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Author(s):

Mark E. Smith, MST-7
Elliot P. Douglas, MST-7
Brian C. Benicewicz, MST-7
J. D. Earls, The Dow Chemical Co.
R. D. Priester, Jr., The Dow Chemical Co.

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HIGH MODULUS LIQUID CRYSTALLINE THERMOSETTING RESINS THROUGH NOVEL PROCESSING TECHNIQUES

M.E. SMITH*, E.P. DOUGLAS*, B.C. BENICEWICZ*, J.D. EARLS†, R.D. PRIESTER JR.†

*Los Alamos National Laboratory, Polymers and Coatings Group, Los Alamos, NM 87545

†The Dow Chemical Company, Organic Product Research, Freeport, TX 77541

ABSTRACT

We have demonstrated the effects of magnetic field alignment for the epoxy resin system, the diglycidyl ether of dihydroxy- α -methylstilbene cured with sulfanilamide. With increasing magnetic field, the tensile modulus of the thermoset can be enhanced by a factor of three, without compromise to the transverse value. Measurements of the coefficients of thermal expansion and the order parameter as determined by x-ray diffraction elucidate the high degree of alignment obtained at field strengths of 15-18 Tesla.

The interrelationship between the reaction kinetics of curing with the molecular alignment process is central to successful processing of this class of thermosets. Preliminary relationships between the field strength, time in the magnetic field, reaction rate, and extent of reaction have been developed. Process control and sequencing allow a wide adjustment in the properties of the produced samples. Our studies demonstrate the increased value of multi-mode processing in the development of tailored property, lightweight materials.

INTRODUCTION

While the use of thermosetting resins has become a mature field in materials science, liquid crystalline materials have not yet been fully exploited in structural applications. Many structural applications employ polymer composites in order to obtain light weight systems. The near endless combinations of reinforcement media and resins require extensive characterization and testing to ensure the desired overall performance of the product. Furthermore, the added variables of coupling agents and fillers confounds the design process such that tried-and-true formulations and process methods are usually relied upon.

Liquid crystalline thermosets (LCTs), provide a unique opportunity to produce internally reinforced parts by alignment of the molecules through electrical, magnetic, or mechanical forces. An immediate advantage is realized in combining electrical or magnetic fields with reactive processing methods since the low viscosity of the monomers allows orientation to occur much more rapidly and uniformly than would be obtainable with a liquid crystalline polymer.

Mechanical alignment methods are constrained by limitations of shear rate in processing, elongational flow in the process system, and the geometry and method of mold filling. In contrast, it is entirely feasible to envision the incorporation of magnetic or electrical fields with the molding process to selectively orient regions of a final part; in this method the alignment due to mechanical forces could be either enhanced or erased in the final molecular architecture of the sample.

Magnetic field orientation of both liquid crystalline polymers¹⁻⁵ and liquid crystalline thermosets⁶⁻⁸ have been reported. However these studies did not yield samples of sufficient size to enable determination of the mechanical property enhancements.

EXPERIMENTAL

The materials used for the following discussion were the diglycidyl ether of dihydroxy- α -methylstilbene (DGE-DHAMS) and the crosslinker sulfanilamide(SAA). These materials were stoichiometrically formulated in the liquid state as 1 equivalent sulfanilamide; 1 equivalent of DGE-DHAMS; and 2 milliequivalents of an organophosphonium catalyst. Once mixed, the resin was cast into the process mold. The mold design consists of electrical cartridge heaters embedded into metal plates, all contained in an insulating teflon cup. Temperature control was maintained throughout the experiment with a PID controller with an accuracy of $\pm 1^\circ\text{C}$.

The magnetic field experiments were conducted in a 20T variable field resistive magnet at the National High Magnetic Field Laboratory. Samples were cured at 150°C with either 5, 30 or 55 min. field exposure. Curing was completed by a total time of 4 hrs. at 150°C ; 1 hr. at 175°C ; and 4 hrs. at 200°C . The final product was a plaque of dimensions 2" x 1.5" x 0.125".

Thermal expansion measurements were performed both parallel and perpendicular to the applied magnetic field direction with an Omnitherm TMA 1000 instrument. The heating rate was $5^\circ\text{C}/\text{min}$ with a 10g mass. Reported values are determined by linear extrapolation of the displacement vs. temperature curve for the temperature range 30° to 60°C .

Tensile properties were measured on ATSM Type V tensile specimens with an Instron 4483 instrument equipped with an MTS 632.26E extensometer.

RESULTS & DISCUSSION

The initially isotropic DGE-DHAMS/SAA formulation forms a smectic phase as the curing reaction proceeds. Under isothermal conditions of 150°C , the smectic structure appears at approximately 20 minutes. Gelation, at which point the molecular weight of the polymer network becomes infinite, occurs at about 45 minutes. The effect of B-Staging is to advance the curing reaction, hence increase the molecular weight, without reaching the gelation point. This technique is commonly employed in thermoset processing methods to improve the handling of the resin and/or decrease the molding time in the process equipment.

The variation of the coefficient of thermal expansion is presented in Table I. Each sample was cured for a period of 55 minutes in the magnetic field at the designated field strengths. With no magnetic field alignment, the values parallel and perpendicular are identical, as expected for an isotropic, homogeneous network.

As the strength of the applied field is increased, the expansion parallel decreases while the perpendicular expansion increases sharply. This is a direct result of the alignment in the long

TABLE I

Field Strength [Tesla]	Coefficient of Thermal Expansion Parallel [$\mu\text{m}/\text{m}/^\circ\text{C}$]	Coefficient of Thermal Expansion Perpendicular [$\mu\text{m}/\text{m}/^\circ\text{C}$]
0	54.1	54.1
3	18.4	71.4
6	6.5	74.9
9	7.6	80.0
12	14.5	70.4
15	4.7	80.7
18	4.4	89.6

axis of the molecules parallel to the field. Thus, the opportunity for the part to expand is constrained almost entirely to increased distance between neighboring molecular segments since the expansion along the chain axis is only covalent bond stretching.

The enhancement of tensile modulus as a function of applied field strength is shown in Figure 1. The data presented corresponds to that listed in Table I. From this figure, one sees that the magnetic field enhancement is significant even at 3 Tesla. The modulus continues to steadily increase from nearly double at 3 Tesla to essentially triple the unoriented modulus at a field strength of 18 Tesla. The decrease at 12 Tesla is most likely attributable to a sample anomaly.

Figure 1: Tensile modulus as a function of applied magnetic field strength. Standard deviations are noted by the error bars. Each data point represents an average of 3 specimens from one plaque.

A functional fit of the data as a simple exponential relation is:

$$E = 438 + 230 x^{(.4)} \quad (1)$$

where E is the tensile modulus, and x represents the field strength. It must be noted that this expression is empirical in nature and cannot be directly related to physical constraints of the alignment process. However, it does suggest that the modulus varies nearly as the square root of the field strength within the experimental range.

In further investigation of the alignment process as a function of the process variables, a statistical design method was employed to investigate the effects of field strength, time in the magnetic field, and the effect of B-stage level. For this system each variable was allowed to hold one of three values: low, medium, and high. Field strength was 5, 10 or 15 Tesla. Time in field was 5, 30 or 55 minutes. The extent of B-stage was 0, 45, or 90 minutes @120°C.

The tensile modulus as a function of the three variables mentioned above is shown in Figure 2. There are three regions denoted on the graph; little or no enhancement ($E/E_{o-field} < 1.5$), enhancement $1.5 \leq (E/E_{o-field}) < 2.0$, and strong enhancement $2.0 < (E/E_{o-field})$. The three zones are identified by the shadings as indicated.

This data set demonstrates that enhancement occurs even with as little as 5 minutes of field exposure and that various levels of enhancement are obtainable through the adjustment of the three process variables shown.

Figure 2: Tensile modulus as a function of applied magnetic field strength. Shadings are represented as: little enhancement ; enhancement ; significant enhancement . Data points exist at the intersections of the lines defining the cubes.

The results of the above data relies heavily on the B-staging factor for each sample. As discussed above, the gelation time becomes critical in the correct determination of process windows. Once the network is formed, external field effects are severely diminished in altering the network structure and molecular orientation. Figure 3 schematically demonstrates this effect.

Figure 3: Tensile modulus as a function of applied magnetic field strength (x) vs. time in field (y). Darkness of data points indicated enhancement factor. Dashed line indicates gelation time for each sample set.

Considering the time for gelation of the resin for each level of B-staging studied, it is readily noted that when the field exposure is significantly less than the gel-time, the molecules can relax out of their orientation prior to being locked into the well aligned network. When the field strength is large enough and the time in field exceeds the gel time, the significant enhancement level is achieved ($E > 2 * E_0$).

In order to evaluate the level of mechanical anisotropy produced by the magnetic field alignment, one sample was sectioned into bars 0.125" x 0.125" x 1" at several angles relative to the magnetic field. The results of the modulus measurements are illustrated in Figure 4.

Figure 4: Tensile modulus as a function of molecular orientation with respect to the stress direction.

The curve is very similar to that measured in unidirectional composites, where the modulus drops rapidly as the direction of measurement increases from the principle orientation axis⁹. The distinct difference from composite behavior is the magnitude of the decrease. The network structure of this material allows the modulus transverse to the orientation vector to remain equivalent to that of an unaligned sample.

The magnetic field effect on existing structure is presented in Figure 5. Samples were prepared by first B-staging the resin for 150 minutes, and injection molding rectangular bars from this material. Each final plaque was made by loading the process mold with the injection molded bars, either parallel or perpendicular to the magnetic field direction, and curing for 5 minutes at the designated field strengths.

Clearly the perpendicular loaded samples dominate in modulus until the highest field strength, 18 Tesla, is reached. The parallel samples do not show strong magnetic enhancement even at 9 Tesla. This result can be attributed to the molecular orientation in the samples prior to the final curing. The injection molded, B-staged bars contain a core region in which the molecules are orientated transverse to the filling direction. This phenomena is due to the fountain flow with which the resin will fill the rectangular cavity. The skin structure will have alignment with the direction of filling; however, the interior of the part will have orientation perpendicular to the filling direction because the resin must fill a larger cross sectional area than the input channel.

Thus, the parallel bars in fact have a core molecular orientation that is 90° offset to the field. The time available prior to gelation is short, the sample viscosity is much larger than the unreacted monomer, and only the high strength field is capable of reorienting the molecules prior to crosslinking. In contrast, the perpendicular bars have many of the molecules nearly aligned with the applied field; therefore moderate field strengths have the ability to improve alignment.

Figure 5: Tensile modulus as a function of prior molecular orientation induced by injection molding B-staged resin bars for additional curing in the magnetic field.

This data set demonstrated the ability of the magnetic field processing to offset prior orientations introduced by mechanical means. In fact the 18 Tesla samples become identical in modulus since the preexisting orientations are erased prior to gelation.

CONCLUSIONS

The use of external magnetic fields in the processing of liquid crystal thermosets yields significant improvement in the mechanical properties of the cured resin. Enhancements of modulus of nearly three times an unoriented sample have been achieved without decreasing the transverse modulus of the sample. The variables of field strength, time in field, extent of B-staging, and gelation time can be chosen to deliver a specific modulus desired for a part. Prior orientations can be selectively removed through the use of magnetic fields during the curing process.

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