Expansion Using Anisotropy in Parts Made from Liquid Crystal Stereolithography Resins

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Abstract

In previous publications we showed that liquid crystal stereolithography resins can be cured in a magnetic field to yield polymers with anisotropic mechanical and physical properties. A modified stereolithography (SL) process developed as a part of this research provides the flexibility to change alignment directions from one layer to the next. This is akin to altering the fiber direction in continuous fiber reinforced composites. In traditional continuous-fiber composites, parts are often constructed of plies containing unidirectional fibers. When the fiber alignment varies from layer to layer throughout the structure, lamination theory developed for composite mechanics can be used effectively to model the characteristic mechanical and physical properties. Of particular interest is that by using such a model, layered polymeric parts with very low thermal expansion coefficients in the x-y plane can be designed. In this paper we demonstrate that composite lamination theory provides a basis for estimating the thermal expansion properties of liquid crystal polymer SL parts with aligned layers.

Introduction

In order to expand the usefulness of stereolithography, it is of interest to develop new resins that have functional mechanical properties at high temperatures. Current SL resins have softening temperatures under 100°C. As a result, they have limited value as high temperature structural materials. By increasing their high temperature mechanical stiffness and strength, SL resins will find new and expanded applications in areas such as direct injection molding, wind tunnel testing, and under-the-hood automotive applications.

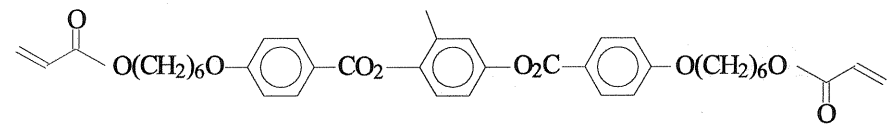
Photo-curable liquid crystal (LC) diacrylate monomers represent a new class of stereolithography resins. These LC materials contain stiff, rod-like molecules, which produce high glass transition (T_g) temperatures. The exact T_g developed depends on the monomer chemical structure and processing conditions. It has been demonstrated that T_g values in excess of 250°C can be achieved [1].

Because the rod-like molecules exhibit liquid crystalline phase behavior, they can be aligned by an external force. When cured in the aligned state, the aligned structure is "locked in" resulting in polymers with anisotropic physical and mechanical properties. By varying the alignment of the layers, properties such as the thermal expansion coefficient can be optimized. In this paper we demonstrate that composite lamination theory effectively provides a basis for estimating the thermal expansion properties of liquid crystal polymer SL parts with aligned layers. Of particular interest is that using

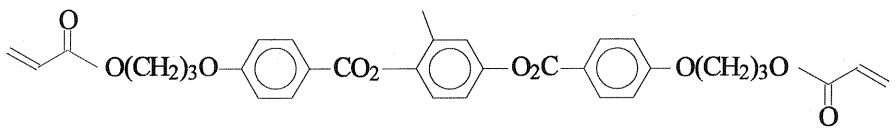
such a model, layered polymeric parts with very low thermal expansion coefficients in the x-y plane can be designed. This is demonstrated by measurements of the thermal expansion behavior for multilayer SL parts fabricated using the prescribed layer alignment sequences.

Experimental

Materials: Two liquid crystal monomers having the structures shown below were studied. The monomers differ only in the length of the alkane spacer groups. Monomer N1 has a spacer length of six -CH_2- groups while monomer N2 has a spacer length of three. Both monomers exhibit liquid crystal phases over a broad temperature range above room temperature. Considerable information has been published on them previously [1-7]. The photo-initiator used was Irgacure 369 (Ciba-Geigy), referred to here as PI-A. The photo-initiator was solvent blended with the monomers and the solvent was removed prior to processing.



(N1)



(N2)

Thermal expansion measurements: The thermal expansion properties of thin films were first evaluated to study the effects of processing parameters on the linear coefficient of thermal expansion values and to establish benchmark values for comparison with thick, multilayer parts made via stereolithography. The thin film specimens were made under carefully controlled conditions by a non-SL method. A description of the method and some results of the thin film CTE measurements were presented in an earlier publication [5]. In this paper we focus on the thermal expansion properties of multilayer SL parts. A TA Instruments model 2940 Thermal Mechanical Analyzer (TMA) was used to measure CTE values. A tensile TMA probe was used for x-y plane CTE measurements; a flat tip probe was used for z dimension (thickness) measurements [8]. Samples were heated at 5°C per minute to just above their glass transition temperatures (to erase thermal history and residual stresses), cooled at 5°C/minute to below room temperature and then heated a second time at 5°C/minute to 120°C or above. All data shown are from the second heat. Due to imposed page constraints, in this paper data are presented only for polymer N1. These data fully illustrate the issues involved. Representative data for polymer N2 will be considered further in the SFF Conference presentation.

Specimen Fabrication: A modified table-top stereolithography apparatus (TTSLA) equipped with a rotating magnetic field was developed as a part of this project [9, 10]. This provides the flexibility to change alignment directions of the LC monomer from one layer to the next. This is akin to altering the fiber direction in a continuous fiber reinforced composite. Multi-layer specimens were made with the TTSLA using an

Argon ion laser tuned to 364 nm. Both the N1 and N2 resins containing 0.5 % Irgacure 369 photo-initiator (Ciba-Giegy) were used for fabicating specimens. The N1 resin temperature was maintained at 85 °C during part building. The N2 resin temperature was set at 100 °C. These temperatures are within the nematic phase temperature range for both resins.

The poles of the magnet used for alignment were adjusted so that the magnetic field was either parallel or perpendicular to the principal build direction. All parts were made using an alternating draw style with a center-to-center spacing of 6 mils (0.152 mm). The layer thickness used was either 10 mils (0.254 mm) or 8 mils (0.203) depending on the part. All parts made for the thermal expansion studies were rectangular in shape with the short side measuring about 10 mm and the long side measuring about 25 mm.

When the magnetic field was aligned parallel to the long direction of the part the orientation was labeled 0 degrees. When the magnetic field was aligned perpendicular to the long direction of the part, the orientation was labeled 90 degrees. The types of multilayer parts made for this study include those with 0 degree, 0/90 symmetric, and 0/0/90 symmetric layer sequences ranging from 12 to 16 layers. The symmetric nomenclature in composite mechanics means that the ply orientation lay-up is symmetric about the mid-plane of the part.

After each part was built, it was removed from the elevator platform and support structures attached to the part were removed before post-cure. The parts were post-cured at an ambient temperature of 150 °C using a broad-band Mercury vapor lamp. They were post-cured bottom-side up for two hours; and then top-side up for two hours.

Results and Discussion

We first consider how the thermal expansion properties of multilayer parts fabricated via stereolithography compared with those of thin films that were made under more ideal conditions. Figure 1 shows the thermal expansion of a 16 layer uni-directional N1 part compared with the thermal expansion of an N1 film. Table 1 lists CTE values above and below the T_g for these specimens. The transverse, or 90 degree, data matched well with no significant differences noted for the 90 degree film and multilayer part. There were greater differences between the 0 degree film and part. The slight differences observed, however, may be due to procedural errors either in aligning the magnet poles before scanning the film or part, or in mounting the sample for thermal expansion measurement.

Table 1 Thermal Expansion Coefficient Values for N1 Films and Multilayer Parts

N1 Specimen	α, from 25 to 40 °C	α, from 85 to 100°C
Film, 0 degree	-17.6 ppm/°C	-139 ppm/°C
Part, 0 degree	7.9 ppm/°C	-102 ppm/°C
Film, 90 degree	179 ppm/°C	315 ppm/°C
Part, 90 degree	180 ppm/°C	328 ppm/°C

Another possibility is that the differences in the slopes of the expansion curves indicate that the molecular alignment in the multi-layer part is not as good as in the thin film. There are certain possible sources for disorder that may result from the laser scanning process. These are:

- Convective flow within the resin at the interface surrounding a new polymer strand--[11]. Such gradients in temperature and density result from the released heat of reaction. Both the scan speed (energy density) and scan pattern will affect thermal gradients and convective flow [11]. Such process parameter variations can influence the properties of the photocured material. As evidence of this, Schultz [13] found that laser draw speed influenced both the degree of anisotropy and the mechanical properties of aligned N2 parts.
- Since the degree of order in the LC state decreases with increasing temperature [7], thermal gradients inherently cause a certain amount of disorder within the monomer phase independent of local convection.

The N1 data in Figure 1 indicate that multilayer parts made with a significant degree of alignment result in anisotropic thermal expansion properties. A similar anisotropy in thermal expansion properties is characteristically found in continuous fiber-reinforced composite plies. In-plane thermal expansion is minimized in composite laminates by arranging the plies at different angles. The same technique was evaluated with aligned layers of the N1 resin. A 13 layer part was made having layers with alignment alternating between 0 degrees (angle between magnetic field and long side of part) and 90 degrees.

For this 13 layer part the thermal expansion in the longitudinal direction was then measured and compared with the thermal expansion of the uni-directionally aligned 16 layer part as shown in Figure 2. As expected, the thermal expansion of the 0/90 part falls somewhere in between the expansion curves for the 0 degree and the 90 degree part. It will be shown below that composite mechanics can be used to predict the thermal expansion properties of multi-angle aligned parts.

Based on the 0/90 symmetric part design, the thermal expansion of the part should be the same measured in the 0 degree direction (length) as it is measured in the 90 degree (width) direction. The thermal expansion properties in the 0 degree, 90 degree, and thickness direction were analyzed and are shown in Figure 3. The curves for the two in-plane directions are nearly the same showing good dimensional stability over the temperature range evaluated. The out-of-plane (part thickness) direction, however, exhibits a large positive thermal expansion coefficient of about 184 ppm/°C below the glass transition temperature.

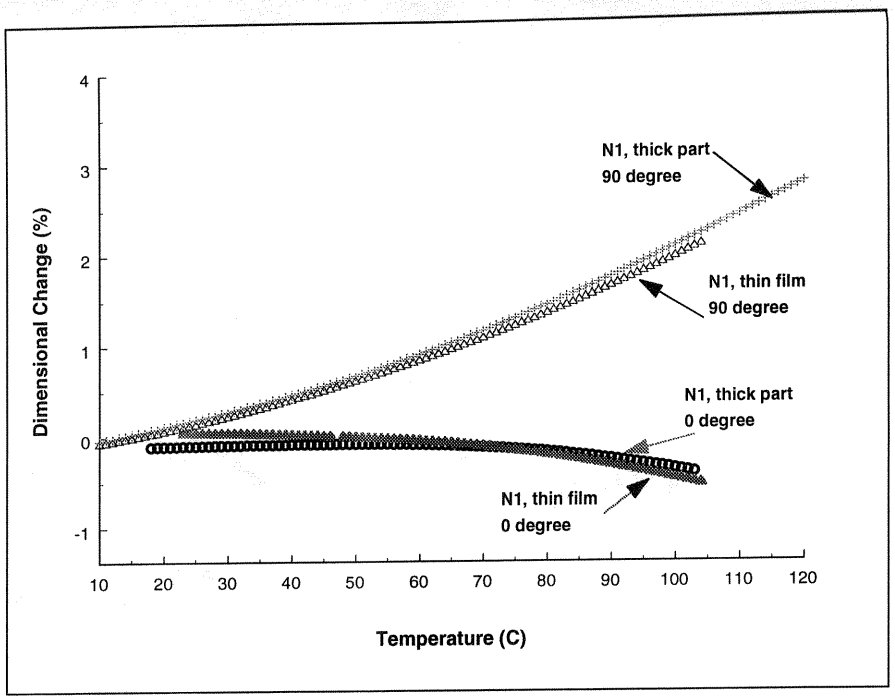


Figure 1. Comparison of linear thermal expansion data for N1 thin film and multilayer part specimens.

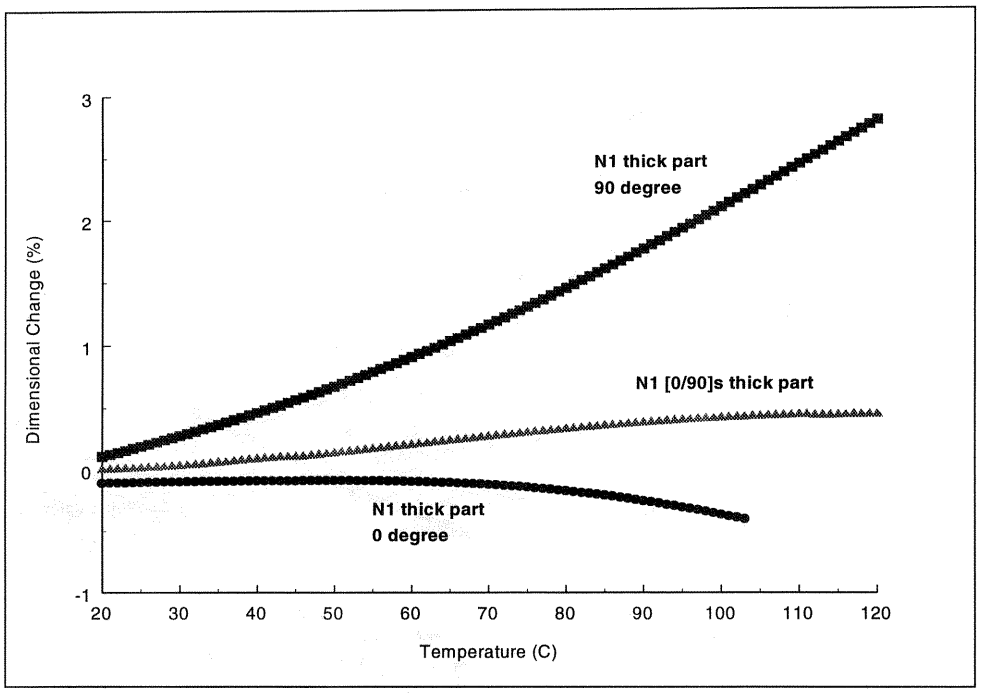


Figure 2. Comparison of N1 thermal expansion data for a 0/90 symmetric part with data for a uni-directionally aligned part.

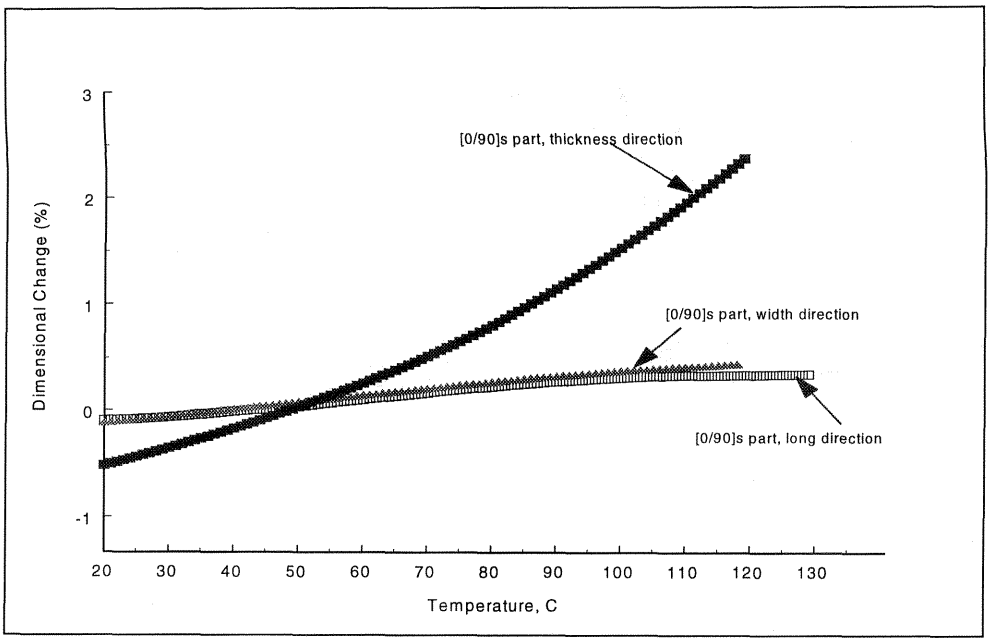


Figure 3. Comparison of N1 linear thermal expansion as a function of part orientation for [0/90]s part.

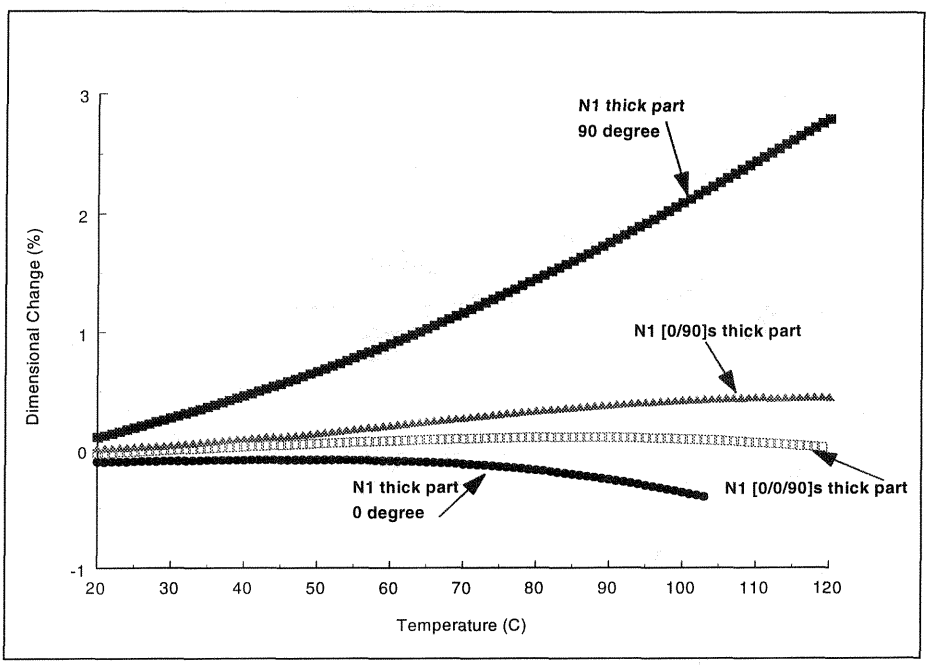


Figure 4. Comparison of the thermal expansion properties of N1 thick parts.

A second multi-angle part, containing a total of 12 layers, was made using a 0/0/90 symmetric layer sequence. The thermal expansion of the part was evaluated in the long direction and the results are shown in Figure 4. The 0/0/90 symmetric part analyzed in the long, or 0 degree, direction has a CTE of 31 ppm/°C below the glass transition temperature and a CTE of –35 ppm/°C above it. Depending on the sequence of alignment angles relative to the part axis system, one may achieve any desired in plane thermal expansion coefficients intermediate between the 0 degree and 90 degree values. Composite mechanics provides a way to predict laminate or part properties as a function of layer properties and stacking sequence.

Composite Mechanics Analysis

In an aligned liquid crystal thermoset, the physical and mechanical properties are anisotropic, with anisotropy similar to that in fiber/polymer lamina. For example, in the direction of orientation the modulus is greater than in the transverse direction and the linear CTE is lower. As a result, it is postulated that composite lamination theory can be used to predict the properties of layered, aligned liquid crystal parts. The thermal expansion of the layered structures fabricated in this study were analyzed by composite lamination theory for symmetric laminate plates where the ply alignment may vary throughout the structure. The analytical treatment of this problem is described in detail by Halpin [12].

A computer spreadsheet analysis program developed by Tsai [14] was used to perform the composite mechanics calculations. The spreadsheet program was developed to do integrated micro-macromechanical analysis and is called Mic-Mac (as discussed in Section 27 of [14]). The user enters a series of material parameters, as well as the laminate ply lay-up sequence and any applied stresses or strains (in our case these are zero). There are also additional parameters that can be entered for hygrothermal expansion and strength degradation. In this study moisture absorption was not considered.

The analysis was performed for the N1 resin. Two operating temperatures were considered: 25 °C and 100 °C. The input single ply (thin film) coefficient of thermal expansion (α) data, the predicted values as a function of part stacking sequence, and the measured values are given in Tables 2 and 3. As shown in Table 2, the composite mechanics approach predicts the in-plane thermal expansion coefficient to be 38.7 ppm/°C in both the x and y directions for the [0/90] symmetric part at 25 °C. The measured α's were somewhat higher and not equivalent in the x and y directions. At 100 °C the predicted values for α_x and α_y were 34 ppm/°C, while the measured values were 21.3 and 44.6 respectively.

The [0/090]s part was only analyzed in the length, or x, direction. At 25 °C the mechanics approach predicts the in-plane thermal expansion in the x direction to be 17 ppm/°C while the measured value was 30.7 ppm/°C. At 100°C there was closer agreement with the predicted value at –30 ppm/°C and the measured value at -23.3 ppm/°C.

Starting with the CTE data for unidirectional parts, the composite mechanics approach provided a reasonable estimate of the thermal expansion coefficients of multi-angle symmetric layered parts at different temperatures. It is thought that closer agreement would be achieved between the model and experiment if the magnet in the TTSLA apparatus were on a precision controlled turntable. This would permit the alignment angle to be more precisely controlled. The effect of process variables such as layer thickness, scan speed, and resin temperature on the degree of alignment achieved was not considered in detail. In order to achieve more exact results these also would need to be considered. It is important to note as well that molecular alignment of the polymers cured in a magnetic field is not perfect as reflected in the order parameter data of Schultz [7, 13]. The theory assumes perfect fiber orientation.

Table 2. Comparison of Measured and Predicted Thermal Expansion Coefficients at 25°C for Multi-Angle Symmetric Parts Made from Polymer N1

Part	One Ply α_x, α_y (ppm/°C)	Predicted part α_x, α_y (ppm/°C)	Measured part α_x, α_y (ppm/°C)
16 layer, 0°	----------	----------	7.9, 180
[0/90]s part	7.9, 180	38.7, 38.7	47.5, 62
[0/0/90]s part	7.9, 180	17.0, 63.0	30.7, (α_y not measured)

Table 3. Comparison of Measured and Predicted Thermal Expansion Coefficients at 100°C for Multi-Angle Symmetric Parts Made from Polymer N1

Part	One Ply α_x, α_y (ppm/°C)	Predicted part α_x, α_y (ppm/°C)	Measured part α_x, α_y (ppm/°C)
16 layer, 0°	----------	----------	-117, 342
[0/90]s part	-117, 342	34.0, 34.0	21.3, 44.6
[0/0/90]s part	-117, 342	-30, 107.0	-23.3, (α_y not measured)

Conclusions

A modified stereolithography (SL) process was developed which uses a magnetic field to align liquid crystal monomers in each layer of a multilayer SL part. This is akin to altering the fiber direction in continuous fiber reinforced composites. Using this process, multilayer SL parts with various layer alignment patterns were fabricated. Multilayer parts were made that contained 13 to 16 layers having unidirectional, 0/90 symmetric, and 0/0/90 symmetric layer sequences. Their thermal expansion behavior in the x-y palne and the z plane were characterized using thermomechanical analysis (TMA).

Analysis of the 0/0/90 symmetric construction in the long, or 0 degree, direction demonstrated a particularly low x-y CTE of 31 ppm/°C below the glass transition

temperature and a CTE of –35 ppm/°C above it. From the results obtained it was noted that, depending on the sequence of alignment angles relative to the part axis system, it is possible to achieve any desired in plane CTE values intermediate between the 0 degree and 90 degree values for unidirectional parts.

When the fiber alignment varies from layer to layer throughout the structure, lamination theory developed for composite mechanics can be used effectively to model the characteristic mechanical and physical properties. Reasonable agreement between the model predictions and experimental CTE values was obtained. Thus it was shown that by using such a model the CTE values of layered polymeric parts may be estimated. By following this procedure multilayer parts can be designed that have very low thermal expansion coefficients in the x-y plane.

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