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PROCESSING OF POLYMERS IN HIGH MAGNETIC
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Many organic molecules and polymers have an anisotropic diamagnetic susceptibility, and thus can be aligned in high magnetic fields. The presence of liquid crystallinity allows cooperative motions of the individual molecules, and thus the magnetic energy becomes greater than the thermal energy at experimentally obtainable field strengths. Our work has determined the effect of magnetic field alignment on the thermal expansion and mechanical properties of liquid crystalline thermosets in the laboratory. Further advances in magnet design are needed to make magnetic field alignment a commercially viable approach to polymer processing.

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Introduction

Orientation of polymers is often used to improve mechanical properties such as modulus and strength. Commercial processing uses shear flows to achieve this orientation. For example, high performance polymer fibers owe their outstanding mechanical properties to orientation of the polymer chains due to shear alignment. However, bulk shear alignment is limited to objects with small dimensions such as fibers. In larger bulk parts that are produced by processes such as injection molding, the orientation is limited to a thin surface layer.¹ The bulk of the part is unoriented because the shear field that is responsible for the orientation dies out quickly as one moves away from the wall of the mold.

It would be desirable to have a technique that could be used for orientation of large parts to achieve property improvements comparable to those currently obtained in fibers. Magnetic field processing has the potential to fill this need because the magnetic field is constant throughout the sample. While magnetic field orientation has been studied in both liquid crystalline polymers (LCP's)²⁻⁶ and liquid crystalline thermosets (LCT's),⁷⁻⁹ there have been no measurements of the mechanical properties resulting from magnetic field orientation. Therefore we have embarked on a program to investigate the feasibility of using magnetic field processing for improving the properties of LCT's. As will be described below, LCT's have certain advantages over LCP's in magnetic field processing due to their lower viscosity, leading to a shorter time and lower field strengths required for orientation. 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.

Physics of Orientation

Magnetic field orientation occurs in organic molecules due to an anisotropy in their diamagnetic susceptibility. One of the strongest such anisotropies occurs in the case of the benzene ring.¹⁰ When an external magnetic field is applied perpendicular to the plane of a benzene ring a current is induced in the electrons that occupy the π orbitals. This ring current induces an additional magnetic field which distorts the external field. By comparison, if the external field is applied parallel to the plane of the ring there is no induced ring current, and thus no distortion of the external field, and the energy is lower. Of course, for a single molecule even the high energy state has an energy orders of magnitude lower than the thermal energy, and thus isolated molecules such as in the gas or liquid phases will not be oriented by any practically obtainable fields.

An additional factor is operative in liquid crystalline molecules.¹⁰ The entropy of packing a concentrated collection of rods favors formation of an ordered (liquid crystalline) phase in which the rods have their axes aligned along a common direction. Due to this ordered phase the global motions of the rods are highly cooperative in nature, and thus the energies for various orientations in a magnetic field described above are multiplied by the number of molecules present. Since the energies associated with the oriented and unoriented states are now much higher than the thermal energy, orientation can be obtained at reasonable field strengths. Although measurements have been made of the degree of orientation of polymers aligned in magnetic fields, there have been no measurements of the resulting mechanical properties. Thus one of the objects of this study has been to define what is meant by "reasonable" field strengths with respect to the final properties of the material.

Experimental

Magnetic Field Processing: The thermoset formulation was prepared by dissolving 0.25 equivalents 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 resistive magnet. 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 Omnistherm 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 dogbones using an Instron 4483 testing machine and an MTS 632.26E extensometer.

Properties of Oriented Polymers

Previous studies of orientation of liquid crystalline materials in magnetic fields have typically been performed by placing the material in a glass capillary or other small container. While this is suitable for measurement of orientation by x-ray diffraction or even thermal expansion measurements,⁷⁻⁹ these studies did not produce the larger samples required for measurement of tensile properties. Our approach to preparing samples results in large plaques from which tensile bars can be machined. Thus, we are able to make the first evaluations of the potential for magnetic field processing of polymers.

The DGE-DHAMS/SAA system forms a smectic phase upon curing. Curing is done at 150° C, which is initially in the isotropic phase. Upon curing a smectic phase is formed due to the increase in aspect ratio of the rod-like 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.

The results from tensile measurements are shown in Figure 2 and Table I. The tensile properties of the unoriented LCT are similar to what is obtained for non-liquid crystalline epoxies based on bisphenol A cured under the same conditions. However, orientation in magnetic fields can result in large increases in the tensile modulus. From the data, it appears that for these curing conditions the maximum enhancement in tensile modulus

occurs at approximately 9 Tesla. The highest modulus value achieved, 1174 ksi, is almost three times greater than the modulus of the uncured material. This high modulus is a result of the orientation present throughout the bulk of the sample due to the effect of the magnetic field, and points to the possibility of using magnetic fields to create materials that can not be obtained with other techniques.

The measurements of thermal expansion shown in Figure 3 parallel the results obtained for modulus. Again, the effect appears to be saturated at a field strength of approximately 9 Tesla. The very low thermal expansion parallel to the orientation direction is a result of the primary axis of the molecules being in the direction of the field, resulting in low thermal expansion. A corresponding increase in thermal expansion is seen perpendicular to the orientation direction.

Orientation Kinetics

A simple model has been developed to describe the orientation kinetics of rod-like molecules in a magnetic field. This model has been described previously for the case in which the viscosity is constant as a function of time.⁵ However, in a curing system such as this one the viscosity increases exponentially as a function of time, and thus we have modified the model to account for this effect. The results of the calculation can be used to help define the processing parameters for magnetic field processing.

Details of the model will be described in a future publication. The model is based on a mean field approach in which one considers the torques acting on a single rod which is surrounded by a continuum representing the average properties of all other rods. We assume that the rod makes an initial angle θ_0 with the field, and calculate the angle θ that the rod makes with the field as a function of time. As shown in Figure 4, there are two torques acting on the rod. The magnetic torque, L_M , defines the torque that tends to align the rod with the external magnetic field. Opposing this is a viscous torque, L_V , which represents the drag on the rod to the rotational viscosity, γ_1 . The equation of motion for this system at steady state is then:

$$L_V + L_M = 0$$

Solving this equation leads to an expression for the angle θ as a function of time. It should be noted that the model is not completely physically realistic, and thus the absolute

magnitudes of the field strengths and times are not correct, but the model does provide a qualitative comparison of the various parameters involved.

Figures 5-8 show various results of the calculation. Figures 5 and 6 illustrate the advantage of using a low viscosity thermoset system compared to a high viscosity polymer, assuming a viscosity that is constant with time. For the thermoset system the orientation is complete very quickly, while for the polymer the increase in orientation is only a few degrees over the same time scale. Of course, the polymer will achieve complete orientation after either a longer time at the same field strength or in the same time by increasing the field strength. However, from a processing point of view both of those options are likely to be impractical.

Figures 7 and 8 illustrate the effect of an exponentially increasing viscosity. In Figure 7 the orientation is allowed to begin at time zero. In this case full orientation is obtained only at the highest field strengths. At lower field strengths the orientation process is halted because the viscosity becomes essentially infinite. This infinite viscosity corresponds to the gel point in the cure, beyond which the epoxy network is formed and molecular level motions are prevented. Figure 8 shows the case where the orientation process does not begin until sometime after the cure starts. This situation corresponds to the fact that the epoxy monomer used in this work is initially isotropic at the cure temperature and becomes liquid crystalline during the cure. In this case the orientation obtained before the gel point is minimal, because there is not enough time for full orientation to occur before the material reaches the gel point. Again, higher field strengths will result in complete orientation, but longer times in the field do not help because of the gel effect. Thus, in defining process parameters for thermoset systems using magnetic fields one must be aware that there is a limit on the amount of time in the field that is useful.

Industrial Applications

While the work described above demonstrates the technical feasibility of improving the properties of polymers through magnetic field orientation, much additional work needs to be done to make magnetic field processing a commercial reality. This will require collaboration among polymer researchers, the polymer processing industry, and the magnet community to address several technical and economic concerns.

The first point that still needs to be addressed concerns the design of magnets for magnetic field processing. It is unlikely that the simple uniaxial orientation described in this paper will be useful for commercial products. Although the specific applications and needs are not yet defined, it is more likely that three dimensional orientation will be required. For example, one could imagine situations in which the orientation is required to lie along the surface of a curved part, or in which the orientation is required at a specific location of the part where stress concentration occurs. Thus, the feasibility of designing magnets which can produce these unusually shaped fields needs to be addressed.

Additional concerns surround the use of magnets in a plant environment. For example, typical superconducting magnet applications require the use of a clean, air-conditioned room; highly skilled and trained operators; and sophisticated software and hardware to operate the magnet. However, typical processing plants do not allow for these conditions. Thus, magnets must be made robust, simple to use, as well as highly reliable for continuous plant operation.

Once the technological are addressed, the next question becomes one of economics. The technical questions outlined above will define the type of magnets that can be used (permanent, resistive, or superconducting), and then the relative cost versus benefit analysis and expected return on investment can be used to determine the most appropriate type of magnet. This economic analysis will also help to determine the amount of property enhancement desired. Looking at the data in Table I, even though a modulus of over 1000 ksi is feasible with very high fields, it may turn out that the expected return on investment does not justify those high fields, and that using a 3 T field to obtain a 750 ksi modulus provides enough benefit at lower costs to allow commercialization.

Summary

The work described here has shown the initial feasibility of using magnetic fields to enhance the properties of polymers. In particular, we can obtain cured epoxy thermosets with a modulus of greater than 1000 ksi. This value of modulus is unheard of for an unfilled epoxy, and demonstrates the potential of magnetic fields for creating new materials with unique properties. We have also started to define the required parameters for magnetic field processing using a simple model to describe the kinetics of orientation. However, a number of technological and economic issues still need to be addressed to make magnetic field processing of polymers a commercial reality.

Discussion

A. Brennan, University of Florida: Is there an influence of field strength on crosslink density?

E. Douglas: There is a substantial amount of postcure that is done outside of the magnetic field, and DSC measurements of the cure exotherm do not show any differences between samples prepared in the field and outside the field. However, it should be noted that there are reports in the Russian literature that magnetic fields can affect the reaction rate of epoxy cure,¹¹ and there could be changes in the network structure due to either changes in the reaction or the molecular alignment.

A. Brennan, University of Florida: Is there anisotropy of properties (stress, modulus, strain) related to field direction?

E. Douglas: Measurements of the properties perpendicular to the field direction show that the transverse modulus is the same as the modulus for the unoriented samples. We are currently making additional measurements on the angular dependence of the modulus with respect to field direction.

A. Brennan, University of Florida: Any information on swelling behavior or creep of the LCT's?

E. Douglas: As these are highly crosslinked systems we would not expect either swelling or creep to be a major issue. However, DMA results indicate a relaxation that occurs around 50° C that may lead to long-term creep. We are currently performing NMR measurements to identify the mechanisms responsible for that relaxation.

H. W. Spiess, Max-Planck Institute for Polymer Research: High orientation of crosslinked LCP's can also be achieved by mechanical forces. This may be easier to implement in an industrial environment. Could you compare the virtues of these two methods, i.e. mechanical versus magnetic forces?

E. Douglas: Elongational flows are certainly more efficient than magnetic fields, but are generally limited to fiber spinning. Mechanical stretching would be limited to rubbery systems that could then be crosslinked further, and the relaxation time would need to be much longer than the cure time in order to lock in the orientation. In addition, mechanical forces are limited to polymeric systems and uniaxial orientation. Thus one loses the advantage of having a low viscosity thermoset and the possibility of having orientations that are not solely uniaxial.

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Table I. Properties of LCT's Oriented in Magnetic Fields

field strength (Tesla)	modulus (ksi)	coefficient of thermal expansion parallel to field ($\mu\text{m}/\text{m}/^\circ\text{C}$)	coefficient of thermal expansion perpendicular to field ($\mu\text{m}/\text{m}/^\circ\text{C}$)
0	432.0 $\pm$ 32.0	54.1	54.1
3	744.9 $\pm$ 43.9	18.4	71.4
6	950.0 $\pm$ 139.5	6.5	74.9
9	1017 $\pm$ 91.4	7.6	80.0
12	819.7 $\pm$ 59.6	14.5	70.4
15	1081 $\pm$ 93.5	4.7	80.7
18	1174 $\pm$ 165.9	4.4	89.6

Figure Captions

Figure 1: Structures of the materials used in this work: top, diglycidyl ether of dihydroxy- α -methylstilbene; bottom, sulfanilamide.

Figure 2: Tensile modulus as a function of field strength.

Figure 3: Coefficient of thermal expansion as a function of field strength.

Figure 4: Schematic diagram showing the torques acting on a rod in a magnetic field. The rod makes an angle θ with the external applied field. L_M is the torque due to the magnetic field B and the anisotropy in the diamagnetic susceptibility of the rod, $\Delta\chi$; L_V is the viscous torque due to the viscosity γ_1 of the surrounding medium.

Figure 5: Calculations of the orientation kinetics of a rod in a magnetic field for the case of constant viscosity with time. The rod initially makes an angle $\theta = 60^\circ$ with the magnetic field, and the viscosity $\gamma_1 = 1$ poise.

Figure 6: Calculations of the orientation kinetics of a rod in a magnetic field for the case of constant viscosity with time. The rod initially makes an angle $\theta = 60^\circ$ with the magnetic field, and the viscosity $\gamma_1 = 10,000$ poise.

Figure 7: Calculations of the orientation kinetics of a rod in a magnetic field for the case of exponentially increasing viscosity with time. The rod initially makes an angle $\theta = 60^\circ$ with the magnetic field, the viscosity $\gamma_1(t)$ at $t = 0$ is approximately 1 poise, and orientation begins at time $t = 0$.

Figure 8: Calculations of the orientation kinetics of a rod in a magnetic field for the case of exponentially increasing viscosity with time. The rod initially makes an angle $\theta = 60^\circ$ with the magnetic field, the viscosity $\gamma_1(t)$ at $t = 0$ is approximately 1 poise, and orientation begins at time $t = 34$ minutes.

Figure 1

Figure 2

Figure 3

Figure 4

$$L_M = -\frac{1}{2}(\Delta\chi)B^2\sin(2\theta)$$

$$L_V = -\gamma_1\left(\frac{d\theta}{dt}\right)$$

Figure 5

Figure 6

Figure 7

Figure 8