LA-UR- 95-4179

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Submitted to: **DOE Office of Scientific and Technical Information (OSTI)**

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Neutron Scattering as a Probe of Liquid Crystal Polymer-Reinforced Composite Materials

Rex P. Hjelm*, Elliot P. Douglas, Brian C. Benicewicz, and David A. Langlois

Abstract

This is the final report of a three-year Laboratory-Directed Research and Development (LDRD) project at the Los Alamos National Laboratory (LANL). This research project sought to obtain nanoscale and molecular level information on the mechanism of reinforcement in liquid crystal polymer (LCP)-reinforced composites, to realize molecular-reinforced LCP composites, and to test the validity of the concept of molecular reinforcement. Small-angle neutron scattering was used to study the structures in the ternary phase diagram of LCP with liquid crystal thermosets and solvent on length scales ranging from 1 - 100 nm. The goal of the scattering measurements is to understand the phase morphology and degree of segregation of the reinforcing and matrix components. This information helps elucidate the physics of self assembly in these systems. This work provides an experimental basis for a microengineering approach to composites of vastly improved properties.

1. Background and Research Objectives

Microengineering of composite materials has been recognized as a potentially important strategy in achieving breakthroughs in improving performance of materials. The design of composites on the nanoscale to molecular level is predicted to improve mechanical properties, such as toughness and strength, by several orders of magnitude. This project involves work to obtain nanoscale and molecular level information on the mechanism of improved mechanical properties in composites, specifically those reinforced by rigid-rod, liquid-crystal polymers. This information is essential to the microengineering approaches of improved composites.

Polymers that exhibit liquid crystalline order in solution or in the melt demonstrate a high degree of order in the solid state, as well, and several such polymers have been

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*Principal investigator, e-mail: hjelm@lanl.gov developed with exceptional physical and mechanical properties such as high strength and high modulus. Some of these have been successfully used as reinforcements in coil-like polymer matrices, and a theoretical framework has been devised for these systems. Based on considerations that the structural strength of these materials is limited by LCP fiber imperfections, fiber fibrillations, poor interfacial adhesion and stress concentrations at the fiber ends, the theory predicts that mechanical enhancement can be improved by about an order of magnitude over present phase-separated systems in the limit that the reinforcing phase is homogeneously dispersed in the matrix [1]. Realizing this molecule composite has proved difficult, and structural studies on the materials that have been made have proven inconclusive; thus the theory has yet to be verified [2].

A successful strategy in the production of molecular reinforced LCP-matrix composites must deal with difficulties in dispersing the LCP in the matrix material. The difficulty is due to unfavorable free energy of mixing between the components [1,2]. Rather complex schemes have been devised to process melts of the polymers into a "homogeneous phase" followed by a deep quench below the glass transition. However, the mixtures almost always show some phase separation limiting the theoretically achievable strength. Further, the mixtures are thermodynamically unstable, and further phase separation inevitably results with time.

There are unexplored strategies to deal with these problems. Our approach is to use a matrix which will better disperse the LCP phase [3,4]. A liquid crystal thermoset (LCT) is mixed with LCP. The mixture is melted, homogenized, and then the temperature of the melt is raised above the thermoset point of the epoxy, making an extended, crosslinked polymer matrix. It is anticipated that this process will give LCP well dispersed in the matrix material. We believe that these materials will offer a new class of composite materials with significant improvements in stiffness, toughness, and strength.

Microengineering, as a strategy for rational design, requires an experimental basis and theoretical framework on which to make predictions on the likelihood of success of a particular strategy. It is important in this approach to understand the phase behavior in solution, its evolution as the gel point is approached, and the morphology in the final dried films. Thus, a complete ternary phase map should be explored for systems that are processed from solution and binary temperature-dependent phase map for systems processed from the melt. Thus films studies, solution studies and studies designed to see how the system evolves as the gel point is approached are to be carried out. All of this is needed to understand self assembly in these systems, as there is little experimental information on system consisting of rods of very different sizes to validate the limited theoretical notions in the literature [5,6]. Further, our interest is to correlate the extent and morphology of phase separation along with interfacial structure with mechanical properties.

2. Importance to LANL's Science and Technology Base and National R&D Needs

This work relates directly to competency in synthesis and characterization of amorphous and microstructural materials that have significantly higher strength and formability than conventional materials. Los Alamos has been responsible for a number of significant developments in new structural materials. Our work in SiC fibers, Mo2Si-based composites, and beryllium alloys are a few examples of such accomplishments. We build on this reputation in structural materials with our discovery and development of liquid-crystal thermoset materials for advanced polymer composites.

This work also relates directly to competency in the development of improved techniques for microstructure characterization by neutron scattering techniques. The Los Alamos Neutron Scattering Center (LANSCE) is the most advanced pulsed neutron source in the United States and the brightest in the world. Extension of established small-angle scattering methodologies to work in composite structures and the development of new methods that are likely to result will aid in further research and utilization of national facilities.

This work also relates to the growing use of polymer composites and the need for even superior materials in applications such as the ATF, stealth bombers and the suborbital supersonic transport. The Navy is seriously considering the development of all organic composite hull submarines. Advantages in lighter weight, greater speed, and lower observability are expected. However, it is known that advances in both materials and processing will be needed to accomplish this task. These materials could also be used in advanced armor for future land vehicles where weight reduction is critical. The light weight and potential strength of these materials are likely to lend themselves well to applications in structural components for more fuel efficient automobiles and other types of commercial transportation applications. Researchers at the Air Force Wright-Patterson Materials Laboratory, NASA-Langley, DuPont, and Dow Chemical have expressed an interest in the new concepts being developed in this project.

3. Scientific Approach and Results to Date

Studies on the structure of composites have relied on several well-established methods. Small-angle scattering techniques, in particular small-angle neutron scattering (SANS) has not yet found widespread application in this area, even though the scales probed by these methods, 10Å - 1000Å, are the most relevant for understanding molecular organization in these materials.

All previous investigations on molecular composites have shown that phase-separated aggregates (approximately 10^2 - 10^3 ångstroms or larger) were present, lending support to this view [2].

We use SANS to study the nanoscale morphology of ternary LCP/LCT/NMP (Fig. 1) systems and binary LCP/LCT systems. In this we use the LQD at LANSCE and other instruments at IPNS and NIST. The measurements and the analysis follow lines already developed for polymer blends and block copolymers. This includes determinations of the characteristic sizes of the phases, the phase morphology and the degree of component segregation among the phases. The organic components are contrasted by specifically labeling one of the components with deuterium. The substitution of protons with deuterons then affords a considerable change in scattering length density.

Analysis of the experiment proceeds by recognizing signatures in the scattering curves. It is well known from the extensive literature in this area that microphase separation leads to correlations which give rise to characteristic scattering patterns, the exact form of which is dependent on the morphology of the phases. On the other hand, a true solution of LCP in matrix would be characterized by scattering from a concentrated solution of rod-like chains.

We have developed new analytical methods to evaluate the amount of segregation of components between phases. These methods are based on the realization that the quadratic intensity-dependence of the intensity at zero momentum transfer on the amount of deuteration of one component (in this case LCP) has coefficients that are related to the difference in the volume fraction distribution of the LCP in each phase [4,5]. This difference is near unity for strong segregation and approaches zero as the segregation, hence phase distinctions, disappear.

LCP-LCT composite films have been cast from LCP-LCT solutions, using nitro-substituted Kevlar that has excellent solubility, and is selectively deuterated to provide the necessary contrast for this phase mapping (Fig. 1 IV). These experiments also test the widely cited liquid crystal miscibility criterion, which states that like liquid-crystal phases should be completely miscible.

The SANS studies on these materials has shown that at 20% loading of LCT in LCP there is microphase separation with morphology being modeled by rod-like inclusions of 80 Å radius in a continuous phase. At 40% loading the microphase separation persists and can be modeled as a system of randomly interpenetrating phases (the Debye-Bueche model). The characteristic length of this is 80 Å [4,5]. In both of these cases the phases appear to be near equilibrium structures, as extensive annealing does not alter scattering. A complete sequence of data has been taken, and preliminary indications are that this can be modeled as a spinodal. We have shown in this latter case that there is weak segregation of the components in the two phases; thus we are approaching the molecular composite ideal without having optimized our system.

An important aspect of this system is in understanding the formation of the films. LCP-LCT solutions are made at the required weight ratio, then heated to the processing temperature, 100°C or 60°C. As expected, the nanoscale structure morphology is dependent on the initial state, though the analysis of this is not complete, and the results given above are for processing from the samples dried at 100°C. The questions are: What is the initial state in solution? What are the changes that occur as the solution concentrates and reaches the gel point? What is the relation of these to the final state measured in the film?

We have used small angle scattering on the solutions [7,8]. The dilute solution results show that at room temperature LCP in NMP forms large domain-like structures as seen by the $I \mu Q^{-4}$ at low-Q. These are broken up by the addition of LCP into combinations of smaller domains and filamentous LCP/LCT structures, which is indicated by the $I \mu Q^{-1}$ dependence when the concentration is 5 wt.% or less, but not at 9 wt.% where the domain-like structure is retained. These results are summarized in Fig. 2. Experiments toward understanding the structure near and at the gel point are planned. We have determined the changes in solution structure as the gel point is approached along different LCP/LCT composition lines. We find that the microscopic biphase found in the dilute solution studies become larger and are readily apparent in the polarization light microscopy at higher concentrations. It is seen that the biphase is a mixture of an isotropic phase and a liquid crystalline phase (Fig. 2), which is probably LCP-rich. As the solution is further concentrated toward the gel point the isotropic phase is not in evidence. Rather, a single liquid crystalline phase is observed. The neutron scattering profiles show a variety of structures that are different from the film morphologies mentioned above. We have not completed the analysis of these structure, however. Some aspects of this research will continue forward under a field work proposal funded by OBES.

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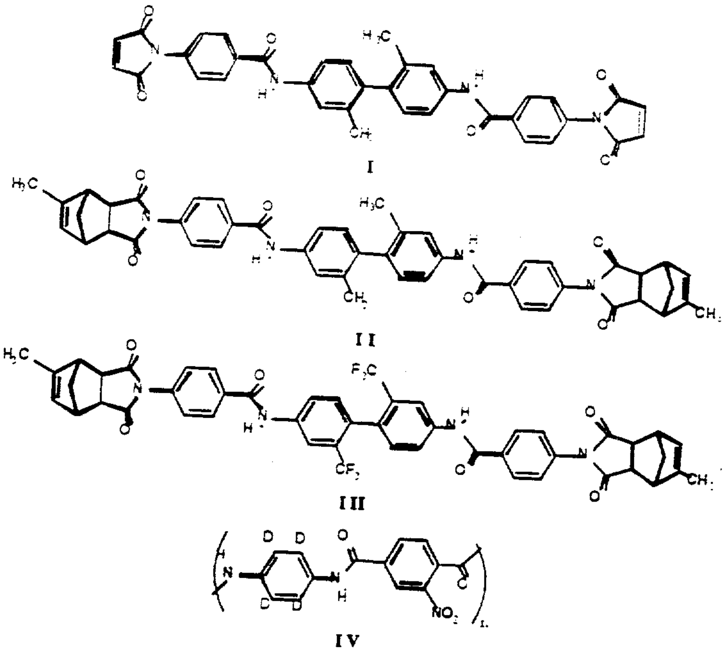

Fig. 1. Liquid-crystal thermosets and liquid-crystal polymer used in this study. Liquid-crystal thermosets: (I) 2,2'-Dimethylbiphenyl Bismaleimide Amide; (II) 2,2' Dimethylbiphenyl Bis(methylnadimide) Amide; (III) 2,2'-Bis(trifluoromethyl)biphenyl Bis(methylnadimide) Amide. Liquid-crystal polymer: (IV) poly(p-phenylene-2-nitroterephthal amide).

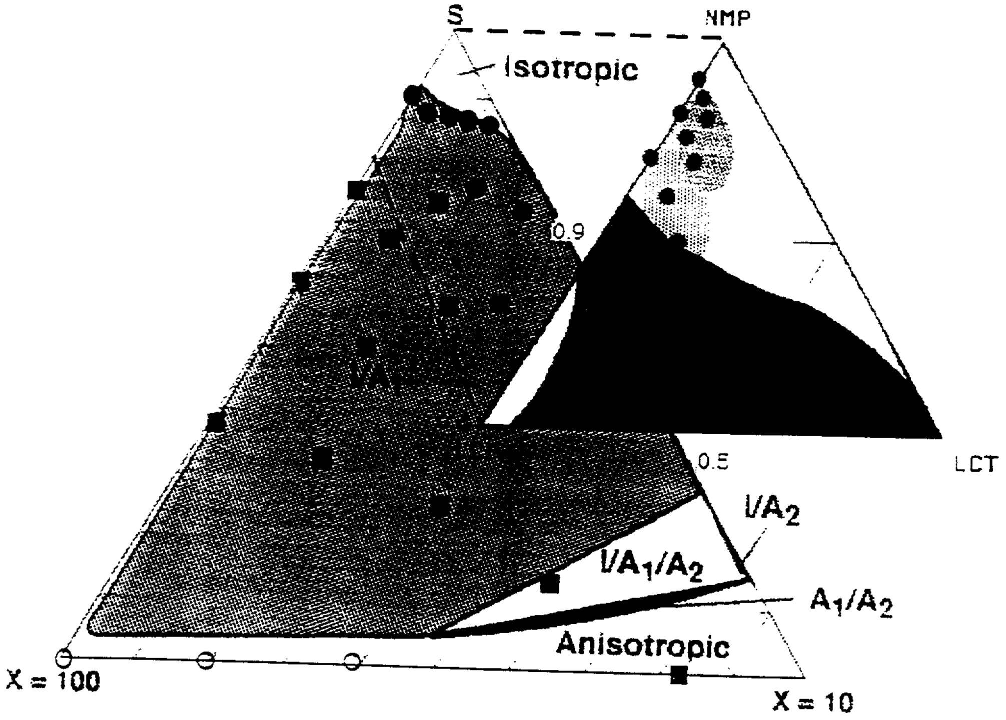

Fig. 2. Calculated phase diagram for a mixture of long (n=100) and short (n=10) rigid-rod polymers [Ref (5)]. I refers to isotropic phases. A1 and A2 refer to, respectively, long (X=100) and short (X=10) rod-rich anisotropic (nematic) phases. The solvent is represented by S. The points on the map sampled in this study are shown by solid circles for biphase samples of isotropic and liquid crystalline phases. Open circles are films. Closed squares are samples found in the liquid crystalline phases. On the expanded solvent corner of the map (upper right), the light and dark regions around the points correspond to domain-like and dispersed solution structure, respectively. The axes are in units of volume fraction.