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Title: EFFECT OF HIGH MAGNETIC FIELDS ON
ORIENTATION AND PROPERTIES OF LIQUID
CRYSTALLINE THERMOSETS

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Effect of High Magnetic Fields on Orientation and Properties of Liquid Crystalline Thermosets

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In this report we provide the first description of the orientation of liquid crystalline thermosets (LCT's) in field strengths of up to 18 T, as well as the first report of tensile properties for both unoriented and oriented LCT's. The LCT we have chosen for study is the diglycidyl ether of dihydroxy-a-methylstilbene cured with the diamine, sulfanilamide. Orientation in magnetic fields leads to an increase of almost three times the modulus compared to the unoriented material. These values are much greater than can be obtained with conventional thermosets. The strain at break is also significantly affected by the chain orientation. The coefficient of thermal expansion and x-ray diffraction of oriented samples show high degrees of anisotropy, indicating significant chain alignment in the magnetic field. We are working to further understand the field dependence of orientation and properties plus the mechanisms of the alignment process.

EFFECT OF HIGH MAGNETIC FIELDS ON ORIENTATION AND PROPERTIES OF LIQUID CRYSTALLINE THERMOSETS

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Introduction

Liquid crystalline thermosets (LCT's) have become recognized over the past few years as an important new class of materials. Numerous reports from our laboratory and others have described their synthesis and phase behavior.[1-10] In particular, we have described important effects due to the orientation of the rodlike molecules in a liquid crystalline phase. We have found that curing rates are enhanced compared to reaction in an isotropic phase,[3] and that the glass transition of the fully cured material can be significantly higher than the final cure temperature.[4]

For structural applications, orientation of LCT's will allow the maximization of mechanical properties. A few studies have described use of magnetic fields to orient LCT's.[8,9] However, the maximum reported field strength was 13.5 T and no measurements were made of the tensile properties. In this report we provide the first description of the orientation of LCT's in field strengths of up to 18 T, as well as the first report of tensile properties for both unoriented and oriented LCT's. The LCT we have chosen for study is the diglycidyl ether of dihydroxy-α-methylstilbene (DGE-DHAMS) cured with the diamine, sulfanilamide (SAA). Structures for these materials are shown in Figure 1. We have cured this thermoset at field strengths of up to 18 Tesla in order to evaluate the effects of very high magnetic fields on the properties of the system.

Experimental

Magnetic Field Processing: The thermoset formulation was prepared by dissolving 1 equivalent of SAA and 2 milliequivalents of an organophosphonium catalyst into 1 equivalent of DGE-DHAMS at elevated temperatures. This mixture was then poured into a mold for the magnetic field experiments. This mold consisted of a Teflon cup into which was placed two aluminum heater blocks, with the thermoset formulation filling the space between the blocks. Temperature control was maintained with a PID controller. Magnetic field experiments were conducted at the National High Magnetic Field Laboratory using a 20 T variable field electromagnet. Curing was done in the field for 1 hr at 150° C. The sample was then removed from the mold by cutting the Teflon cup and separating the aluminum plates. The final cure was done

in a conventional oven, and consisted of an additional 3 hrs at 150° C, 1 hr at 175° C, and 4 hrs at 200° C. Plaques approximately 2" x 1.5" x 0.125" were obtained.

Thermal Expansion: Thermal expansion measurements were performed parallel and perpendicular to the field direction using an Omnitherm TMA 1000 with a heating rate of 5° C/min and a mass of 10 g. Values of CTE reported are calculated by linear extrapolation of the displacement-temperature curve over the temperature range 30 to 60° C.

Tensile Properties: Tensile properties were measured on ASTM Type V specimens using an Instron 4483 testing machine and an MTS 632.26E extensometer. The results given here are the average of at least three different samples for each field strength.

X-ray Diffraction: X-ray diffraction was performed using a rotating anode generator and a two dimensional position sensitive detector. Calculation of the orientation parameter was done using the equation

$$f = \frac{1}{2}\left(3\left\langle \cos^2 \phi \right\rangle - 1\right)$$

where the average value of $\cos^2 \phi$ is given by

$$\left\langle \cos^2 \phi \right\rangle = \frac{\int_0^{\pi/2} I(\phi)\sin\phi\cos^2\phi \, d\phi}{\int_0^{\pi/2} I(\phi)\sin\phi \, d\phi}$$

Results and Discussion

The DGE-DHAMS/SAA system, which is initially isotropic, forms a smectic phase upon curing at 150° C. The formation of the smectic phase is due to an increase in aspect ratio of the rodlike molecules as the reaction proceeds. Under these conditions, the smectic phase forms after approximately 20 minutes of cure, and the gel point is reached in approximately 45 minutes. Curing in the magnetic field was done for 1 hour in order to ensure that any orientation induced by the field was locked into the network structure.

Tensile properties of the cured LCT at 0, 15, and 18 T are shown in Table I. Numbers in parentheses are the standard deviations. The tensile properties of the macroscopically unoriented material are similar to those obtained with epoxies based on bisphenol A cured under the same conditions. The unique advantages of the liquid crystalline epoxy are realized when the material is oriented in magnetic fields. Particularly noteworthy is the increase in tensile modulus. Orientation in magnetic fields leads to an increase of almost three times the modulus compared to the unoriented material. The strain at break is also significantly affected by the chain orientation. The reduction in strain at break and the in-

crease in the modulus are due to the decreased elasticity of chemical bonds in the direction of orientation, as compared to the interchain interactions which dominate the stress-strain behavior in the unoriented sample.

Measurements of the coefficient of linear thermal expansion, shown in Table II, also indicate a high degree of anisotropy in samples prepared in magnetic fields. Again, the CTE values of the unoriented sample are similar to those of conventional epoxy thermosets. Alignment in magnetic fields causes a significant decrease in the thermal expansion parallel to the field direction and a significant increase in the thermal expansion perpendicular to the field direction. This is also consistent with the molecules being aligned parallel to the direction of the field.

In order to quantify the orientation, x-ray diffraction measurements were performed. The orientation parameter was determined by integrating the scattered intensity around the azimuthal angle ϕ at a given value of the scattering angle 2θ according to the equations given above. The orientation parameters calculated are 0.93 and 0.90 for 15 and 18 T, respectively, where a value of 1.0 indicates complete orientation. These two values are the same within experimental error. X-ray results confirm that the molecular axes and the smectic layer normals are aligned parallel to the field direction.

Conclusions

This report describes preliminary results on magnetic field processing of liquid crystalline thermosets. We have provided the first information on the mechanical properties of liquid crystalline thermosets, both unaligned and aligned in high magnetic fields. To our knowledge these are the highest fields used to date for alignment of liquid crystalline molecules, and the degree of order obtained is higher than previously reported. Mechanical properties show significant increases in tensile modulus, giving values much greater than can be obtained with conventional thermosets. We are working to further understand the field dependence of orientation and properties plus the mechanisms of the alignment process.

Acknowledgments

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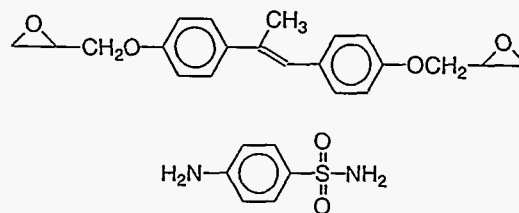10. Barclay, G. G., Ober, C. K., Papathomas, K. I., Wang, D. W. Macromolecules, 25, 2947, (1992).

Figure 1: Chemical structures of materials used in this study. Top: liquid crystalline epoxy. Bottom: sulfanilamide curing agent.

Table I: Tensile Properties

	0 T	15 T	18 T
modulus (ksi)	443 (32)	1081 (93)	1174 (166)
strain at break (%)	8.9 (1.6)	0.8 (0.3)	1.0 (0.03)
stress at break (psi)	13,010 (621)	8117 (1105)	9985 (500)

Table II: Coefficients of Thermal Expansion

	0 T	15 T	18 T
CTE parallel to field (μm/m/°C)	54	4.7	4.3
CTE perpendicular to field (μm/m/°C)	——	99.6	111.2