[illegible]

[illegible]

3[illegible] 402

p8

Cooperative Agreement NASA NCC1-150

Preparation, Fabrication, and Evaluation of Advanced Polymeric and Composite Materials

Final Report

Robert A. Orwoll, Principal Investigator
Department of Applied Science
P.O. Box 8795
College of William and Mary
Williamsburg, VA 23187-8795

From 1991 until December 31, 1997, funding from the cooperative agreement NCC1-150 supported the dissertation research of six doctoral students and two masters students at William and Mary. It also provided funding for a ninth student who left the graduate program prematurely without earning a degree (in order to move with her spouse's new job location). In some of these cases, students originally supported by NCC1-150 moved to other NASA funding (e.g., GSRP). In addition, this cooperative agreement supported one postdoctoral research associate on the William and Mary faculty.

The thesis titles, names of the eight students, and the abstracts of their theses are given below:

Physical and Mechanical Behavior of Amorphous Poly(arylene ether-co-imidazole)s and Poly(arylene ether-co-imidazole) Modified Epoxies

Patricia D. Roberts-McDaniel, Ph.D., 1994

> Due to the high crosslink density of cured epoxy resins, they generally lack damage tolerance. A significant amount of research has been expended to improve the toughness of epoxies. Research into the area of thermoplastic epoxy modifiers has begun to overcome some of the limitations of early methods of epoxy toughening (i.e., lower modulus and thermal stability).

This study examines the physical and mechanical properties of random poly(arylene ether-co-imidazole) (PAE-co-Is) and the characterization of epoxies modified with poly(arylene ether-co-imidazole)s.

Poly(arylene ether-co-imidazole)s exhibited the highest solubility in N,N,N',N'-tetraglycidyl-4,4'diaminodiphenyl methane (TGMDA) based resins. The high molecular weight polymers caused significant decreases in melt flow behavior of the modified systems. Modification of TGMDA resins with PAE-co-Is significantly decreased the tetrahydrofuran sensitivity of the cured system and did not significantly affect the moisture absorption properties. One system modified with 10% w/w polymer exhibited increases in fracture toughness 1.7 times that of the unmodified system.

The Requirements of Patentability as Applied to the Chemical Arts

Joy L. Bryant, M.A., 1994

The purpose of this thesis is to discuss and teach by way of actual examples what is required in order to obtain a patent for an invention relating to the chemical arts.

A patent provides an inventor with the right to exclude others from making, using and selling his invention in the United States in exchange for public disclosure. Patent law is the legal system which provides a means for protecting property in technology. The United States patent system has a long evolutionary history and is constantly subject to change in order to meet the needs of the public.

The patentability of an invention is subject to meeting the requirements set forth in Title 35 of the United States Code (35 U.S.C.). These requirements are both non-technical and technical. The subject matter of the invention must be classified as statutory subject matter (non-technical) and must be novel, useful and nonobvious (technical).

Patent prosecution is the process of obtaining a patent. It is during this process whereby the claims in an application are evaluated in order to determine whether the invention meets the non-technical and technical requirements of patentability.

The individual cases presented show that each case is unique and the strategy which is used in arguing the patentability of an invention differs depending on the facts in the case.

Fabrication of Thermoplastic Polymer Composite Ribbon

Donald A. Sandusky, Ph.D., 1995

The goal of this research was to develop a controllable process to convert a thermoplastic powder-coated carbon-fiber towpreg into uniform and consolidated ribbon. The approach comprised four primary activities. 1) The patent and processing literature was studied to evaluate the state of the art. 2) A functional ribbon fabrication technique was developed by scaling-up, in a novel configuration, hardware components found in the literature. 3) The *ex parte* ribbonizing process was characterized by calibrating equipment, determining steady state and studying cause and effect between process parameters and ribbon quality. 4) Process design and control methods were derived from heat transfer and pulling force analyses.

The *ex parte* ribbonizer process comprises a material handling system, a preheat region, a heated stationary bar assembly, and a cooled nip roller assembly. Appropriate timing of important contacts is key to fabricating quality ribbon. Process characterization and analyses revealed key flow mechanisms. Ribbon microstructure changes most at the bars. Ribbon macrostructure changes most at the nip. An Isothermal bar contact is a practical processing constraint for ensuring uniform squeeze flow bar spreading. All bar drag force is attributed to shear stress in the interfacial viscous boundary layer between the towpreg and the stationary bar surface. Continually sensing pulling force is a good indication of process control.

The research goal was achieved because the *ex parte* ribbonizer can be used to convert polymer powder towpreg into uniform and fully-consolidated ribbon in a controllable manner.

Blends of Reactive Diluents with Phenylethynyl-Terminated Arylene Ether Oligomers

Rachel L. Knudsen, M.A., 1995

The purpose of this study is to improve the physical properties of phenylethynyl terminated poly(arylene ether) (PETAE) oligomers while decreasing the melt viscosity to improve processability. The approach is to blend phenylethynyl containing reactive diluents with PETAE oligomers. The diluents plasticize the oligomers during processing but become incorporated into the network when the blend is cured.

Five diluents were synthesized and bended with each of three PETAE oligomer backbones at two diluent/oligomer ratios, giving a total of thirty blends and three non-blended oligomer controls. Experiments were performed to test solvent resistance, glass transition temperature, tensile strength and modulus, melt viscosity, and Ti/Ti tensile shear strength. Two blends were selected which best met the goals of the research. These blends, 10A-80/20 and 20A-80/20, contained the same diluent and backbone but different diluent/oligomer ratios.

Cured films of the selected blends either did not swell at all or swelled less than the control in the solvents tested. The glass transition temperatures of the cures blends increased by 15 to 16°C as compared to the control.

The cured film of 10A-80/20 showed an increase of 34% in tensile strength and16% in tensile modulus at room temperature as compared to the non-blended oligomer control. Films of the two selected blends showed an increase in tensile properties at 177°C, with a strength increase as high as 47% over the control and a modulus increase up to 14%. The minimum melt viscosities of both blends decreased as compared to the controls, and the viscosity of one blend, 20A-80/20, was a factor of ten lower than the control.

The Ti/Ti tensile shear strengths of both selected blends were higher than those of the control in all test conditions. Improvements of 40 and 31% were seen at room temperature and 177°C, respectively, and improvements of 22 to 84% were seen in the room temperature test following a 48 hr soak in one of several solvents.

The results suggest that an increase in crosslink density occurs from the addition of the diluents, and improved properties are being attained because of this increase.

The Synthesis, Characterization, and Application of Ether-Containing Polyimides

Catherine Croall Fay, Ph.D., 1995

Polyimides are a family of heterocyclic polymers that have received extensive evaluation as adhesives, fibers, films, moldings, composite matrices, insulators, coatings, membranes, and resists. Their outstanding thermal stability, excellent mechanical and electrical properties, and chemical resistance make them attractive for many applications.

The purpose of this research was to develop ether-containing polyimides for three applications: liquid crystalline polyimides as processing aids, polyimides for microelectronic applications, and polyimides for harsh environments. The approach consisted of three primary activities: (1) develop novel diether dianhydrides for polyimide fabrication, (2) develop, characterize, and evaluate polyimide architectures based on the material application requirements, and (3) provide extensive structure-property relationships utilizing a number of unique groups in the polymer backbone and their contributions to the resultant polymer features.

Several novel extended diether dianhydrides were synthesized. When these flexible dianhydrides were combined with rigid diamines, an alternating flexible/rigid polymer backbone resulted and hence the potential was created for liquid crystallinity. Incorporation of rigid groups such as naphthalene and biphenyl, or spacers containing -CH_2- groups like butane or hexane, provided the potential to achieve liquid crystallinity in the resultant polyimides. The potential liquid crystalline polyimides developed exhibited crystallinity and other desirable properties, but data were inconclusive regarding their liquid crystallinity. Extensive knowledge was gained in the synthesis of novel dianhydrides and their precursors. Additionally, structure-property relationships based on a variety of novel dianhydride moieties resulted.

High performance polymer film and coating materials are increasingly being used by the electronic circuit industry. Electrical behavior is critical for polymers used in these applications. Materials are needed with substantially lower dielectric constants. Fluorinated dianhydrides and polyimides therefrom were synthesized to achieve lower dielectric constants. Additionally, a series of copolyimides was developed, using commercial and experimental monomers, for use as interlayer dielectrics and encapsulants. Several combinations were achieved that optimized mechanical, physical, and chemical properties required for the applications.

Polyimides for use in harsh environments were developed and evaluated. Two media of particular interest were high pH to determine the polyimide's hydrolytic stability and high-energy radiation to determine utility of the polyimides in geosynchronous orbit. New and existing polyimides were evaluated through physical, mechanical, and chemical means to determine possible substitutes for wire and cable insulators that were degrading in the presence of alkaline cleaners. These candidates also have other utility in applications requiring hydrolytic stability. Also, squaric acid containing polyimides were developed and evaluated for potential space applications. These polyimides exhibited a combination of attractive properties, especially their resistance to the radiation component of

geosynchronous orbit.

The Synthesis of Reflective and Electrically Conductive Polyimide Films Via an In Situ Self-Metalization Procedure Using Silver (I) Complexes

Robin E. Southward, Ph.D., 1996

Optically reflective polyimide films have been prepared by the incorporation of silver (I) acetate and a β-diketone solubilizing agent, hexafluoroacetylacetone (HFAH) into a dimethyl acetamide solution of the poly(AMC acid) formed from 3,3′,4,4′-benzophenonetetracarboxylic acid dianhydride (BDTA) and 4,4′-oxydianiline (4,4′-ODA). Optically reflective and conductive polyimide films have been prepared by replacing the β-diketone (HFAH), with the less substituted β-diketone, tetrafluoroacetylacetone (TFAH). The former system has been both cast directly from the poly (AMC acid) resin and cast from the poly(AMC acid) resin onto a fully imidized BTDA/4,4′-ODA case (formally a metalized topcoat). Thermal curing of the silver (I)-containing poly(AMC acid) leads to imidization with concomitant silver (I) reduction, yielding a reflective silver surface, when TFAH is the solubilizing agent. The metalized BTDA/4,4′-ODA films retain the essential mechanical properties of undoped films and have good thermal stability particularly in nitrogen atmospheres. The system which forms a metalized topcoat also exhibits the essential mechanical and thermal properties of the parent polymer while minimizing the silver required to form the reflective surface, and has outstanding metal-polymer and polymer-polymer adhesion attributed to mechanical interlocking. Films were characterized by X-ray, DSC, TGA, XPS, TEM, SEM, AFM.

The Thermal Cure of Phenylethynyl Terminated Polyimides and Selected Model Compounds

Karen H. Wood, Ph.D., 1997

The ability to process high performance polymers into useful adhesives and high quality composites has been significantly advanced by synthetic techniques in which oligomers terminated with reactive groups cure or crosslink at elevated temperature after the article has been fabricated. Several matrix resin systems of considerable interest to the aerospace community utilize phenylethynyl terminated imide (PETI) technology developed at the Langley Research Center to achieve this advantage. This work addresses the cure chemistry of PETI oligomers.

The thermal cure of selected oligomers and model compounds was studied using a variety of analytical techniques including differential scanning calorimetry, high pressure liquid chromatography, Fourier transform infrared, nuclear magnetic resonance, electron spin resonance and mass spectroscopies and liquid chromatography-mass spectroscopy. Model compound studies indicate that the cure is extremely complex. Many stable products were isolated and attempts at identification were made. Initial cure mechanisms have been proposed based on experimental results. The intent of this research is to provide fundamental insight into the molecular structure of these new engineering materials so that their performance and durability can be more adequately appreciated.

The Synthesis, Characterization, and Molecular Modeling of Cyclic Arylene Ether Oligomers

Sheeba Ahmed, Ph.D., 1997

Cyclophanes are a family of bridged cyclic aromatic compounds that have found extensive applications in host-guest chemistry, molecular recognition, biomimetics and most recently as precursors in ring-opening polymerizations.

This research presents the synthesis of several novel cyclic arylene ether oligomers, based on 1,2-bis(4-fluorobenzoyl) benzene with 3,3′-methylene diphenol and 3,3′-(ethylene dioxy) diphenol, and their characterization by LC-MS/MS, 1-D H-NMR and x-ray crystallography. Electrospray ionization (ES) along with MS/MS was used to characterize cyclic oligomers of molecular weights up to 1600 Da. The thermal properties of these cyclic oligomers were studied by differential scanning calorimetry (DSC) and thermal gravimetric analysis (TGA).

These cyclic oligomers were synthesized in high yield by regulating reaction time, concentration, temperature, and solvent systems. The relevance of reaction conditions was investigated by selected reaction monitoring (SRM).

Molecular dynamics and potential energy calculations were also carried out to understand the molecular characteristics of the bisphenols that lead to formation of these cyclic species. Furthermore, the molecular modeling studies assisted in predicting the conformations of the small macrocyclic rings. The predicted structures indicated the cavity size and relative orientation of the oxygen atoms.

In addition to providing stipends, equipment, supplies, chemicals, travel funds, etc. for students carrying out dissertation research, grant #NCC1-150 also supported Dr. Steven P. Wilkinson who held a position on the William and Mary faculty as Postdoctoral Research Associate. He taught an Applied Science lecture class on composites and conducted a polymer laboratory course. Dr. Wilkinson also carried out research related to prepregging and processing of high-performance composite materials.

The major focus of Dr. Wilkinson's research was to achieve a better understanding of prepregging high performance polymers onto carbon fibers. The NASA-Langley multi-purpose tape machine was delivered during Dr. Wilkinson's appointment at William and Mary. He devoted considerable effort in surveying the literature about prepregging science and in learning the machine's operation. Five different resins were prepregged initially. The mechanical properties of laminates made from the tape machine's prepreg were found to be superior to those prepared from drum-wound prepreg material.

Dr. Wilkinson wrote a technical memorandum describing the tape machine and its basic operation. In the memorandum he identified a number of research areas that helped to focus the research effort. A suitable methodology was needed for predicting the resin solids content on the carbon fibers utilizing typical machine operating parameters. A method was devised that involved calibrating the machine with a series of solutions and describing these solutions with a prepreg flow number. Through a superpositon principle which incorporates solution viscosity and production rate, a research grade solution could be prepregged and made to act in the same manner as the calibration solutions. This method helped in predicting the necessary operating parameters for obtaining desired resin solids contents on the carbon fibers.

The effects of pressure on fiber impregnation was analyzed. It appeared that capillary pressure may be an important contributor to the overall effective pressure. To study this effect, evaluation of the wetting characteristics of the polymer solutions on the carbon fibers has to be determined. A wicking rate technique was evaluated to measure the change in surface energy which occurs when polymer solutions wet the carbon fibers. The technique gave excellent reproducibility although standard deveiations were large (15%). The surface topology of the carbon fibers was characterized by scanning tunneling microscopy.

Also, Dr. Wilkinson made progress in consolidating polymeric matrix resins for "out-of-autoclave" applications. Chain extendible thermoplastics with specific end-group functionality were found to produce quality laminates under vacuum bag pressure only. He evaluated a number of oligomeric NASA resin systems, and he studied novel solvent systems for improved solvent removal during prepregging.

Thus, cooperative agreement NCC1-150 played a very important role in the education and training of eight graduate students in Applied Science at William and Mary. They and Postdoctoral Research Associate Steven Wilkinson carried out wide ranging studies on advanced polymeric and composite materials. (Photocopies of student theses are available on request from the Principal Investigator.)