

## Ceramic Fiber Reinforced Polymer Matrix Composites

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### **Abstract**

The processability of random, non-woven ceramic fiber reinforced composites with a polymer matrix was investigated. Two forms of fiber were used: random, non-woven fiber preforms and loose, chopped fiber. Resin film infusion, RFI, was the method by which composites were made using the preforms and vinyl ester resin as the matrix. The loose fiber was injection molded, IM, with polyphenylene sulfide as the matrix. All composites underwent a series of characterization and mechanical tests. Ultrasonic C-scan, scanning electron microscopy, and fiber volume fraction measurements were performed. The range of volume fraction of fiber for RFI and IM were 30 to 40vol% and 10 to 20vol%, respectively. Tensile tests were run to measure initial modulus, strength, and strain-to-failure.

# MECHANICALLY ALLOYED GRAPHITE REINFORCED NYLON MATRIX COMPOSITES

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## **Abstract**

Composite materials of graphite powder in a nylon 6,6 matrix were prepared by the mechanical alloying process. Powders ranging from 0 to 10 volume percent graphite were milled for 5 hours with a 4:1 charge ratio. The milled composite powders were melt consolidated via hot press into sheets at 290°C and 300°C. Each composition and melt temperature sheet was characterized mechanically through tensile testing. Differential scanning calorimetry was used to determine the degree of crystallinity of the polymer matrix of only a portion of the samples produced at 290°C. Comparison with previous studies of silica in a nylon 6,6 matrix show that graphite promoted higher levels of crystallinity in the semicrystalline polyamide matrix. Graphite particle inclusions created a more brittle material with a higher Young's modulus than the unreinforced nylon. The tensile strength of the composite material was surprisingly lower than that of the pure polymer matrix. Preliminary conclusions about the unexpected weakening and the improved stiffness as related to the graphite particles and crystallinity were drawn.

# EXPERIMENTAL DETERMINATION OF AN INITIATION CRITERION FOR FATIGUE CRACKING IN ADHESIVE BONDS

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## **Abstract**

Adhesive joint fatigue life was examined with respect to two stress singularity parameters derived from the specimen geometry and applied load. By varying these parameters it may be possible to generate a fatigue failure criterion that could be used to predict fatigue life without extensive prototype testing. Preliminary points on this theoretical graph were obtained by mechanically cycling adhesively bonded wedge samples. These specimens consisted of an epoxy wedge bonded to an aluminum substrate. A fatigue testing fixture was constructed to analyze these specimens.

EVALUATION OF AMORPHOUS POLYESTERS FOR POTENTIAL USE AS  
POLYCYANURATE TOUGHENERS

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**Abstract**

The toughening effectiveness of four amorphous polyesters (Vitel 3200, 3300, 3500 and 3550) and hydroxyl terminated butadiene-acrylonitrile copolymer (HTBN) for polycyanurate networks was studied. Blends containing the toughener and polycyanurate were prepared at a 10 % ( wt.) level. Dynamic mechanical analysis (DMA) was employed in the determination of the glass transition temperature (T<sub>g</sub>) and low temperature transitions and used to evaluate the extent of phase separation. Thermogravimetric analysis was used to investigate the thermal stability of the systems. Atomic Force Microscopy (AFM) was used to examine the microstructure of the samples. Finally, a fracture toughness test, using a single-edge notch beam technique, was performed to determine the extent that the polyesters and HTBN toughened the polycyanurate. Only the Vitel and the HTBN significantly improved the toughness of the polycyanurate matrix by over forty percent. The Vitel 3300, 3500, and 3550 were not effective tougheners.

# EFFECTS OF ENVIRONMENTAL EXPOSURE ON SOLVENT AND WATER-BASED EPOXY SYSTEMS

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## **Abstract**

The dielectric properties of three types of epoxy systems were investigated: solvent-based, extracted water-based, and unextracted water-based. Samples from each of these three groups were fabricated via casting and exposed to humid environments in an environmental chamber at room temperature and elevated temperature, a steam bath at various temperatures, and finally soaked in boiling water. The microwave frequency dielectric properties of the three systems after each environmental exposure were measured with a network analyzer. Thermogravimetric analysis was used to detect the presence of surfactant within the water-borne samples. Under identical conditions, water-borne epoxy systems absorbed more water than solvent-based systems and also allowed more free water into the samples. The critical moisture content of the water-borne samples was approximately 4.0 wt%, whereas the critical moisture content of the solvent-borne samples was approximately 2.5 wt%. Extraction of water and soluble components in the resin had no effect on the dielectric properties of the water-borne samples. TGA was not sensitive enough to detect the presence of surfactant in the water-borne samples. Because of the presence of high quantities of free water at moisture fractions beyond 4.0 wt%, the differences between the dielectric properties of solvent and water-borne epoxy systems appear to be due to morphology.

# Characterization of Waterborne Epoxy Resin Using Dynamic Mechanical Analysis and Atomic Force Microscopy

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## **Abstract**

Environmental concerns have promoted the switch from solvent-based coatings and adhesives to water-based coatings and adhesives. However, the effect of the added surfactant needed to stabilize the waterborne emulsion is unknown. In this study, atomic force microscopy (AFM) and dynamic mechanical analysis (DMA) were used to determine the long term behavior and performance of water-based epoxy films. The distribution of the surfactant in the polymer was studied using AFM. Viscoelastic properties were characterized by DMA. AFM studies revealed that the surfactant was miscible with polymer in polymer-surfactant systems. The microstructure seen in some cases is not detected by dynamic mechanical analysis. In the dynamic mechanical analysis studies, the effect of a substrate on the polymer-surfactant system was investigated. Master curves were constructed to describe the performance over the waterbased epoxy films over time. A plot of normalized log storage modulus versus log frequency between bulk samples and bulk samples cast on the glass cloth was not illuminating. However, the shift factors could be fitted to the Williams-Landel-Ferry (WLF) equation. C1 and C2 constants were calculated and used to determine the activation energy at the glass transition. Activation energies were higher for samples cast on the glass cloth, suggesting more thermal energy is required for cooperative motion at the glass transition. In addition, the temperature sensitivity of the shift factors or fragility was analyzed. Based on previous work in our laboratory, fragility increased with decreased amounts of surfactant. In the current work, samples cast on the glass cloth exhibited increased fragility. Thus, it is believed that the surfactant migrates toward the interface of the material, leaving the matrix.

AN INVESTIGATION OF PHYSICAL AGING ABOVE THE GLASS TRANSITION IN  
POLY(ETHER ETHER KETONE) USING CREEP MEASUREMENTS

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**Abstract**

Physical aging above the glass transition in a semicrystalline polymer, Poly (ether ether ketone) or PEEK, was investigated using creep measurements. This paper outlines the specimen preparation, including the melt from powder and subsequent cold crystallization at 200, 210, 220, 230, and 240°C. Physical aging was investigated at 180°C in a dynamic mechanical analyzer (DMA). Creep curves were then horizontally and vertically shifted to form a master curve. Horizontal shift rates at the different cold crystallization temperatures were then determined from master curves. The results showed that as the cold crystallization temperature was increased, the horizontal shift rate increased. A possible mechanism, secondary crystallization, was suggested for physical aging above the glass transition. As the cold crystallization temperature is increased, it is widely accepted that the spherulitic morphology coarsens. This increases the driving force for more secondary crystallization to occur, which increases the crystallinity and constrains the residual amorphous regions. Differential Scanning Calorimetry (DSC) was used to investigate if secondary crystallization was occurring. The DSC results confirm that secondary crystallization is the mechanism for physical aging in PEEK above the glass transition temperature.

(Keywords: physical aging; glass transition; creep; semicrystalline polymers; PEEK)

PEEK/Carbon Fiber Composites: An Evaluation of Particle Size and Processing Method on Final Composite Properties

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**Abstract**

Thermoplastics would be a great matrix material except that high melt viscosities hinder the wetting of the reinforcing fibers. One method of fabricating such composites is called powder prepregging. Powder prepregging localizes the polymer enabling materials with high viscosities to still consolidate well. Prepregging is done by spreading a tow of fibers and "shaking" the polymer powder onto the fiber. The effect of particle size and distribution is unknown in all aspects of the process. This paper reports the results of the effect of particles size on the mechanical properties. It was concluded that the particle size does not effect either the longitudinal or transverse moduli or the interlaminar shear strength. Likewise, the longitudinal strength did not vary significantly with particle size. In the transverse direction, as the particle size increases, the transverse strength increases from 40 MPa to around 70 MPa. The decrease in strength is attributed to the small particles. The smaller particles tend to agglomerate. The agglomerated particles form large particles which hinder the flow of the polymer, leading to a less uniformly consolidated composite.



# EVOLUTION OF THE LOW ENDOTHERM AND CRYSTALLINITY DURING SECONDARY CRYSTALLIZATION OF SEMI-FLEXIBLE CHAIN POLYMERS

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## **Abstract**

The effect of prior thermal history on secondary crystallization and on the low endotherm in poly(ethylene terephthalate) (PET) and poly(ether ether ketone) (PEEK) were evaluated. PET samples were cold-crystallized for various times at 165 °C and analyzed using DSC and pycnometry. Both the low endotherm temperature and heat of fusion were found to increase with crystallization time. Possible explanations for the large increases in low endotherm temperature and heat of fusion are given in detail. Amorphous and crystal densities were calculated from the pycnometry and DSC data, and compared with literature values. PEEK samples with various annealing/crystallization histories were prepared and analyzed using DSC. The primary crystallization process in PEEK was shown to be independent of prior annealing in the melt below  $T_m$ , but the endotherm corresponding to annealing at 245 °C was shown to be dependent upon prior annealing in the melt.

## Synthesis of Ferrocene Dimers Linked by Fluoroarenes

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### **Abstract**

Ferrocene polymers are investigated for potential application as "molecular wires." Small molecular weight co-polymers have been made using hexafluorobenzene as the co-monomer, but low solubility made characterization difficult and optimization impossible. The approach we chose was to substitute new fluoroarene monomers in place of hexafluorobenzene in order to discourage solid-state packing which should, in turn, improve the solubility. Substituting decafluorobiphenyl for hexafluorobenzene as the co-monomer did not improve solubility. Octafluoronaphthalene gave a complex mixture of products. We also synthesized monomeric and dimeric models of the polymers in order to construct a chemical shift database of  $^1\text{H}$  and  $^{19}\text{F}$  spectra for use in polymer characterization. Synthesis of the monomeric and dimeric units was successful in some degree and the NMR spectra obtained will be useful in the future characterization of these polymers. Dimers can also be used to "grow" medium molecular weight polymers which could be tested for their mechanical and electrical properties.

# SYNTHESIS AND CHARACTERIZATION OF *p*-PHENYLENEDIAMINE BASED POLY(ETHER IMIDE) THERMOPLASTIC AND THERMOSETTING SYSTEMS

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## **Abstract**

The synthesis and characterization of an insoluble polyimide system based on 2,2'-bis[4-(3,4-dicarboxyphenoxy)phenyl]propane dianhydride or bisphenol A dianhydride (BPA-DA) endcapped with either phthalic anhydride or 4-phenylethynylphthalic anhydride is described. The use of the 4-phenylethynylphthalic anhydride allowed curing of the polymer giving a thermoset. Imide oligomers of  $M_n = 5000 \text{ g mol}^{-1}$  and high molecular weight ( $20\,000 \text{ g mol}^{-1}$ ) were synthesized by the use of the ester acid of the dianhydrides and *p*-phenylene diamine in solution. It was determined that a direct relationship between molecular weight and particle precipitation upon cooling from NMP solvent was observed, as well as a relationship between concentration and precipitation temperature. High molecular weight materials were found to remain soluble in the reaction solvent. Particle sizes appeared to be related to concentration for the phthalic anhydride endcapped oligomers while results were inconclusive for the 4-phenylethynylphthalic anhydride endcapped polymers. Melting points ( $T_m$ ) for the *p*-PDA polymer were determined to be around  $280^\circ \text{C}$ , observed on the first heat only, in contrast to the amorphous *m*-PDA based polymer made commercially which showed no  $T_m$ . The glass transition temperatures ( $T_g$ ) of the *p*-PDA based system endcapped with 4-PEPA was observed to be as much as  $15^\circ \text{C}$  higher than that of the *m*-PDA systems.

TPER-BPDA SEMICRYSTALLINE POLYIMIDE STRUCTURALADHESIVE: 1.  
DURABILITY STUDIES OF LAP SHEARADHESIVE BONDS; 2. MORPHOLOGICAL  
STUDIES

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**Abstract**

Durability studies of lap shear adhesive bonds formed with TPER-BPDA (1,3-bis (4-aminophenoxy) benzene - 3,3',4,4'-biphenyltetracarboxylic dianhydride) were performed. The bonded samples were subjected to aging temperatures of 23°C, 177°C, and 232°C for times of 1 week, 3 weeks, and 7 weeks. The strengths, however, were found to vary considerably only with testing temperature with average strengths of 6111 psi, 4449 psi, and 2984 psi; for testing temperatures of 23°C, 177°C, and 232°C respectively. The only exceptions were samples stored at 232°C for 7 weeks which showed some decrease in strength. Exposure to common solvents, with the exception of acetone, for 9 days was found to have no affect on the strengths of lap shear bonds made with TPER-BPDA. A 72 hour water boil reduced the room temperature test strength to 4700 psi. The failure mode was found by SEM to be cohesive in all cases.

Morphological studies of TPER-BPDA were carried out to study the effects of melt temperature, crystallization temperature, and molecular weight on crystallization kinetics and morphology. It was found that the crystalline morphology was strongly dependent on crystallization temperature. A lower isothermal crystallization temperature resulted in a higher nucleation density and thus a smaller average spherulite size. At a temperature approaching 330°C, the nucleation density became so high that only a fine grainy morphology was apparent. The spherulitic growth rate increased as crystallization temperature was varied from 365°C to 330°C. The spherulitic growth rate was not affected by melt temperature for the range studied. The growth rate was decreased by a factor of ~70 percent as the molecular weight (Mn) was increased from 15 kg/mol to 30 kg/mol.

## SYNTHESIS OF POLYETHER DENDRIMERS VIA A DIVERGENT ROUTE

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### **Abstract**

A reaction sequence was studied to synthesize precursors for a dendron repeat unit, (1?OH)<sub>4</sub>[G<sub>1</sub>]-OTHP. This dendron would be used for the divergent synthesis of a (aBr)<sub>48</sub>[G<sub>4</sub>] polyether dendrimer and a (Ph)<sub>16</sub>[G<sub>5</sub>]-OPhBr polyether dendritic wedge. Several protecting groups were tested, including methyl ethers, benzyl ethers, tetrahydropyranyl ethers, benzoate esters, and acetate esters. Benzyl ethers were used as a protecting group in a reaction sequence converting 5-hydroxyisophthalic acid to precursors for a first generation dendron repeat unit. The (CO<sub>2</sub>Me)<sub>4</sub>[G<sub>1</sub>]-OTHP dendron precursor to the (1?OH)<sub>4</sub>[G<sub>1</sub>]-OTHP was also synthesized.

# SURFACE PREPARATION AND BOND DURABILITY OF Ti-6Al-4V WITH A POLYIMIDE ADHESIVE

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## **Abstract**

The surface preparation of Ti-6Al-4V using base/acid and weak base (aqueous) treatments were studied. The objective was to maximize the hydroxide concentration on the surface of the metal so that a chemical reaction could enhance bonding to a polyimide adhesive. The analyses of these preparations were performed by finding the concentration percentages of elements on the surface and performing curve fits with the oxygen peaks to compare the hydroxide concentrations. The XPS was used for this study. An aqueous 50% (v/v) NH<sub>4</sub>OH weak base treatment was selected for use before bonding and/or priming. Base/acid, weak base, and alumina grit blast treated titanium were all bonded in a single lap shear configuration with an FM-5 adhesive supplied by Cytac with a cure cycle of 250°C for 1/2 hour and 350°C for 1 hour at 75 psi. The durability of lap shear specimens using different surface treatments was tested. Samples were subjected to tests at room temperature, after a three-day water boil, and after maintenance at 177°C for two weeks, and 204°C for two weeks before being tested in an Instron. Samples were also bonded with FM-5 after priming with PETI-5 and TPI-2000 polyimides. These samples were then tested in the Instron after being held at room temperature and after immersion in boiling water for three days. Scanning Electron Microscopy (SEM) and X-ray Photoelectron Spectroscopy (XPS) were used to determine how the failure occurred. The TPI-2000 primed and bonded specimens that were tested at room temperature gave the highest strength of approximately 7000 psi. However, the PETI-5 primed samples gained strength following testing in boiling water.

## CARBON FIBER REINFORCED VINYL ESTER MATRIX COMPOSITES

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### **Abstract**

Styrene diluted "vinyl ester" oligomers comprise a class of resins for thermoset polymer matrix materials used in carbon fiber reinforced composites becoming increasingly important for infrastructure. A lower viscosity derivative of the vinyl ester resin has been synthesized, which can be diluted with less styrene to achieve a pultrudable viscosity. Less styrene results in less shrinkage of the matrix and improved properties of the composite. Recent research shows that fibers sized with a thermoplastic yield enhanced performance of polymer matrix composites. The sizing material interacts with the matrix resin to form an interphase region with properties different from the matrix and the sizing material (Figure 1). The "interphase" is a region of finite mass located at the fiber/matrix interface that can drastically affect composite performance. Understanding the relationship between the carbon fiber and the cured matrix network will allow optimization of composite mechanical properties. Water dispersible and water soluble poly(hydroxyether) thermoplastic sizings have been investigated. To study the interphase between thermoplastic sizings and the vinyl ester matrix, bilayers and single fiber model composites were examined by atomic force microscopy.