

# **Investigation of Solvent Diffusion Studies for a Model Epoxy Adhesive**

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## **ABSTRACT**

Diffusion studies are reported for a model epoxy system. Epon 862, a bisphenol F epoxy resin was chosen, and 1-methyl imidazole (1 parts per hundred resin) was used as the curing agent. Two different curing pathways were investigated. The first pathway was an isothermal cure at 175 °C for two hours. In the second pathway, samples were cured at 175 °C for one hour and postcured at 200 °C for one hour. DSC, DMA, dielectric, and dilatometry indicated a glass transition temperature of 65 °C for the isothermally cured samples and 85 °C for the postcure samples.

During a period of 20 days there was a 5% weight increase when water was the swelling agent, and a 2.5 decrease in weight when 1,5-pentanediol was used as the swelling agent. During a period of 10 days, a 5% weight increase occurred when a 90% water/ 10% 1,5-pentanediol (by volume) mix was used as the swelling agent. The energy to debond the adhesive from a poly (ethylene terephthalate) substrate indicated that isothermally cured samples soaked and dry as well as postcured samples dry exhibited similar critical strain energies.

# Cresol Novolac Networks Containing Maleimide Reagents

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## ABSTRACT

A p-cresol maleimide endcapping reagent for a novolac oligomer and a maleimide monomer, 4-hydroxyphenylmaleimide, were synthesized for use as crosslinking agents in cresol novolac-epoxy networks. The synthesis of both maleimide monomers was monitored with  $^1\text{H}$  NMR. Differential scanning calorimetry was used to study the thermal crosslinking reactions of these monomers. Crosslinking of novolac oligomers endcapped with p-cresol maleimide was performed at 200°C with triphenylphosphine and bisphenol-A diepoxide. Novolac oligomers with 4-HPM were crosslinked with bisphenol-A diepoxide at lower temperatures and then postcured. All novolac networks with p-cresol maleimide groups had voids after curing. However, novolac networks with 4-hydroxyphenylmaleimide monomer were synthesized without voids. Thermal gravimetric analysis of p-cresol maleimide showed the onset of weight loss around 150°C and 20% weight loss at 200°C. Weight loss for 4-hydroxyphenylmaleimide began around 170°C and has less than 5% weight loss at 200°C as shown by thermal gravimetric analysis.

# **An Investigation Into The Behavior Of Concrete-Filled FRP Tubes For Pile Foundations Under Axial Loading**

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## **ABSTRACT**

Professors George Filz and Jack Lesko of the Departments of Geotechnical Engineering and Engineering Science and Mechanics, respectively, and Miguel Pando, a Ph.D. Student in the Geotechnical Engineering Department, are currently under taking an extensive research program at Virginia Tech in order to evaluate the performance of these concrete-filled FRP Tubes as bridge foundations. This involves the assessments of the driveability, axial and lateral capacities and the long-term performance or durability of these piles. As a SURP Student at Virginia Tech during the summer of 2000 I became involved in this joint venture. My area of concentration in the research program involved the investigation of the behavior of these concrete-filled FRP Tubes under axial loads.

The project comprises a four part experimental program conducted over the summer of 2000. The following gives a brief outline of this program:

- Axial compression tests carried out on FRP Tubes filled with 1500 psi concrete, which were approximately 5 feet in length, had an average outer diameter of about 12 ½ inches and an average thickness of about 5/16 of an inch. (currently underway)
- Tension tests carried on the FRP Tubes alone which were cut into small strips approximately 1"x 10" in size.
- Axial compression tests carried out on empty FRP Tubes approximately 2 feet in length.
- Burn offs of small strips of FRP Tubes approximately 1"x 2" in size.

# Synthesis and Properties of Epoxy-Siloxane Networks Containing Phosphine Oxides

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## ABSTRACT

A novel diepoxide containing a phosphine oxide moiety was synthesized by reacting bis-(hydroxyphenyl)phenyl phosphine oxide with epichlorohydrin. The epoxy was characterized using  $^1\text{H}$  NMR and was found to have 33% chain extension. This epoxy resin, as well as a bisphenol-A based diepoxide, was reacted with 1,3 bis-(3-aminopropyl)tetramethyldisiloxane. The incorporation of the phosphine oxide group exhibited increased glass transition temperature and increased char yield when compared to the networks prepared with the bisphenol based epoxy resin. The bisphenol based epoxy/siloxane network was shown to be exceptionally ductile with a fracture toughness of  $2.68 \pm 0.52 \text{ Mpa}\cdot\text{m}^{1/2}$ . Lap shear analysis was performed to assess the adhesive properties of the epoxy/siloxane networks with steel. Samples prepared with bisphenol and bisphenol/phosphine oxide blends resulted in interfacial failure and were in a structural regime. The incorporation of a phosphine oxide diepoxide demonstrated mixed mode failure which is suggestive of better adhesion to steel.

# Controlling Dewetting in Ultra-thin Films

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## **ABSTRACT**

Thin organic films play important roles as adhesives, coatings for controlling a solid surface's wetting properties and compatibility with its environment, and in microelectronic and optical devices. For thin enough films ( $< \approx 1000\text{\AA}$ ) subjected to thermal annealing above the glass transition temperature,  $T_g$ , film destruction can occur through a process known as dewetting. The work contained in this report is an optical microscopy study of ultrathin layers demonstrating how isopentylcellulose cinnamate (IPCC) can be used to control the stability of poly(*t*-butyl acrylate) (PtBA) films on silicon wafers prepared by the Langmuir-Blodgett (LB) film technique. Three principles were demonstrated regarding PtBA stability: 1) Placing IPCC between PtBA and silicon (Si/IPCC/PtBA/Air) induces dewetting which worsens as the IPCC layer thickness increases; 2) Thicker PtBA layers on Si/IPCC/PtBA/Air dewet more slowly; and 3) Placing a little as two monolayers of IPCC on top to form a trilayer sandwich of Si/IPCC/PtBA/IPCC/Air substantially stabilizes the film.

# **Electric Field Tunable Materials for Thin Film Microwave Switching Devices**

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## **ABSTRACT**

Novel organic materials can be used in microwave switching devices as a substitute for inorganic ceramic ferrite materials because of their cheap and easy processability. The velocity of propagation of can be varied by the external electric field or magnetic field. In our organic materials, external electric field is used to vary dielectric constant and therefore velocity of propagation of microwaves. Our new devices are arranged as parallel plate capacitors where the thin polymer film is in-between the capacitor plates. The thickness of the film ranges form 200-1000nm. All the films are spin-coated. This thin polymer film consists of guest dye molecules incorporated into the polymer host material. When voltage is applied the electric field is established between the electrodes and all of the dye molecules orient in the direction of the electric field. This reorientation of the dye molecules causes the dielectric constant to change. The changes of dielectric constant are measured through capacitance. Our devices gave the reversible change in capacitance up to 25% over 7V.

# **Initial Stages Of Crystallization In Bisphenol-A Polycarbonate**

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## **ABSTRACT**

The early stages of crystallization of a bisphenol-A polycarbonate were investigated using differential scanning calorimetry, infrared spectroscopy, wide- and small-angle X-ray scattering. The conditions were established in order to perform identical isothermal crystallization experiments with the techniques mentioned above. Preliminary SAXS results on a polydisperse polycarbonate sample are consistent with a preordering process during the induction period.

# Synthesis of High Refractive Index Polyphosphonate Adhesives and Their Hydrolytic Stability

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## ABSTRACT

The synthesis of aromatic polyphosphonates based upon various bisphenols and dichlorophenyl phosphine oxides was investigated. The materials have been only discussed briefly in the literature, although it has been recognized that the phosphorus would contribute important fire resistant characteristics. Major problems with obtaining high molecular weight and preparing materials with sufficient hydrolytic stability had been encountered. In principle, the materials are analogous to the well-known and very important aromatic polycarbonates. This study has been conducted as a solution polymerization using catalysts based upon either imidazoles or dimethyl amino pyridine. The catalysts were able to very effectively produce high molecular weight, tough ductile materials with a high degree of optical clarity. In contrast to the aromatic polycarbonates, the refractive index could be increased from 1.58 to 1.60 (for the bisphenol-A based system) and as high 1.64 for a biphenol based system. The latter was still an amorphous soluble polymer due to the non-coplanar nature of the phenyl phosphine oxide bond. The second issue was the poor hydrolytic stability. The polyphosphates were successfully endcapped with cumylphenol by altering the stoichiometry of the dichloro phenyl phosphineoxide biphenol ratio, to control the molecular weight with an excess of the dichloride and then to cap the active chain ends with the monofunctional cumylphenol. The results were quite successful; predicted molecular weights of 25,000 were obtained, as verified by both gel permeation chromatography and NMR endgroup analysis. Moreover, preliminary rheological studies show that the endcapped systems are melt stable at 200°C, whereas the systems of initially higher molecular weight but without any endcapping clearly degraded quickly -- probably an acid catalyzed hydrolysis process. Thus, the materials are at this stage shown to be tough ductile, transparent materials with high refractive index that have a substantial degree of hydrolytic stability, if properly endcapped to eliminate acidic functionalities. Future work should further compare the hydrolytic stability of these optimized systems, in comparison to polycarbonates to ascertain whether the phenyl phosphonates are potentially competitive to the polycarbonates. Furthermore, copolymers of the phosphonates with the polycarbonates should be prepared to take advantage of the well known, but also demonstrated in this work, extensive high char yields that can be produced upon pyrolysis in either nitrogen or air.



# Chemical Modification and Oxidative Degradation Studies of Poly(1,3-Cyclohexadiene)

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## **ABSTRACT**

Degradation studies of novel poly(1,3-cyclohexadiene) (PCHD) homopolymers focused on oxidative degradation as a function of temperature and catalysts such as cobalt (II) 2-ethylhexanoate. The effects on molecular weight as well as chemical composition were studied using GPC, IR, *insitu* IR and NMR. Epoxidation of poly(1,3-cyclohexadiene) was performed using m-chloroperoxybenzoic acid. The resultant polymer was studied to determine degree of conversion, change in molecular weight and molecular weight distribution, and effects on thermal properties. Initial attempts at other modifications of PCHD such as bromination, ozonolysis, hydrogenation and reaction of epoxidized PCHD with amines, anhydrides, inorganic acids and nucleophiles generally yielded insoluble products or proved to be non-quantitative processes that were not characterized at this time.

# **Durability Studies of Room Temperature Curing Silicone Adhesives: Mode I and Mode II Testing**

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## **ABSTRACT**

Durability studies were carried out under various environmental conditions using adhesively bonded aluminum adherends that had undergone a P2 etch surface treatment. The treated aluminum adherends were adhesively bonded with unmodified and modified silicone adhesives. The samples were tested via Mode I – wedge geometry - (peel stress) and Mode II – three-point bend geometry - (shear stress) methods. Tests of environmental durability were carried out for specimens maintained under Mode I and Mode II stress conditions by exposing the specimens to air at room temperature and by immersion in water at room temperature and also by immersion in boiling water. For Mode I testing, no significant variation in adhesive performance was noted when comparing specimens bonded with unmodified and modified adhesive. Furthermore, no significant change was found in durability when comparing specimens tested in different environments. For the Mode II testing, a change in performance occurred for specimens tested in water at room temperature water compared to tests in boiling water. In all testing, the failure mode was cohesive. It was determined that the P2 etch surface treatment clearly enhanced performance compared to another surface treatment involving the cleaning of aluminum with iso-propanol. The pretreatment of aluminum using the P2 etch procedure is a reasonable adherend pretreatment method to improve adhesive performance in severe environmental conditions.

# Synthesis of a Cryptand for Complexations with High Association Constants

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## ABSTRACT

The synthesis of cryptand **5** in order to determine its ability to complex with paraquat diol **1c** was attempted. The cryptand contains a pyridine moiety, which is expected to assist complexation and result in a larger association constant. Large association constants are necessary to prepare high molecular weight noncovalent polymers. Several methods to produce the cryptand were explored and some problems of the synthesis have been identified. Several derivatives of 32-crown-10 were produced as part of the synthesis, including the diacid chloride **12** precursor to the cryptand.

# **Effects Of Changes In Aluminum Surface Morphology On Underwater Adhesion**

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## **ABSTRACT**

Surface morphology modifications caused by anodization and anodization pre-treatments were studied. Aluminum samples (alloy 6063) were pre-treated by sanding with steel wool, rinsing in potassium hydroxide, and/or in methyl ethyl ketone and/or etching with chromic acid before anodization. The anodization process involved either chromic or phosphoric acid oxidation. These samples were subjected to a series of tests including contact angle measurements, strength testing and scanning electron microscopy (SEM). Contact angle measurements were used to determine surface energy as it may affect sample wettability. Scanning electron microscopy was then used to determine what effect pre-treatments had on the aluminum oxide layer porosity. Finally, strength testing was used to measure the underwater adhesion of a photocurable acrylic resin to the modified aluminum surface. It was determined that cleaning aluminum prior to anodization was unnecessary. However, etching by chromic acid markedly increased the bonding properties of the anodized samples compared to un-etched samples. This pre-treatment combined with phosphoric anodization produced the best adhesive properties in an underwater environment. This result was supported by contact angle measurements.

# **Synthesis and Characterization of Magnetic Polydimethylsiloxane Fluids**

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## **ABSTRACT**

A series of poly(dimethylsiloxane-b-(3-cyanopropyl)methylsiloxane-b-dimethylsiloxane) triblock copolymers with various molecular weights were synthesized. The copolymers were used as steric stabilizers for stable dispersions of cobalt particles. The dispersions were prepared in toluene with stabilizers where anchor blocks adsorbed onto the particles and tail blocks provided steric stability. These copolymers formed micelles in toluene and dicobalt octacarbonyl diffused into the center of the micelles where cobalt metal particles formed. The concentration limits at which a stable dispersion can be formed were studied. Also the effect of the reaction parameters on particle size was investigated.

# ***In-situ* Sub-Micron Photo-Luminescent Particle Synthesis by Surface Modification**

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## **ABSTRACT**

A new method for the formation of particles of zinc sulfide on a polymer surface was developed. Films of polystyrene were exposed to corona discharge, soaked in a solution of zinc acetate, and exposed to hydrogen sulfide gas. X-ray photoelectron spectroscopy (XPS) confirmed the presence of zinc sulfide on the surface, and atomic force microscopy (AFM) revealed that the particles had an average length of between 100 and 200 nm and a thickness of 10-15 nm. A detailed study of the corona discharge treatment showed that the water contact angle could be tailored by regulating several experimental parameters. The corona discharge step could be made site selective by exposing the sample through a mask.

# **Bimaterial Curvature Measurements For Characterizing Coefficients Of Thermal And Diluent Expansion Of Structural Adhesives**

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## **ABSTRACT**

A bimaterial curvature approach has been developed that allows one to characterize the coefficient of thermal expansion (CTE) and the coefficient of diluent expansion (CDE) of commercially available epoxy resins. Intrinsic property mismatches such as CTE and CDE lead to residual stresses that cause bimaterial strips composed of a glass substrate coated with epoxy to bow. The phenomenon arises as a result of temperature change or solvent diffusion. This technique uses a dynamic mechanical analyzer to measure curvatures resulting from thermal expansion or diffusion induced swell.

A quantitative calculation of the CTE for epoxy resins was proven to be feasible via this technique. Coating thickness was observed to play a significant role in the measured values of CTE. Additionally, some conclusions about diffusion induced curvature changes were made. Experimental observations indicate that final curvature values correlate directly with saturation mass uptakes for 4 different diluents. Likewise, the rate of curvature change also correlates directly with the corresponding diffusion coefficient of each diluent.