**Fifteenth Asilomar Conference on Polymeric Materials**

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FIFTEENTH ASILOMAR CONFERENCE ON POLYMERIC MATERIALS

February 9-12, 1992

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SUBMITTED BY

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CONTENTS

1. Program
2. Attendees
3. Abstracts
PROGRAM

FIFTEENTH ASILOMAR CONFERENCE

on

POLYMERIC MATERIALS

FEBRUARY 9-12, 1992

in

PACIFIC GROVE, CALIFORNIA
INVITED SPEAKERS FOR

FIFTEENTH ASILOMAR CONFERENCE ON POLYMERIC MATERIALS

FEBRUARY 9-12, 1992

"PROCESSING AND CHARACTERIZATION OF HIERARCHICALLY STRUCTURED CERAMIC-POLYMER COMPOSITES"

PROFESSORS ILHAN AKSAY & MEHMET SARIKAYA
UNIVERSITY OF WASHINGTON
SEATTLE, WA

"SCALE, INTERACTION AND ARCHITECTURE IN POLYMERS"

PROFESSOR ERIC BAER
CASE WESTERN RESERVE UNIVERSITY
CLEVELAND, OH

"HIGH PERFORMANCE BLENDS WITH LIQUID CRYSTALLINE POLYMERS"

PROFESSOR DON BAIRD
VIRGINIA POLYTECHNIC INSTITUTE AND STATE UNIVERSITY
BLACKSBURG, VA

"RECENT PROGRESS IN ADVANCED CARBONACEOUS MATERIALS FOR REMOVAL OF TRACE CONTAMINANTS"

PROFESSOR JAMES ECONOMY
UNIVERSITY OF ILLINOIS
URBANA, IL
"DETERMINATION OF STRESS STATE AND ADHESION IN POLYMERIC SYSTEMS"

PROFESSOR RICHARD FARRIS
UNIVERSITY OF MASSACHUSETTS
AMHERST, MA

"POLYMERIC HARD ELASTIC BEHAVIOR AND MICROPOROUS PROPERTIES"

DR. HAROLD FISHER &
DR. JAMES LOWERY
HOECHST CELANESE CORPORATION
CHARLOTTE, NC

"READING FRACTURE SURFACES OF POLYMERIC MATERIALS"

PROFESSOR ANNE HILTNER
CASE WESTERN RESERVE UNIVERSITY
CLEVELAND, OH

"HIERARCHY IN THE MATERIALS SCIENCES"

DR. GEORGE MAYER
INSTITUTE FOR DEFENSE ANALYSES
AXELANDRIA, VA

"MOLECULAR DESIGN OF PROCESSABLE HIGH Tg THERMOPLASTIC MATRIX RESINS AND STRUCTURAL ADHESIVES"

PROFESSOR JAMES MCGRATH
VIRGINIA POLYTECHNIC INSTITUTE AND STATE UNIVERSITY
BLACKSBURG, VA
"FUTURE DIRECTIONS IN POLYMER MATRIX COMPOSITES"

DR. ROGER MORGAN
MICHIGAN MOLECULAR INSTITUTE
MIDLAND, MI

"SYNTHESIS AND POLYMERIZATION OF NOVEL IMINES"

DR. ANNE PADIAS
UNIVERSITY OF ARIZONA
TUCSON, AZ

"PHASE BEHAVIOR AND INTER-REACTION IN POLYPESTYRE SYSTEMS"

PROFESSOR ROGER PORTER
UNIVERSITY OF MASSACHUSETTS
AMHERST, MA

"DAMAGE TOLERANCE IN POLYETHYLENE FIBERS & COMPOSITES"

DR. DUSAN PREVORSEK
ALLIED-SIGNAL INC.
MORRISTOWN, NJ
ATTENDEES

15th Asilomar Conference on Polymeric Materials

February, 9-12, 1992

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In this presentation we will illustrate the feasibility of utilizing biomimetic processing procedures in the processing of materials. Four specific examples will be illustrated: (i) the use of biopolymers as dispersants in the colloidal processing of ceramics; (ii) synthesis of nanometer-sized, multicomponent particles with phospholipid vesicles; (iii) processing of laminated ceramic-metal and ceramic-polymer composites as analogs of mollusk shell; and (iv) the modification of wood properties through partial mineralization. In the first area, we will illustrate that rheological properties of ceramic particle-containing suspensions can be modified by growing the alginate-producing bacterium, Azotobacter vinelandii directly in the presence of aluminum oxide particles. Mechanisms leading to suspension stabilization will be discussed with respect to the role played by polymannuronic and polyguluronic acid components of water-based biopolymers may provide an opportunity to process ceramics by ecologically balanced processing procedures. In the second area, our examples will build onto the pioneering works of Janos Fendler and Stephen Mann on the formation of nanometer-sized particles in vesicles. As a follow-up to their studies, we will highlight the advantages of vesicle-mediated particle processing and consolidation in nanocomposite processing. Particular emphasis will be on the lubricating properties of bilayers. In the third area, we will illustrate the advantages of mimicking mollusk nacre structure as laminated B_xCl-Al and ceramic-polymer composites. In comparison to methods used in biological systems, although our mimicking approaches are very crude, the improvements in properties are significant enough to warrant further research in this area. The last illustration will be on the modification of wood properties through the formation of ceramics (SiO_2 and/or AlOOH) in the cell walls and cells.
CHARACTERIZATION OF HIERARCHICALLY STRUCTURED NATURAL CERAMIC-POLYMER COMPOSITES

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Biological hard tissues, such as bone, dentin, and seashells, are composite materials incorporating both the inorganics (phosphates and carbonates) and organics (macromolecular structural units including proteins). These materials have unprecedented physical properties, which are often multifunctional due to their highly ordered structures through the dimensional scale from molecular to submeter. Biological composites are a source of inspiration for design and processing of synthetic materials based on both their structure, biomimicking, and processing, bioduplication. In this presentation, we will discuss our current work that focuses on nacre section of the abalone and pinctada (oyster) shells where the hard tissue has a brick and mortar structure at the submicron and nanometer scales, respectively. Here the bricks are aragonite (orthorhombic CaCO$_3$) constituting over 95 v/o, and mortar as a composite of macromolecules and proteins. The material has a combination of high strength (180 MPa/(g/cc)) and fracture toughness (8 MPa-m$^{1/2}$) which are due to the characteristics of interfaces, and structures and properties of both the inorganic and the organic components. Studies on the morphology and crystallography, by high resolution TEM, revealed that platelets are multiply tiled based on hierarchical twinning. This suggests that the active sites for nucleation in the organic matrix has a pseudo-hexagonal ultrastructure and that the template growth mechanism is operational during nacre formation. Furthermore, based on growth pattern on a wide dimensional scale, the structure of the organic may have a direct consequence on the final shape formation of the shells. We will, furthermore, discuss the current understanding of the biochemistry and structures of the organic matrices based on the results in the literature and the collaborative groups.
Hierarchical structure in biocomposite systems such as in collagenous connective tissue have many scales or levels, have highly specific interactions between these levels, and have the architecture to accommodate a complex spectrum of property requirements. As examples, the hierarchical structure-property relationships will be described in three soft connective tissues; tendon, intestine and intervertebral disc. In all instances, we observed numerous levels of organization with highly specific interconnectivity and with unique architectures that are designed to give the required spectrum of properties for each oriented composite system. From these lessons in biology, the laws of complex composite systems for functional macromolecular assemblies will be considered. Finally, demonstrations of the application of these laws to simple synthetic composites will be given including continuous multilayered polymeric materials, liquid crystalline polymers, and "hard elastic" membranes. Again it will be shown that structure-property relationships can only be described, and in some instances predicted, if these complex synthetic materials are accurately defined in terms of their hierarchical structure.
High Performance Blends with Liquid Crystalline Polymers

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There has been considerable interest in using liquid crystalline polymers (LCP's) to reinforce thermoplastics, because the reinforcement is generated during processing. Factors which control the formation of the reinforcing fibrils are the viscosity ratio, interfacial surface tension, and the strength of the flow (e.g. elongational versus shear flow). Most combinations of LCP and thermoplastic studied to date are immiscible and hence two distinct phases are present. Recently in our laboratory we have found that certain LCP's based on hydroquinone (HQ) and phenylhydroquinone (PHQ) are at least partially miscible with polyetherimide (PEI). The first part of the presentation is concerned with establishing the presence of miscibility in binary systems consisting of a PEI and LCP's based on HQ and PHQ and the effect of miscibility on the physical properties of the blends. In particular miscibility is studied by means of differential scanning calorimetry (DSC), dynamic mechanical thermal analysis (DMTA), scanning electron microscopy (SEM), and wide angle x-ray diffraction scattering (WAXS). For comparison similar results are reported for an immiscible system consisting of PEI and a LCP based on PHB and HNA (Vectra A). It is observed that for the miscible system the tensile modulus and strength can exhibit a synergistic effect in that they deviate from a simple law of mixtures over the whole concentration range while for the immiscible system, the properties only deviate from the law of mixtures at very high LCP content. Although miscibility appears to play an important role in determining the physical properties of the blend, especially at low LCP compositions, the properties of the LCP are also important.

The second part of the presentation is concerned with ternary systems based on PEI, PEEK, and LCP's based on HQ and PHQ. Using DMTA and the analysis of fracture surfaces by means of the SEM, the miscibility of the ternary compositions as well as the various binary compositions (i.e., PEEK/LCP and PEEK/PEI) was determined. The PEEK/LCP blend was found to be miscible up to 50 wt% LCP and partially miscible above this amount. The PEI/LCP blends were found to be partially miscible over the whole composition range. As a result of the partial miscibility for each of the above binary systems, some ternary compositions exhibited only one phase while others exhibited two phases. By adjusting the ratio of components one can obtain blends with a desired balance of properties. For example, at a composition ratio of 10/60/30 PEI/PEEK/LCP one can obtain a material with similar modulus and tensile strength but a higher elongation at break than that of the pure LCP.
Activated carbon granules have been available for many years and find extensive use as purification systems for both air and water. On the other hand the technology on activated carbons has changed very little over the past 50 years even though the needs have become far more sophisticated. Equally as serious is the fact that a fundamental understanding as to the mechanisms of adsorption by the activated carbons is not available, further hindering progress in this field.

In this presentation work is described which attempts to distinguish between three key variables which appear critical to the mechanism of adsorption, namely, the chemical nature of the pore surface, the surface area and the shape of the pore. Recent progress on new kinds of adsorption systems is described.
The determination of residual stresses in a coating is crucial to the prediction of coating failure by cracking or delamination. A few thicknesses away from any free edges, the state of stress in a coating is entirely within the plane of the coating. This means that the interface between the coating and the substrate is totally stress free. One can therefore remove an internal section of the substrate, creating a tensioned drumlike membrane without altering the state of stress. Time-averaged holographic interferometry of vibrationally excited membranes was used to evaluate the in-plane stresses in the membrane, two normal stresses and a shear stress. This technique provides a very high degree of redundancy from the many resonant modes obtainable. It is valid for all materials and requires no knowledge of material properties other than density. Reducing the degree of constraint by cutting the membranes and re-evaluating the stresses, provides direct information on Poisson's ratios and other coefficients for coatings having orthotropic linear elastic properties. Such information is necessary to predict inhomogeneous states of stress near free edges and holes. In addition, the peel adhesion experiment is analyzed using a deformation calorimeter so that both the heat and the work of peeling could be assessed. Experiments were conducted on metal coatings peeled from polyimide films and from polyimide films peeled from metal. In both cases most of the energy consumed in separating the two materials was either liberated as heat or stored in the peeled material. The true energy of adhesion has only a minor role in the balance of energy. The influence of stored elastic energy in highly stressed coatings was also studied. It was verified that thick coatings could be made to delaminate spontaneously when they were cut; this procedure was accompanied with little energy release when compared to the energy required for peeling.
Abstract

The development of morphological structure during the extrusion of polymers is often a hindrance to the goals of the manufacturer. On the other hand, in the manufacture of microporous films and fibers using the "hard elastic" phenomenon, polymer morphology determines far more than tensile properties, optical clarity, etc. The most important product characteristics (the number, size, and shape of micropores) are dependant upon induced crystallization in the extrusion stage.

The production of hard elastic precursors is dependant on polymer properties (structure, molecular weight, polydispersity, and crystallinity) and extrusion conditions (temperature, quench, and draw-down). Conversion of the hard elastic precursors to stable microporous structures is accomplished by a two-step stretching process. The first creates fissures between the row-lamellar crystallites. The second stretching operation, performed near the melting point, deforms both amorphous and crystalline phases. Scanning electron microscope photomicrographs provide graphic evidence of morphological structure.

Examples of applications of microporous films and fibers are given.
READING FRACTURE SURFACES OF POLYMERIC MATERIALS

by

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Abstract

Fractography has been used in the post-failure analysis of single edge notched specimens of injection molded blends of polycarbonate (PC) and ABS. The mode of ductile tensile fracture of single edge notched specimens depended on composition. Plane stress shear tearing was observed in the composition range PC/ABS 90/10 to 70/30 by weight where PC was the continuous phase. Intermediate compositions, PC/ABS 60/40 to 40/60, had a co-continuous or almost co-continuous phase morphology; these blends fractured by mixed mode pop-in where a tunneling center crack relieved the triaxiality and permitted plane stress shear lips to form near the edges. Herringbone fracture, a plane strain mode characterized by discontinuous crack growth, was observed when ABS was the continuous phase, PC/ABS 30/70 to 10/90. An S-shaped relationship was observed between the ductile-to-brittle transition temperature and the composition. Addition of ABS to PC increased ductility up to PC/ABS 70/30 and 60/40 which were the most ductile compositions. Further addition of ABS decreased the ductility and the least ductile compositions were PC/ABS 30/70 and 10/90.
ABSTRACT

Complex structures which have been resolved at various hierarchical levels in rigid natural composites have been linked to mechanical properties that are, at times, superior to those which have been designed into synthetic composite materials comprised of organic, metallic, and ceramic constituents. Some of the lessons learned from the design of rigid biological systems will be described, along with what is known and what is unknown about constituent components, and interfaces. Functional hierarchical approaches to designing with and the mechanical analyses of synthetic composites will be described, in combination with lessons learned from biology.
ABSTRACT

Molecular Design of Processable High Tg Thermoplastic Matrix Resins and Structural Adhesives

High performance monomers based upon structures 1 and 2 shown below have recently been generated. The resulting monomers are important intermediates for a variety of thermally stable polymers such as polyimides, polyaryleneethers, and polybenzoxazoles. The pendent aryl group in both systems is non-planar and affords polymeric systems that are amorphous but also soluble and processable. The aryl groups also contribute to excellent thermal oxidative stability and indeed the systems shown are comparable to the better known "six F" based systems. The phosphorous containing monomer also contributes a high glass transition temperature, processability and flame resistance. The synthesis and characterization of processable aromatic polyimides, polyaryleneethers, and polybenzoxazoles will be reported. Glass transition temperatures of 420°C have been achieved with the polyimide derived from the 3F diamine and pyromellitic dianhydride. The resulting materials show excellent thermooxidative stability and are soluble in NMP. The materials are candidates for 700°F matrix resin and structural adhesive applications. An overview of the synthesis and characterization of these materials will be provided.

$\text{CF}_3$

1. $X = F, \text{NH}_2, \text{OH}, \text{COOH}$

2. $Y = F, \text{NH}_2, \text{OH}, \text{COOH}$

3F Monomer Systems

Aryl Phosphine Oxide Monomer System
ABSTRACT

FUTURE DIRECTIONS IN POLYMER MATRIX COMPOSITES

Roger Morgan
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New developments in materials, processing and performance of polymer matrix composites will be described in relation to future applications and economics.

In the materials area, the development of (i) tough, high modulus and temperature compression resistant, processible bismaleimide thermosets, (ii) tough processible syndiotactic polystyrene, and (iii) multiperformance materials will be described.

Experimental techniques and the physics and chemistry that influence (i) fast composite processing via powder prepregging and resin transfer molding and (ii) the control and manipulation of macroscopic composite fabrication stresses will be presented.

In the composite service performance area, a durability test program is described that covers (i) specific molecular, microscopic and macroscopic failure modes, (ii) resulting synergistic degradation experiments as a function of stress, temperature and moisture environments, and (iii) accelerated test procedures based on the most probable critical failure path for future composite applications. A number of chemical and physical composite matrix, fiber and interfacial degradation mechanisms will be critically discussed.
Origins of Damage Tolerance in Polyethylene Fibers and Composites

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Abstract

Spectra® polyethylene fibers and composites are known for their unmatched damage tolerance and capability to absorb energy. Therefore, their utilization in the technology of survival, where Spectra® composites are used to protect people, equipment and apparatus, is expanding very rapidly.

The origins of the damage tolerance are in the composite structure of Spectra® fibers. They consist of long near-perfect needle-like crystals imbedded in and covalently bonded to a rubbery matrix consisting of same molecules. It has been recognized that such composite fibers are not only the most damage tolerant material known to date, but that it is impossible to conceive another polymeric fiber that would be more damage tolerant than Spectra®.

The second, no less critical factor in damage tolerance of Spectra® polyethylene is the multitude of low energy crystal defects, dislocations, disclinations, etc. that are activated by high stress and allow crystals to participate in energy absorption. This is different from other high performance organic fibers such as polyaramids, PBT, carbon fibers etc. where crystals provide reinforcement but contribute little to the energy absorption of the system.

To exploit the damage tolerance of Spectra® in large structure it is necessary to use a uniaxial composite prepreg where the microstructure of Spectra fibers is replicated on a larger scale to minimize reflections of shock waves and insure that the energy absorption characteristics of the fiber are effectively translated into the performance of composites.

Examples will also be presented showing that it is possible to design Spectra composites whose impact resistance and energy absorption characteristics improve on repeated impact, a characteristic which is essential for many armor applications. We know of no material that would exhibit this unique impact behavior, that "appears to violate" the well known laws of cumulative damage. This unique behavior originates in the capability of Spectra fibers to undergo plastic deformation without failure. A response that cannot be duplicated by other fiber reinforced composites. Several laboratories are now investigating whether Spectra fibers can also be used to improve the impact characteristics and damage tolerance of structural composites of glass, Kevlar and carbon fibers. To this end, the experimental data and analysis will be presented to identify hybrid structures offering the best combination of properties for structural applications.