TPL-AD14-FR

BARIUM TITANATE/POLYMER NANOSCALE COMPOSITES WITH
CONTROLLABLE ARCHITECTURES

Reporting Period: 9/2/98-4/8/99
Contract period of performance: 9/2/98-4/8/99

Grant No: DE-FG03-98ER82699

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1.0 PROGRAM SUMMARY

1.1 Objectives

Composites have been developed to combine the desired properties of their component materials. This is often in response to an application which demands properties which are currently unavailable in a monolithic material. In most cases, composites require a sacrifice of one or more properties to enhance the properties of interest. At reduced length scales, where on surfaces become an appreciable percentage of the total number of atoms, surface effects can dominate. It is only recently that the properties of nanoscale composites are being explored. This is due in large part to a lack of processing knowledge to make the materials.

The goal of the Phase I program was to develop a novel processing method for nanoscale composites. The method makes use of the tendency of copolymers to microphase separate. Model systems have shown lamellar, cylindrical and spherical morphologies with length scales of tens of nanometers. The current research was aimed at introducing a ceramic precursor into the block copolymer that was capable of partitioning into one of the copolymer regions. Hydrothermal attack of the precursor was then initiated to form a crystalline ceramic. Specifically, a copolymer of polyimide and polydimethylsiloxane was chosen as the matrix into which a discontinuous, hydrothermally grown barium titanate was to be incorporated. The dielectric properties of this composite were to be measured.

1.2 Summary Of Technical Achievements

Several polydimethylsiloxane/polyimide copolymers were synthesized. Polyimic acid containing amine, phenyl and cyano pendant groups was reacted with commercially available polydimethylsiloxane as well as siloxanes produced by TPL. The nature of the siloxane portion was not observed to strongly affect the polymer behavior; however, differences in wetting and phase separation were seen depending on the functional groups of the polyimic acid. Three copolymers were synthesized which showed phase separation.

Several commercially available titanium alkoxides were added to the copolymers. All of the alkoxides caused immediate gelling of the copolymer. It is believed that the titanium served as a crosslinking agent shedding weakly held ligand groups and attacking functional groups of the copolymer, presumably of the polyimic acid. Two titanium alkoxides which are not commercially available were synthesized by TPL. These alkoxides also gelled the polymer.

Because of the intractable problem of gelling, several alternative polymer systems were investigated. Polystyrene/polybutadiene was studied as a model system for composite synthesis since its phase separation behavior is well known. Polystyrene/polyacrylonitrile was also studied because it was felt that the dielectric properties of this polymer would be superior to the polystyrene/polybutadiene. Notably,

the dielectric loss of polybutadiene is expected to be high. A polysiloxane/epoxy polymer matrix was studied because it is known to result in good dielectric properties.

The polysiloxane/epoxy system was found to degrade when exposed to barium hydroxide systems ; therefore, work was discontinued on this system. The phase separation behavior of the polystyrene/polybutadiene system with and without barium titanate was observed. Dielectric property measurements of this system and the polystyrene/polyacrylonitrile system were made.

2.0 TECHNICAL ACHIEVEMENTS

2.1 Polymer Synthesis

A brief description of the synthesis routes for several of the polymer matrices used in this research follows.

Polyimides are produced through a two step reaction involving the condensation synthesis of diamines with dianhydrides in aprotic solvents to produce polyamic acids. Polyamic-acids, or polyimide pre-polymers are converted to polyimides through water removal at elevated temperatures. To produce block copolymers, commercial polysiloxanes are functionalized and reacted with the polyimide pre-polymer prior to the dehydration.

Methyl-hydro siloxanes were functionalized with amine, cyano and phenyl groups to vary the properties of the siloxanes. The various chemical structures are seen in Figure 1. Addition of amine groups increased the crosslink density of the polymer while the addition of cyano and phenyl groups altered the surface tension of the polymer. It was possible to change the length scale of the phase separation from millimeters to microns by controlling the concentrations of these groups.

Figure 1: Chemical structure of siloxane.

Hydro-containing siloxane oligomers were modified by silanol condensation with amine functional silanols to create a branch structured amine. The reaction schematic is shown in Figure 2. Methoxy groups on the silane reacted at hydride sites to form flexible Si-O-Si bonds and liberate methane. The branch structure of this material allowed for a

high crosslink density and; therefore, good mechanical integrity while maintaining flexibility.

Figure 2: Silanol condensation of amine-methoxysilane with methyl-hydro-siloxane.

The polyimide/polysiloxane copolymer was produced by reacting the aromatic dianhydride, benzophenonetetracarboxylic acid dianhydride (BTDA), with the carbon-based diamine, phenylenediamine, and the functionalized siloxane polymer. This material was dehydrated to form the polyimide/polysiloxane copolymer. The reaction schematic is shown in Figure 3.

Figure 3: Polyimide condensation.

The general reaction procedure was based upon published synthesis condition.¹ The dianhydride was dissolved in dry N-methyl pyrrolidinone (NMP) at approximately 10 weight %. The solution was slowly dripped into 50 weight % diamine dissolved in NMP at 0°C. The mole ratio of total diamine to dianhydride was kept at 1:1. After addition, the reaction was heated to approximately 150°C to complete the condensation between the siloxane, carbon-based diamines and the anhydride.

Co-Polymerization Of Siloxanes And Epoxy

¹ Ahn and Sherrington, 1996, Macromolecules 29, 4164-4165.

Functionalized polysiloxane oligomers were co-polymerized with epoxy resin. Amine terminated polydimethyl siloxanes were used to catalyze the oxirane ring opening on the epoxy resin as shown in the reaction schematic of Figure 4. The reaction rate of the copolymerization step was affected by varying the ratio of amine versus vinyl and phenyl groups on the siloxane oligomer; however, the mechanical strength of all of the samples was adequate for testing.

Where R = siloxane pendant groups such as vinyl or phenyl

Figure 4: Amine Catalysis of epoxy ring opening. Copolymerization of amine containing siloxane and epoxy.

Other Polymer Matrices

Two other polymer systems were investigated in the course of this research. Commercially available polystyrene/polybutadiene copolymer (PS/PB) was obtained from Shell Chemical and polystyrene/polyacrylonitrile (PS/PA) from Aldrich. The first material consisted of 30% PS and 70% PB. This ratio of PS to PB governs the phase separation behavior such that the material phase separates into cylinders of PS in a PB matrix. This phase separation is seen in Figure 5. The second material, PS/PA, consisted of 30% polyacrylonitrile. Since the morphology of phase separation is dependent on the surface tension as well as ratio of components, it was not possible to know the morphology of this material a priori.

2.2 *Incorporation of Ceramic*

Hydrothermal synthesis has been used to convert a variety of titanium sources (titanium dioxide, titanium hydroxide gel, titanium alkoxide, titanium metal) into crystalline barium titanate. Exposure of the titanium to an aqueous barium solution at elevated temperature and high pH yields barium titanate. It has been shown that alkoxides mixed into polymers can be converted into barium titanate by hydrothermal processes demonstrating that the polymer does not interfere with the conversion.² Barium titanate is studied since it forms under relatively mild conditions and is

² E.B. Slamovich, I.A. Aksay, *Journal of the American Ceramic Society*, 1996, 79 239-247.

technologically useful. The steps to produce such a polymer/barium titanate composite are: 1) Mechanical mixing of a titanium alkoxide into a polymer solution, 2) Casting of the solution into a film, and 3) Hydrothermal treatment of the film in barium hydroxide. TPL followed this procedure to manufacture barium titanate/polymer composite.

Figure 5: TEM image of polystyrene/polybutadiene film after annealing.

The intent of the Phase I program was to produce barium titanate/polymer composites in which the ceramic is patterned at the nanoscale. This was to be accomplished by encouraging phase separation of the polymer matrix anticipating that titanium alkoxide would preferentially partition into one of the polymer phases. The film can then exposed to hydrothermal conditions suitable for synthesizing barium titanate in the matrix and the properties of the composite could be tested.

The hydrothermal synthesis was conducted at 85 C in 1 M barium hydroxide solutions for one hour. These conditions proved to be sufficient for forming barium titanate in PS/PB polymer matrices as seen below. As will be described later, polymer films which could not withstand these hydrothermal conditions were treated under the more mild conditions of 0.5 M barium hydroxide for longer time periods.

2.3 Demonstration of Barium Titanate Patterning

In the Phase I program, films of a block copolymer of polybutadiene and polystyrene were produced. Titanium diisopropoxide bisethylacetoacetate was added (at concentrations of 20 to 80% relative to the polymer) to solutions of the polymer in toluene or methyl ethyl ketone. These solutions were spun cast on to thin stainless steel shim stock and allowed to dry. Some of the films were annealed in a vacuum oven at 150 C for several hours in order to promote microphase separation. Microscopy of the polymer films revealed partitioning of the barium titanate in the polymer matrix; *i.e.*, annealing of the films revealed significant changes in the morphology of the barium titanate formed. Figures 6 and 7 are SEM images of composites with the same initial compositions; however, before hydrothermal processing, one of the films was annealed. Note that not only has the size of the barium titanate been reduced, the morphology of the ceramic is reminiscent of the microphase separated polymer matrix seen in Figure 5.

Figure 6: TEM Image of polystyrene/polybutadiene nanocomposite containing barium titanate hydrothermally synthesized prior to annealing.

2.4 Microphase Separation in the Desired Copolymer System

Parallel research investigated synthesis methods for more technologically useful polymer matrices in which the processing approach could be used. Copolymers of polyimic acid and polydimethylsiloxane were prepared as described above with varying concentrations of amine, diphenyl and cyano- groups. Films of these copolymers were produced and examined in cross-section by SEM to identify signs of microphase separation. Figure 8 is an image of a copolymer which displayed good microphase separation. In this image, microdomains of polysiloxane approximately 1 micron in diameter can be observed. This success led to the next step in the program incorporation of titanium alkoxide.

Titanium alkoxides were added to polyimide-polysiloxane copolymers which exhibited phase separation. The addition of the alkoxide gelled the polymer. Regardless of the polyimide composition (varying ratios of amine, diphenyl and cyano- groups), gelling occurred. Titanium butoxide, titanium ethylhexoxide, titanium diisopropoxide bisethylacetoacetate, titanium diisopropoxide bispentanedionate, and titanium triisostearoyl isopropoxide were added to the polyimide/polysiloxane copolymer without success. In addition, ligand exchange syntheses were performed at TPL on titanium isopropoxide with tetrahydrofurfuryl alcohol and glycerol to yield unique alkoxides. Unfortunately, these alkoxides also gelled the polymer. Due to this apparently intractable problem, a study of other copolymer systems was initiated. Polymers were chosen for their dielectric properties, likelihood of phase separation behavior and ease of synthesis.

Figure 7: TEM image of a polystyrene/polybutadiene nanocomposite containing barium titanate. Hydrothermal synthesis was performed after annealing.

2.5 Investigation of Alternative Polymer Systems

The problem of gelation in the polyimide/polysiloxane system was believed to be due to the functional groups of the polyimide. Therefore a logical step was to replace that component with epoxy. A description of the epoxy synthesis was described earlier. Copolymers of epoxy and polydimethylsiloxane synthesized at TPL have been found to possess good dielectric properties. In order to identify possible processing difficulties, all

of the processing steps were attempted with a few select copolymers before studies on phase separation or alkoxide partitioning were performed.

Titanium alkoxides were introduced into several epoxy copolymer compositions. The mixtures proved compatible and were spun cast into films. The films were thermally cured to promote crosslinking. Although many epoxy systems can withstand exposure to strong base, there is a possibility of attack of the epoxy crosslink. Treatment of these films under the standard hydrothermal conditions resulted in disintegration of the film. Attempts to process the film at barium hydroxide concentrations of 0.5 M and temperatures as low as 70 C still degraded the film to an extent that it could not be handled. No further work was performed on this system.

Figure 8: SEM image of polyimide/polysiloxane copolymer showing microphase separation.

Copolymers of polystyrene and polyacrylonitrile were studied because they can be synthesized with relative ease and possess good dielectric properties. The polymer was found to be compatible with several titanium alkoxides. Further, these films could withstand the hydrothermal synthesis conditions. Unfortunately, both polystyrene and polyacrylonitrile are brittle species and films containing titanium alkoxide displayed microcracks. Because of the other good qualities, further study of the system seemed warranted. With the addition of the plasticizers to the system, the cracking problem was overcome and testable films were produced. It was anticipated that the addition of

plasticizers, notably benzyl butyl phthalate, might alter the dielectric properties of the film; therefore, all of the films (with and without alkoxide and before and after hydrothermal treatment) contained equal amounts of plasticizer.

The phase separation behavior of polystyrene/polyacrylonitrile films was not studied. It was felt that dielectric testing should be performed to determine the effect of barium titanate on the composite before an examination of the morphology of the films was conducted.

2.6 Dielectric Properties

Polymerized films were tested for dielectric constant and loss factor as a function of frequency following ASTM D150. The dielectric constant and loss characteristics were measured from 30 Hz to 1.8 GHz using a HP 4279A LCR meter, and a HP 4291A RF impedance analyzer. Bulk resistivity was measured using a Keithly 6517 electrometer/high resistance system. Since the films were cast on stainless steel shim stock, only top electrodes needed to be added. Gold electrodes were deposited by vacuum metal evaporation to establish the second contact required for material properties characterization. The reported values are the average of three test locations.

The dielectric properties of polystyrene-polybutadiene films were tested in one of six conditions: 1) as cast, 2) cast and annealed, 3) cast with added titanium alkoxide, 4) cast with added titanium alkoxide and annealed, 5) cast with added titanium alkoxide and hydrothermally treated or 6) cast with added titanium alkoxide, annealed and hydrothermally treated. The results for films containing 60% alkoxide relative to polymer are seen in Table 1. Surprisingly, only small differences in the dielectric constant or loss tangent could be measured despite the dramatic structural changes observed after annealing and the presence of barium titanate. Some decreases (order of magnitude) in loss tangent were observed for some of the unannealed films; however, no basis for this change could be identified. Data was also obtained for polystyrene/polyacrylonitrile films. As with the PS/PB films, the effect of added barium titanate was not found to be significant. Upon further reflection, the result was attributed to a low percentage of barium titanate that formed in the composite. This can be qualitatively observed in Figures 6 and 7 and verified by the following calculations.

Table 1
Dielectric Properties of Polystyrene/Polybutadiene Films

Sample	Annealed	Alkoxide	Hydrothermal	Constant @ 1kHz	Loss @ 1kHz
PS/PB	No	No	No	3.94	0.015
PS/PB	Yes	No	No	4.17	0.021
PS/PB	No	Yes	No	3.95	0.002
PS/PB	Yes	Yes	No	5.14	0.016
PS/PB	No	Yes	Yes	4.33	0.002
PS/PB	Yes	Yes	Yes	5.76	0.030

Titanium alkoxides, on average, contain about 10 wt% titanium. Since polymers were cast from solutions containing about 10 wt% solids, limited amounts of alkoxide could be added to the polymer films. More significant alkoxide concentrations diluted the polymer to an extent where the films could not maintain their integrity either as-cast or after hydrothermal treatment. Even an addition of 60 wt% alkoxide to the polymer solution results in only 7 vol% barium titanate! Due to problems such as variations in film thicknesses and irregularities in the electrode area, the effects of the ceramic addition are washed out.

3.0 CONCLUSIONS

Among the data obtained in the Phase I program, three results should be kept in mind: 1) Hydrothermal synthesis of barium titanate was demonstrated in the model system, 2) Annealing of the copolymer system resulted in a dramatic redistribution of hydrothermally synthesized barium titanate and 3) The solution casting approach to film formation does not allow for incorporation of sufficient titanium alkoxide to ultimately affect the dielectric properties of the film.

Given the dramatic affect of annealing on the size and shape of barium titanate, further study of this method of particle size control is warranted. The effect of the redistribution of barium titanate on dielectric properties could not be demonstrated because of the relatively low ceramic content of the titanium precursors used. The next logical step is to demonstrate patterning of barium titanate by a processing method that will allow for greater solids loading of barium titanate. The logical approach is to attempt melt processing of the copolymer. If the polymer was formed without solvent, stresses caused by shrinkage during drying would be avoided and increases in the alkoxide concentration would be possible. The low yield of titanium alkoxides is thus mitigated by elimination of the solvent from the forming process. Nanocomposites with a solids loading approaching 30 vol% barium titanate could be achieved by melt casting with less dilution of the polymer than when cast from solution.