

# SYMPOSIUM U

## Advanced Fibers, Plastics, Laminates, and Composites

November 26 – 30, 2001

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\* Invited paper

## SESSION U1: NATURAL FIBERS AND PROPERTIES

Chair: Hong Li  
Monday Morning, November 26, 2001  
Liberty (Sheraton)

### 8:30 AM \*U1.1

#### FIBERS OF BAMBOO AND HEMP PALM TREE.

Shigeyasu Amada, Gunma University, Dept of Mech Engineering, Kiryu, Gunma, JAPAN.

Bamboo and Hemp Palm tree are typical composite materials which are reinforced by the strong fibers. The measured strength of the fibers ranges from 500 to 1000MPa which is higher than steel. Furthermore, the fibers are distributed based on a functionally graded structure, which adapts to a stress distribution due a bending load. These plants construct a hierarchical structure as well as a functionally graded one. Both the structures can lead to a marvelous structural properties under the environmental loading conditions.

### 9:00 AM \*U1.2

#### PRODUCTION AND CHARACTERIZATION OF YARNS AND FABRICS UTILIZING TURKEY FEATHER FIBERS. Alimohammad Evazynajad, Holly Mc Bride, and Brian George, Philadelphia University, School of Textiles & Materials Technology, Philadelphia, PA.

Currently, between two and four billion pounds of feathers are produced annually by the poultry processing industry (1). These feathers are usually converted to animal feed in an attempt to recycle it rather than dispose of these feathers in landfills (2,3). However, this method can result in diseases being passed along to the ingestors of this feather meal. Until recently there was no method of removing the quill from feather, but a method of effectively stripping the feather fibers from the quill without damaging the fibers has been patented, and as a result research is being conducted to determine uses for these fibers (4). The topic of this paper is the production of yarns and fabrics containing turkey feather fibers. Materials containing up to thirty percent turkey feather fibers were produced utilizing novel techniques as well as commercial textile equipment. The yarns produced were tested to determine their mechanical properties. As the percentage of turkey feather fibers increased, the tenacity and strain of the yarn decreased while the modulus increased. The yarns were knitted into fabrics which were then thermally tested to determine their insulation capabilities. It was found that as the percentage of turkey feather fibers in the fabric increased that the insulating capabilities also increased. Other research has focused on producing nonwoven fabrics from turkey feather fibers for use in erosion control applications. Several nonwoven fabric production methods have been utilized to produce fabrics suitable for this application.

#### References:

1. Walter Schmidt, Agricultural Research Service, USDA, November 1, 1999.
2. J.M. Choi, P.V. and Nelson, "Developing a slow release nitrogen fertilizer from organic sources. II. Using poultry feathers." J. Am. Soc. Hortic. Sci. v. 121, n. 4, 634-638, (1996).
3. Vincent Corporation:  
<http://www.vincentcorp.com/apps/animal.htm>, November 9, 1995.
4. D. Comis, "Chicken feathers: eco-friendly 'plastics' of the 21st century?" Agricultural Research Service News, February 9, 1998.

### 10:00 AM \*U1.3

#### SILK FIBERS AND MATERIALS - PROPERTIES AND PROCESSING. Greg Altman, Regina Valluzzi, Rebecca Horan, Helen Lu, David Kaplan, Dept Chemical & Biological Engineering, Tufts University, Medford, MA.

Fibrous proteins can be viewed as complex copolymers that are amenable to detailed study of structure-assembly relationships. Silks, as a group of fibrous proteins, self-assemble into structural materials critical to the survival of silkworms and spiders. The relationships between structure and assembly among these proteins are useful to study with respect to building a fundamental understanding of the development of structural hierarchy in these materials, as well as for an understanding of the complexity of biological responses to these materials. Ongoing studies are directed at gaining insight into hierarchical assembly through the systematic alternation of primary sequence, blockiness, control of polymer-polymer interactions, and environment as they relate to the formation of structural hierarchy. Important issues such as conformational polymorphism, chirality, triggered assembly, and the formation of lyotropic phases are key areas of current focus. In addition, silk fibers and films provide useful scaffolds for tissue engineering. Current studies are focused on matching fiber/yarn architecture to desired tissue mechanical properties, cellular responses to these materials related to biocompatibility, and use of the yarns for the formation of tissue engineered ligaments.

### 10:30 AM \*U1.4

#### ENGINEERING PROPERTIES OF SPIDER SILK. Frank K. Ko,

Fibrous Materials Research Center, Department of Materials Engineering Drexel University, Philadelphia, PA; Sueo Kawabata, Mari Inoue, and Masako Niwa, Department of Materials Sciences, University of Shiga Prefecture, Shiga, JAPAN; Nara Women University, Nara, JAPAN; Stephen Fossey and John W. Song, US Army Natick Research and Development, Engineering Center, Natick, MA.

Strength and toughness are usually considered mutually exclusive properties for materials. In spite of the progress made over the past century in polymeric fiber science and technologies, the search for a truly strong and tough fiber continues. It is of practical and scientific interest to explore the limit of strength and toughness of fibrous materials; and to examine the factors which contribute to the development of a combination of strength and toughness in materials. The answers to these questions may be found in nature.

In the world of natural fibers, spider silk has long been recognized as the wonder fiber for its unique combination of high strength and rupture elongation. Earlier study indicated spider silk has strength as high as 1.75 GPa at a breaking elongation of over 26%. With toughness more than three times that of aramid and industrial fibers, spider silk continues to attract the attention of fiber scientists and hobbyists alike.

In this paper, the mechanical properties of *Nephila clavipes* spider silk provided by the US Army Natick R&DEC are presented to illustrate the unique combination of strength and toughness and the anisotropy of spider silk. Specifically, the tensile properties of the silk of *Nephila clavipes* spider were characterized by simple elongation, transverse compression and torsion under various humidity conditions using the Kawabata ultra-sensitive testing system.

### 11:00 AM \*U1.5

#### MICROCRYSTALLINE KERATIN: FROM FEATHERS TO COMPOSITE PRODUCTS. Walter F. Schmidt, Environmental Quality Laboratory, Agricultural Research Service, USDA, Beltsville, MD.

Feather fibers are shorter, straighter, and finer than wool keratin. A process to convert feathers into fiber was patented by USDA/ARS in early 1998. Within the year, three companies licensed this process. Two of them have working pilot plants which each can generate an estimated 1,000 kg per day of fiber. Production of a third independent pilot plant is in progress. Typical poultry plants generate 5,000 kg / hr of feathers, which translates into 1-2 billion kg of feathers produced in the US annually, half of which can be extracted as feather fiber. The level of feather fiber available commercially depends directly upon the amount processed from this already existing abundant and renewable supply of feathers. The fiber half of feathers has a unit diameter of 6 microns, a maximum length of about 1 cm. It has good flow and processing characteristics. The uniform fiber is by design colorless to white. The alpha-helical molecular structure in the fiber explains its microcrystalline properties. In porous composites, the high surface area and microscopic structure of feather fiber are valuable in forming absorbent filters. In more solid composites, the fiber imparts microcrystalline properties to composites comparable to adding nylon fibers of similar dimensions. Chemically the components in the quill fraction are also keratin. This fraction is morphologically and macroscopically quite non-uniform. Morphologically, the quill is the hardened glue that holds the fibers in their designed space. After processing into microscopically uniform material, this keratin fraction can be used as a filler within a plastic composite. The quill fraction is both less microcrystalline and less resistant to mechanical and thermal stress than the fiber.

## SESSION U2: NATURAL FIBERS AND NATURAL PLASTICS

Chair: N. Chawla  
Monday Afternoon, November 26, 2001  
Liberty (Sheraton)

### 1:30 PM \*U2.1

#### KERATIN PROTEIN NANO-FIBER FOR REMOVAL OF HEAVY METALS AND CONTAMINANTS. M. Misra, P. Kar and G. Priyadarshan, Metallurgical & Materials Engr., University of Nevada, Reno, Reno, NV; Carlo Licata, Maxim LLC, Pasadena, CA.

Keratin Protein Fiber has strong affinity for heavy metals and nano-scale contaminants from different systems. Keratin protein is a hydrophobic fibrous material. The main constituent of fiber is the naturally occurring fibrous protein. Keratin protein fibers are strong and have an intricate network of microscopic sites which have a strong metal binding capacity. It has a demonstrated potential in filtration of contaminants from water. Due to good tensile strength and pore

structure, these materials can be reused through a large number of adsorption/desorption cycles. Keratin protein fibers are biodegradable and a renewable source of raw materials. The University of Nevada, Reno is working with Maxim Biosystems to develop this nano-technology for water purification and filtration of nano-scale contaminants.

#### 2:00 PM \*U2.2

LENZING LYOCCELL - A VERSATILE FIBER. D. Eichinger, H. Firgo and Ch. Rohrer, Lenzing AG, AUSTRIA.

Cellulosics have a very balanced set of general features, with its unique specific control of moisture resulting in widely accepted physiological benefits and wearing comfort. This gives interesting future prospects for the man-made cellulosics Viscose, Modal and Lyocell by Lenzing/Austria.

One decade of Lyocell technology brought a lot of new opportunities in textile and technical application due to the very interesting properties of this solvent spun cellulose fiber, mostly cited are the very good mechanical properties as well as the fibrillation tendency of Lyocell. Further the ecological benefits of the technology have been recognised: Lenzing Lyocell was awarded the "European Award for the Environment 2000" by the European Community.

In this lecture we will give an introduction into today's Lyocell technology from Lenzing and the different cellulosic products made with this technology. Two special types of fibres will be discussed in more detail: Lyocell LF - a cross-linked textile variant - and Lyocell FILL - a new cellulose fiber for filling material.

With Lyocell LF, Lenzing has developed a fibre in which the tendency towards fibrillation is suppressed by chemical cross-linking at the production stage. For the properties of the product it is decisive that this cross-linking takes place in a never dried condition whereby the typical fibre properties of Lyocell are largely maintained. The mechanical, chemical and structural properties of Lyocell LF and the impact on textile application will be presented.

Lyocell FILL is a new cellulose fill fiber with very interesting physiological properties, which are the result of a special moisture management resulting in an excellent moisture transportation and vapour absorption index. The prerequisites for a fill fibre will be discussed on the basis of mechanical properties and morphology and comparison with other types of fibers for this special end-use will be made.

#### 2:30 PM \*U2.3

SOME ASPECTS ON PREPARATION AND PROPERTIES OF ALGINATE AND CHITOSAN FIBRES. Henryk Struszczyk, Institute of Chemical Fibres, Lodz, POLAND.

A demand for special fibres produced on the base of natural polymers such as alginate, chitin or chitosan, starch, keratin or biosynthesised cellulose is a function of their unique properties and growing application areas. Institute of Chemical Fibres, Lodz, Poland develops continuously above fibres, both filament and staple, based on selected natural polymers, also distinguished by controlled bioactivity. The aim of this paper is to present some aspects on preparation and properties of fibres based on calcium-sodium alginate or chitosan. The wet spinning method was used for their manufacture using modified spinning solutions of above natural polymers.

Alginate fibres were prepared on the base of aqueous alkaline solution of sodium alginate with average molecular weight higher than 100 kD. A spinning solution, after original modification using either additives or ageing process, were spun into acidic coagulation bath containing calcium salts. Prepared fibres based on the calcium-sodium alginate were characterized by titre of 2-4 dtex, tenacity of 15-20 cN/tex and elongation of 10-30%.

Chitosan fibres with controlled molecular, super-molecular and morphological structure, distinguished by titre of 2-4 dtex, tenacity of 12-16 cN/tex and elongation of 15-30%, were prepared using an initial chitosan, obtained from the crab or shrimp shells, with average molecular weight ranged from 100 to 400 kD and acetylation degree not higher than 20%. These fibres were spun from acidic solution of chitosan into alkaline coagulation bath. The properties of above fibres, including their biodegradability and bioactivity, are presented. Some special applications of chitosan and alginate fibres in medical field are also discussed.

#### 3:30 PM \*U2.4

A NEW POLYMER PLATFORM FOR THE FUTURE - SORONA FROM CORN DERIVED 1,3-PROPANEDIOL. Joseph V. Kurian, Technical Group Manager R&D, DuPont Experimental Station, Wilmington, DE.

DuPont Company recently introduced a new polymer platform, Sorona™, based on 1,3-propanediol. Currently, we are scaling-up a biological process for large-scale production of 1,3-propanediol. DuPont recently dedicated world's first continuous polymerization plant for making Sorona™ 3GT polymer. Fabrics made from

Sorona™ fiber are exceptionally soft and comfortable. They offer unique "comfort" stretch and recovery characteristics and can be dyed easily under atmospheric conditions. DuPont has licensed Sorona™ fiber technology to a number of fiber manufacturers for applications development. This presentation will give an overview of Sorona™ polymer developments with an emphasis on recent trends in materials from renewable sources.

#### 4:00 PM \*U2.5

A REVIEW OF CASTOR OIL AND OTHER TRIGLYCERIDE-BASED INTERPENETRATING POLYMER NETWORKS.

L.H. Sperling, Materials Research Center, Center for Polymer Science and Engineering, Depts. of Chemical Engineering and Materials Science and Engineering, Lehigh University, Bethlehem, PA.

Castor oil has three hydroxyl groups, one from each organic acid residue, that can be reacted to form crosslinked polyurethanes and polyesters. The result is an elastomer of significant commercial value of itself. When combined with crosslinked polystyrene or other plastic, an interpenetrating polymer network, IPN, can be formed. A few other triglyceride oils also possess special functional groups, including veronica oil and lesquerella oil, both wild oils now being researched. These, too, can be formed into IPNs. Depending on composition, the IPNs form tough, leathery materials or impact-resistant plastics. This review paper will summarize the results of this and other laboratories.

#### 4:30 PM \*U2.6

SOY PROTEIN ADHESIVES FOR WHEATSTRAW COMPOSITES.

X. Susan Sun, Department of Grain Science and Industry, Kansas State University, Manhattan, KS.

The construction and furniture industries comprise an extremely large and diverse market of plywood, composites, and fiber/particle boards. Agricultural fibers, such as wheat straw, are renewable resources annually, abundant, and have been underused, which can be good alternatives. Urea formaldehyde (UF) and phenol formaldehyde (PF) are the major adhesives used in wood particleboard formation, constituting about 98% of the 7.5 billion lb of adhesives used for plywood and particleboard manufacturing annually in the U.S. Formaldehyde-based adhesives often cause environmental pollution during manufacturing and distribution of products. Also, these resins have poor bonding performance with wheat straw fibers because the inherent nonpolar and hydrophobic properties of the straw surface are not compatible with the polar and hydrophilic nature of the UF and PF resins. Soy proteins are large complex molecules and have been considered as potential alternative adhesives for agricultural fibers. Soy protein gluing is related to the dispersion of the protein molecules and their unfolding in solution. The unfolded protein molecules have increased contact areas and interactions with the substrate. This paper will focus on utilizing soy protein adhesives for wheat straw composites, and discuss effects of soy protein modifications and chemical treatments of wheat straw surface on mechanical properties of the wheat straw composites.

### SESSION U3: NATURAL PLASTICS AND COMPOSITES

Chair: Christian Rohrer  
Tuesday Morning, November 27, 2001  
Liberty (Sheraton)

#### 8:30 AM U3.1

LOW COST PLASTICS AND COMPOSITES FROM PLANTS.

Richard P. Wool, John J. LaScala, Wim Thielemans, Erde Can, Jue Lu and Shana P. Bunker, Department of Chemical Engineering and Center for Composite Materials, University of Delaware, Newark, DE.

Using plant oils (soy, corn, cotton, olive, sunflower, linseed, etc), natural fibers (straw, flax, hemp, jute, kenaf, bamboo, poultry, etc) and lignin, it is possible to make a broad range of new high performance, low cost materials which can have a significant impact on the environment. By controlling the fatty acid distribution function of plant oils via computer simulation and the molecular connectivity (US Patent No. 6,121,398), we control the molecular architecture and chemical functionalization to produce linear, branched, lightly cross-linked and highly crosslinked polymers by free radical and condensation polymerization. These bio-based materials can be used as Pressure Sensitive Adhesives (linear and branched thermoplastics), Elastomers and Rubbers (lightly crosslinked), Adhesives and Composite Resins (highly crosslinked thermosets). When combined with natural fibers, glass fibers and lignin, new low cost composites are produced which can be applied to many high volume applications heretofore forbidden because of cost. These include agricultural equipment (tractors and farming machines), automotive sheet molding (SMC) compound (car and truck parts), civil (bridges and highway components), marine (pipes and offshore equipment), rail

infrastructure (carriages, box cars and grain hoppers) and the construction industry (hurricane resistant housing). Several examples are given for the synthesis, manufacturing and properties of both the plant-based resins and the glass, flax, lignin and hemp composites. Supported by NSF, USB, DE-SB, MD-SB and John Deere and Company

#### 8:45 AM \*U3.2

DESIGN AND ENGINEERING OF STARCH BASED MATERIALS. Ramani Narayan, Department of Chemical Engineering and Materials Science, Michigan State University, East Lansing, MI.

Sustainability, industrial ecology, and green chemistry are the new principles that are guiding the development of the next generation of materials, products and processes. Thus, new materials/products have to be designed and engineered from cradle to grave incorporating a holistic life cycle thinking approach. The use of annually renewable resources and the biodegradability or recyclability of the product is becoming an important design criterion. Starch, an abundant annually renewable agricultural product, offers the functionality for conversion to biodegradable, thermoplastic materials that can be used for a number of packaging and single-use disposable products. Starch is a natural polymer comprised of anhydroglucose monomer repeat units. On heating starch degrades, however using water and or glycerol as a plasticizer one can plasticize the starch. We have used this in developing biodegradable loose-fill packaging material that dissolves in water and readily assimilated by the soil microorganisms. These materials are eco-friendly substitutes for the polystyrene or polyethylene foam sheet and loose fill packaging. We are exploiting the lightweight, non-toxic, water wettable adhesive property of the extrusion foamed starch articles in toys, educational materials, arts & crafts, currently being commercialized. The thermoplastic starch can also be blended with other biodegradable polyesters to yield resin formulations that can be made into film and molded articles. Modification of the starch -OH groups by esterification forms starch esters of appropriate degree of substitution (1.5 to 3.0 ds). This imparts thermoplasticity and water resistance. Unmodified starch shows no thermal transitions except the onset of thermal degradation at around 260°C. Starch acetate of ds 1.5 shows a sharp glass transition at 155°C and starch propionate of same ds had a  $T_g$  of 128°C. The starch ester resin reinforced with biofibers has properties comparable to general-purpose polystyrene.

#### 9:15 AM \*U3.3

PHENOLIC AND LIGNOPHENOLIC MATRICES REINFORCED WITH LIGNOCELLULOSIC FIBERS. Elisabete Frollini, Jane Paiva, Sandra Silva, Ilee Tanaka, Wanderson Trindade, Universidade de Sao Paulo, Instituto de Química de Sao Carlos, Sao Carlos, SP, BRAZIL.

Lignin, extracted from sugarcane bagasse by the organosolv process, was used as a partial substitute of phenol (40%, w/w) in the preparation of resol phenolic matrix. Lignocellulosic fibers, as for instance sugarcane bagasse, sisal, jute and curaua, were used as reinforcement in these polymeric matrices, in order to obtain fiber-reinforced composites. These lignocellulosic materials were modified by chemical and/or physical methods (mercerization, esterification, ionized air) and characterized regarding its chemical composition and tensile strength. Thermoset polymers (phenolic and lignophenolic) and related composites were obtained by compression molding and characterized by mechanical tests such as Impact, Differential Mechanical Thermoanalysis (DMTA). The treatment of fibers with ionized air (a 'dry method') is promising, because the impact strength results obtained when these treated fibers were used were similar or higher than those obtained with mercerized fibers. Compared with the other lignocellulosic materials used, sisal composites presented an exceptional impact strength, which increases with the fiber length. Probably, its high spiral angle is an important structural parameter acting on this property. The inner part of the fractured samples was analyzed by Scanning Electron Microscopy (SEM) and the results indicated adhesion between fibers and matrix, because the fibers are not set free, suggesting they suffered a break during the impact test. The results as a whole showed that it is feasible to replace part of phenol by lignin in phenolic matrices, without loss of properties.

#### 10:15 AM \*U3.4

BIOPOLYMER-SILICA HYBRID AEROGELS CONTAINING TRANSITION METAL SPECIES; STRUCTURE, PROPERTIES, AND REACTIONS. Xiangjun Hu, Shuang Ji, and William M. Risen, Jr., Dept of Chemistry, Brown Univ, Providence, RI.

Novel transition-metal containing hybrid biopolymer-silica aerogels have been synthesized as transparent monolithic structures. The compositions include Ru(III), Rh(III), Co(II), and Pd(II) species, silica and chitosan, an amine-group-containing biopolymer derived from chitin. Due to its aqueous solubility and hydrogen bonding properties, chitosan was homogeneously incorporated into the silica

network. These aerogels have densities in the range of 0.25 - 0.30 g/cm<sup>3</sup>, BET surface areas in the range of 500 - 900 m<sup>2</sup>/g, and refractive indexes below 1.17 (at 632.8 nm). Infrared spectroscopy shows that chitosan is effectively introduced into the silica aerogels, and the transition metal ions can coordinate with the amine sites on chitosan. This combines the metal-ion interaction of chitosan with that of silica aerogels. Transmission electronic microscopy indicates that the particle sizes of silica are about 2 nm. Small angle neutron scattering (SANS) has been used to study the microstructure of these aerogels. A new Small-Particle Mass-Fractal model scattering function, derived from the Teixeira Mass-Fractal scattering function, was used to fit the SANS data. It was found that chitosan helps to form an open aerogel structure. It supports a structural model in which there are primary particles that connect with each other closely to form clusters, and these clusters serve as a secondary structural unit to form the chitosan-reinforced aerogel network. It also indicates that chitosan reinforces the interparticle connections. The local environments, structures and chemistries of the transition metal ions have been explored. Of special interest in this regard are the magnetic properties of the Ru(III) containing materials, which are consistent with anti-ferromagnetic coupling, and the reactions of the Rh(III), Ru(III), and Pd(II) species with small gaseous molecules.

#### 10:45 AM \*U3.5

A NEW HYBRID AEROGEL APPROACH TO MODIFICATION OF BIODERIVED POLYMERS FOR MATERIALS APPLICATIONS. Mingzhe Wang, Xipeng Liu, Shuang Ji, and William M. Risen, Jr. Department of Chemistry, Brown University, Providence, RI.

Novel hybrid aerogels consisting of the bioderived polymers chitosan, pectic acid or alginic acid and silica have been synthesized as clear monoliths from clear gels by supercritical fluid extraction. These renewable resource polymers, which are soluble and typically unassociated in aqueous systems, are separately arranged in an aerogel scaffolding. This makes them exposed and available for reactions that would not be possible in aqueous systems. Thus, it is possible to react the amine groups of chitosan, a polymer derived from chitin, with isocyanate terminated prepolymers to form urea linkages and to form new linked-chitosan materials. Following the reactions, the scaffold can be dissolved and the new material isolated. Variations lead to hydrophobic or hydrophilic materials. The reactions of aerogel scaffolded bioderived polymers to form urethane-, or amide-group linked materials also will be presented and the properties of newly formed materials will be described. Further reactions enabled by the approach, including ones leading to radiation curable polymeric systems will be presented.

#### 11:15 AM \*U3.6

REDUCTION OF MOISTURE SENSITIVITY IN NATURAL FIBRES, G.T. Pott, Ceres B.V., Wageningen, THE NETHERLANDS.

When natural fibres are used as reinforcement for polymer composites, a number of problems have to be overcome. A very serious problem is the moisture sensitivity, causing fibre swell and ultimately rotting through fungi attack. A number of technologies deal with changing the chemical and/or physical composition of the fibre, thereby reducing the moisture sensitivity. To this category belong acetylation and hydrothermal treatment. In acetylation, acetic anhydride is used as a chemical that reacts with reactive OH-groups of the lignocellulose material, increasing hydrophobicity. In hydrothermal treatment no chemicals are used, only water and energy. The presentation will focus on the reduction of moisture sensitivity of bast fibres, such as flax, jute and hemp. Acetylation is reviewed briefly, but the hydrothermal treatment, especially the Duralin process is discussed in more detail. A brief survey is given of the structure and composition of bast fibres and the moisture adsorption and desorption mechanisms in these fibres.

The Duralin process involves three steps, hydrothermolysis, drying and curing. The raw material for the Duralin process applied to flax is green rippled flax straw. This eliminates the need for the traditional dew-retting, where the freshly harvested flax stems lay on the field for about four weeks. The Duralin process reduces moisture absorption and biological degradation, the fibre yield is higher than after dew-retting and the shives can be used as a filler material in polymers and for making a water proof particle board. The three main causes of reduced water uptake after Duralin treatment are the extraction of hemicellulose, the network formation through cross-linking of degradation reaction products of hemicellulose and lignin, and the increased crystallinity of cellulose.

Duralin fibres have shown to have higher tensile strength and higher flexural modulus than fibres extracted from dew-retted flax. Compounds reinforced with these fibres have, apart from decreased moisture sensitivity a better mechanical performance. Both the amount and the release rate of decomposition products resulting from compounding with polypropylene are significantly less for Duralin fibres than for dew-retted or green fibres.

11:45 AM **U3.7**

NOVEL STRUCTURAL MATERIALS FROM NATURAL SOURCES BY MEANS OF GREEN NANOTECHNOLOGY. Wang Weixing, Gong Kecheng, Polymer Structure & Modification Research Lab, South China University of Technology, Guangzhou, CHINA.

Cement, ceramics, and plastics are popular structural materials around us. But their drawback and virtue are all distinct. How to make novel structural materials with good high-temperature strength like ceramics, high-toughness like plastics, and low cost like cement at ambient temperature and atmosphere is challenging. Green nanotechnology[1] is the perfect combination bionics with nanotechnology to prepare novel materials with good performance by means of the soft solution process (SSP) from natural source. Here we describe a simple, cheap way of preparing structural materials from abundant and cheap natural source such as kaolinite, soybean cake, rice husk etc. by green nanotechnology. Manipulation of materials' structure at nanometer and micron with biomacromolecules, reactive monomers or surfactants is the key to obtain high performance. And tough laminate with hierarchical structure thinner than 1mm with high hardness and smooth surface like enamel has been obtained. [1] Gong Kecheng, and Wang Weixing et al. "Chemical, polymer, ceramics, and composites from Green Nanotechnology", Proceedings of 3rd Ints Workshop on Green Chemistry, 2000, p202, China.

#### SESSION U4: COMPOSITES FROM NATURAL FIBERS AND/OR PLASTICS

Chair: Frank K. Ko

Tuesday Afternoon, November 27, 2001  
Liberty (Sheraton)

1:30 PM **\*U4.1**

APPLICATIONS OF BIO-COMPOSITES IN INDUSTRIAL PRODUCTS. P.V. Kandachar, Faculty of Design, Construction and Production, Delft University of Technology, Delft, THE NETHERLANDS.

Available as agricultural resources in many countries, natural fibres, such as flax, hemp, kenaf, exhibit mechanical properties comparable to those of synthetic fibres like glass. But they are lighter, biodegradable, and are often claimed to be less expensive. Composites with these natural fibres have the potential to be attractive alternative to synthetic fibre composites. The natural fibres, however, exhibit more scatter in their properties, are thermally less stable and are sensitive to moisture absorption. The choice of matrix to reinforce with these fibres therefore becomes critical. Currently, synthetic non-biodegradable polymers, such as polypropylene, polyester, etc., are being explored as matrix materials, for applications in sectors like automobiles and buildings. Biodegradable polymers, as alternatives to synthetic non-biodegradable polymers, if made available in sufficient quantities at affordable prices, pave way for bio-composites in future. With both matrix and fibres being biodegradable, bio-composites become attractive candidates from the environment point of view. Currently, extensive and reliable property data on natural fibre composites and/or on bio-composites, are lacking, making product design with these materials rather tedious. Once the database is available, design & manufacture of products with natural fibre composites and biocomposites offer several opportunities and challenges.

2:00 PM **\*U4.2**

THE COMPETITIVENESS OF NATURAL FIBERS BASED COMPOSITES IN THE AUTOMOTIVE SECTOR. Alcides Leao, Nestor Giacomini, Vera Salazar, Dept of Natural Resources, UNESP, Botucatu, BRAZIL.

The development of new materials based on natural renewable resources have to be considered due environmental and economical concerns, for construction, furniture, packaging and mainly for automotive industries. The development of new materials is particularly attractive when a good part of this materials is based on natural renewable resources that not further stress the environment, are lighter and even stronger in some aspects when compared to man-made materials. Cost and weight are key aspects in the automotive sector. A broad review of natural fibers based composites are presented in exterior and interior application in the automotive sector. Process such as RTM, SMC, Injection Molding and Thermoforming are described and compared to the counterparts made of non-renewable sources.

2:30 PM **\*U4.3**

NATURAL FIBER REINFORCED PLASTICS IN AUTOMOTIVE INDUSTRY - ASPECTS OF SUSTAINABLE MOBILITY. H. Flegel and T.P. Schloesser, DaimlerChrysler AG, Research and Technology, Advanced Manufacturing Engineering, Ulm, GERMANY.

Ever since launching their first automobiles, Mercedes-Benz has used components made of renewable raw materials in car manufacturing. Today, more than 30 components made of renewable raw materials are used in the production of Mercedes C-, E- and S-Class automobiles. Our tests, which will be discussed, show that natural fibers are suitable both for manufacturing interior components and for reinforcing plastic materials, even for external semi-structure trim parts. The engine encapsulations of EvoBus busses like Mercedes Travego and Setra TopClass are made with natural fiber reinforced UP-resin, a commercial solution that realizes a cost and weight reduction of 5 percent. The natural fiber reinforced engine encapsulations is worldwide the first exterior component made from natural fibers.

The paper will also show that natural fibers, such as flax, hemp, kenaf and sisal are responsible for high transverse and tensile strength.

When embedded in plastic, natural fibers achieve a strength similar to that of fiberglass-reinforced plastics and are, therefore, well suited as a replacement. Even though the mechanical attributes of natural fibers embedded in plastic are comparable to glass fibers reinforced components, they have a much lower density and therefore a much lower part weight. In our R&D work, we have - for the first time - been able to deploy natural fibers within an entire process chain. The lecture will therefore also discuss (1) fiber selection and specification, (2) fiber preparation and processing, (3) component manufacture and quality, (3) materials and component approval, (4) recycling and ecological situation and (5) technology transfer to emerging countries. This procedure is transferable to foreign emerging countries. The use of locally growing natural fibers for a local production of plastic components is part of the global DaimlerChrysler strategy to increase the local content in different areas of the world.

3:30 PM **\*U4.4**

STRUCTURAL BIO-COMPOSITES PRODUCED FROM ENGINEERED NATURAL FIBERS AND PETRO AND/OR BIO POLYMERS. Lawrence T. Drzal, Amar Mohanty, Manju Misra, Michigan State University, Composite Materials and Structures Center, Dept of Chemical Engineering and Materials Science, East Lansing, MI.

Natural/Bio-fiber composites (Bio-Composites) are emerging as a viable alternative to glass-reinforced composites with particular advantages for automobile and infrastructure applications. Natural fibers, which traditionally were used as fillers for thermosets, are now becoming one of the fastest growing performance additives for thermoplastics. Advantages of natural fibers over man-made fibers such as glass and carbon are: low cost, low density, competitive specific mechanical properties, reduced energy consumption, carbon dioxide sequestration, and biodegradability. The combination of bio-fibers like Kenaf, Hemp, Flax, Henequen and Sisal with polymer matrices from both non-renewable and renewable resources to produce composite materials that are competitive with synthetic composites requires special attention to the biofiber-matrix interface, and its resulting adhesion, as well as to the processing methods used to produce these materials. While much attention has been given to the combination of polypropylene with natural fibers for making bio-composites of industrial value, the resulting composites are not completely eco-friendly due to the non-biodegradable nature of the matrix. Substitution of petro-based plastic with bio-plastic such as soy-based plastic, starch plastic and cellulosic plastics derived from renewable resources is the next generation of matrices being considered. Mechanical properties of biocomposites depend on the choice of fiber type. Bast fiber based bio-composites produce the best tensile and flexural properties; while leaf fiber based bio-composites produce excellent impact behavior. The development of useful bio-composite materials also requires that fiber-matrix adhesion be optimized to insure good mechanical properties. Since a significant attraction of bio-composites is the low cost of bio-fiber, inexpensive yet effective biofiber surface treatments are necessary. Water-based sizings or dry coupling agents have been studied as useful approaches to designing bio-composites of commercial value. Our research shows that blending of suitably surface treated bast and leaf fiber in the correct proportions, which we call - 'Engineered Natural Fibers' or 'ENF' allows biocomposites to be designed and produced in which the flexural and impact properties can be altered and optimized. The potential of biopolymers such as cellulosic plastic (commercial bio-plastic) and formulated soy-based plastics, developed at MSU, in bio-composites will also be highlighted. The incorporation of bio-resources such as plant-derived fiber and crop-derived plastics to composite materials can reduce dependency on petroleum. Through bio-fiber surface treatment, biopolymer modification, and adequate processing techniques, novel bio-composites can be designed and engineered so as to substitute/supplement glass fiber composites in various applications.

4:00 PM **\*U4.5**

LAMINATES FROM THE SOY-BASED POLYURETHANES AND

NATURAL AND SYNTHETIC FIBERS. Zoran S. Petrovic, Wei Zhang, Ivan Javni and Andrew Guo, Kansas Polymer Research Center, Pittsburg State University, Pittsburg, KS.

Two polyols were prepared from soybean oil, one by epoxidation route and the other via hydroformylation. The polyol obtained by epoxidation has secondary groups and has gel time of more than one hour when reacted with crude MDI to produce polyurethanes.

Hydroformylated polyol has gel time with MDI of several minutes and is more suitable for reinforced reaction injection molding (RRIM). First group of polyurethanes had glass transition close to 80°C while the hydroformylated gave about 30 degrees lower T<sub>g</sub> and comparable strength but higher elongation. Adding glycerin as the crosslinker could increase both T<sub>g</sub> and strength.

Two series of laminates were prepared using several types of glass fabric, carbon fiber, polyester, cotton, jute fabrics and natron paper as reinforcements. Both the hydroformylated and epoxidized polyol based polyurethane composites were of comparable strength. Composites from organic fibers were lighter and more flexible than the glass reinforced samples. For comparison glass reinforced epoxy and polyester were prepared and tested. Organic fibers give lower stiffness and strength than the corresponding glass or carbon fiber. Although the neat polyester and epoxy resins had somewhat higher strengths than the polyurethanes from soybean oil, mainly due to the higher crosslinking density, the composites from the soy oil-based resin displayed superior properties. Glass transition and mechanical properties of the soy-based polyurethanes was varied from about 70°C to 140°C with added crosslinkers. Processing time of the soy-polyurethanes resins was shorter than that of other two resins.

#### SESSION U5: GLASS, CARBON AND OTHER REINFORCING FIBERS

Chair: X. Susan Sun

Wednesday Morning, November 28, 2001

Liberty (Sheraton)

##### 8:30 AM U5.1

#### VALUE-IN-USE OF COMPOSITE REINFORCING FIBERS.

Frederick T. Wallenberger, PPG Industries, Inc., Fiberglass Science and Technology, Glass Technology Center, Pittsburg, PA.

Reinforcing fibers are a key component of polymer-matrix composites, ceramic-matrix composites, and metal-matrix composites. They all increase, but to various degrees, the strength and the stiffness of the given matrix material. In addition, they will selectively offer other valuable properties, which will obviously differ from application to application, such as low dielectric constants, high temperature resistance or high creep resistance. Depending on the in-use requirements for a given composite, it is possible to select the most suitable composite-reinforcing fiber for a given end-use and to design the desired composite part at the lowest possible cost. This review analyzes the fiber properties, the reinforcing potential, the unit cost and therefore the value-in-use of important composite reinforcing fibers. The reinforcing fibers under review include metal fibers such as Brunsmet; carbon and graphite fibers, such as Panex, Toroyca and Thorne; oxide ceramic fibers such as Nextel; non-oxide ceramic fibers such as Tyranno, Hi-Nicalon and SCS-6; oxide glass fibers, including conventional and boron-free E-glass; aramid fibers such as Kevlar, Technora and Twaron; and new natural composite reinforcing fibers such as Kenaf.

##### 8:45 AM U5.2

#### RECENT ADVANCES IN OXIDE GLASS FIBER SCIENCE.

Frederick T. Wallenberger<sup>1</sup>, Ernest Lawton<sup>2</sup>, and Hong Li<sup>1</sup>, PPG Industries, Inc., Fiberglass Science and Technology; <sup>1</sup>Glass Technology Center, Pittsburg, PA and <sup>2</sup>Fiberglass Technology Center, Lexington, NC.

Oxide glass fibers are among the most versatile industrial materials known today. They are readily produced from raw materials, which are available in practically unlimited supply. The major oxide ingredients, are silica, calcia, alumina, magnesia and/or boron oxide. These fibers exhibit useful properties such as hardness, transparency, chemical resistance and inertness, as well as desirable fiber properties such as strength, flexibility and stiffness and commercial properties such as low dielectric constants. The technical literature and recent scientific advances will be summarized.

##### 9:00 AM U5.3

#### GLASS FIBERS FROM VISCOUS AND INVISCID MELTS,

Frederick T. Wallenberger<sup>1</sup>, University of Illinois, Urbana-Champaign, IL, and Norman E. Weston (retired), Micron Analytical Services, Wilmington, DE. <sup>1</sup>Present Address: PPG Industries, Fiberglass Science and Technology, Glass Technology Center, Pittsburg, PA.

Glass melts, which are viscous (have viscosities of log2.0 - log4.0 poise), are either strong melts or fragile melts. Amorphous glass fibers can be formed from both strong and fragile oxide melts. Glass melts, which are inviscid (have viscosities of only 1.0 - 2.0 poise), can also yield amorphous oxide glass fibers. This paper shows that strong melts exhibit a continuous, nearly linear decrease in melt viscosity with increasing temperature, especially below and above the liquidus temperature. Fragile melts, like strong melts, exhibit a continuous decrease, in melt viscosity up to the liquidus with increasing temperature. But, unlike strong melts, their viscosity drops much more rapidly above the liquidus with further increases in temperature. In this temperature range their viscosity is very low. Inviscid melts, unlike strong or fragile melts have sharply defined melting points, rather than ranges of high viscosity. This paper also shows that amorphous oxide glass fibers, formed from each melt including inviscid melts, must have a melt viscosity log 2.5-3.0 poise at the point of fiber formation. To meet this requirement, fragile melts must be up-drawn and inviscid melts must be super-cooled and/or the resulting fiber surfaces must be chemically modified.

##### 9:15 AM U5.4

#### CONTINUOUS CARBON NANOFIBERS FOR NANOFIBER

COMPOSITES. Yuris Dzenis, Yongkui Wen, Dept of Engineering Mechanics, Center for Materials Research and Analysis, University of Nebraska-Lincoln, Lincoln, NE.

Continuous carbon nanofibers were manufactured using electrospinning technique. The as-spun polyacrylonitrile (PAN) nanofibers were stabilized and carbonized to convert them into carbon nanofibers. The diameters of typical carbon nanofibers were in the range from 100 - 500 nanometers. Compared to the vapor growth carbon nanofibers, the electrospun carbon nanofibers are continuous, uniform in diameter, and solid. The nanofiber samples do not require any purification. The carbon nanofibers were characterized by scanning electron microscopy, transmission electron microscopy, and atomic force microscopy. Electron diffraction patterns were obtained from individual carbon nanofibers. Carbon nanofibers and their nanocomposites are expected to retain many good properties of regular carbon fibers and advanced composites. These include high specific modulus and strength, good fatigue durability, and excellent corrosion resistance. Carbon nanofibers can be used to improve mechanical properties of matrices in conventional composites. Reinforcement of interfaces with carbon nanofibers as a means to improve interlaminar fracture toughness and suppress delamination was also explored.

##### 9:30 AM U5.5

#### DIELECTRIC PROPERTIES OF NANOPOROUS CARBON FIBER

COMPOSITES. Mohamed Nasr, Burt Lee, and Michael Ellison, Clemson Univ, School of MS&E, Clemson, SC.

Nanoporous carbon fibers or activated carbon fibers (ACFs) having high surface area and reactivity were prepared through treatment of commercial ACFs with transition metal salts and a carbonaceous sol binder followed by thermal treatment in an inert atmosphere. The electrical properties of the treated ACFs were examined and exhibited enhanced properties. These treatments created new interfaces through which extra charges could be localized, transferred, or stored. Dielectric impedance measurements such as relative permittivity and impedance of ACF and ACF composites exhibited that the electric double-layer capacitance of the ACF were higher than the untreated ACFs. Surface area analysis by BET method and pore volume characterizations revealed the changes on the pore structure affected by the treatments. It was found that the relative permittivity of ACF increased as the number of interfaces between the structure of ACF and the conductive filler increased. At the same time, the impedance of ACF decreased due to the presence of conductive filler. The as-received as well as the treated ACF behaved as a pure resistor with almost no capacitive effect. It is shown that nanoporous carbon fabrics treated by the unique process developed in this work are good candidates for use as polarizable electrodes in double-layer capacitor applications.

##### 9:45 AM U5.6

#### THEORY AND SIMULATION OF TEXTURE FORMATION IN

MESOPHASE CARBON FIBERS. Jun Yan, Alejandro D. Rey, McGill University, Dept. of Chemical Engineering, Montreal, QC, CANADA.

Abstract Carbonaceous mesophases are spun into high performance carbon fibers using the melt spinning process. The spinning process produces a wide range of different fiber textures whose origins are not well understood. Planar polar (PP) and planar radial (PR) textures are two ubiquitous ones. This paper presents the theory and simulations of the formation process of the PP texture using the Landau-de Gennes mesoscopic theory for discotic liquid crystals, including defect nucleation, defect migration, and overall texture geometry. The simulated PP texture geometry is thoroughly explained

using analytical methods. The computed PP and PR textures phase diagram, given in terms of temperature and fiber radius, is used to establish the processing conditions and geometric factors that lead to the selection of these textures.

**10:30 AM \*U5.7**

**CARBON NANOFIBER SURFACE TREATMENT EFFECTS ON POLYPROPYLENE COMPOSITE PROPERTIES.** David J. Burton, D. Gerald Glasgow, Max L. Lake, Choongyong Kwag, and Joana C. Finegan\*, Applied Sciences Inc., and \*General Motors R&D Center, Warren, MI.

Carbon nanofibers (CNF) are vapor grown carbon fibers grown catalytically from gaseous hydrocarbons using metallic catalyst particles. Good adhesion between these fibers and matrix resins is essential for the performance of CNF based composites, so the mechanical properties of composites are strongly influenced by fiber surface morphology and chemistry. This presentation examines the fiber-matrix adhesion problem as influenced by CNF fiber surface area and energy. It will be shown that optimal fiber surface areas and energies for providing significant reinforcement in PP composites can be defined. In addition the influence of the fiber surface on electrical properties of selected organic matrix composites will be discussed.

**11:00 AM \*U5.8**

**YAG- AND RARE EARTH ALUMINATE-COMPOSITION GLASS FIBERS OBTAINED DIRECTLY FROM THE LIQUID PHASE.** J.K. Richard Weber, Paul C. Nordine, Containerless Research, Inc., Evanston, IL.

Glass fibers of the YAG-composition (Y3Al5O12) and of a wide range of rare earth oxide - aluminum oxide compositions can be pulled directly from the liquid phase. The process occurs at a temperature below the equilibrium melting temperature, where a liquid viscosity sufficient for fiber pulling operations is readily achieved under containerless processing conditions. The fiber making process, mechanical properties of the fibers, and recent research on optical properties of rare earth dopants in these fibers will be presented.

**11:30 AM \*U5.9**

**NOVEL MULTI-LAYER MELT BLOWN MICROFIBER WEBS.** Eugene G. Joseph, 3M Company, St. Paul, MN.

Melt blowing is rapidly growing in the field of non-wovens. It is a melt extrusion process where the resulting webs consist of microfibers. This work relates to multi-layer blown microfiber webs where multiple layers have been introduced within each microfiber. The layers are alternating and a wide variety of polymer combinations have been evaluated. The structure-property behaviour of these materials has been studied utilizing techniques such as electron microscopy, thermal and dynamic mechanical analysis etc. The mechanical and adhesive properties have been varied by changing the number of layers within the fiber in a controlled fashion and a working model has been developed to assist in understanding observed behaviour. The presentation will cover the structure - property behaviour of these multi-layer microfiber webs.

**SESSION U6: POLYMER AND RESIN MATRIX MATERIALS**

Chair: Eugene G. Joseph  
Wednesday Afternoon, November 28, 2001  
Liberty (Sheraton)

**1:30 PM \*U6.1**

**MORPHOLOGICAL AND ORIENTATION EFFECTS ON THE OPTICAL AND ELECTRONIC PROPERTIES OF CONJUGATED ELECTROACTIVE ORGANIC POLYMERIC FIBERS AND FILMS.** Richard V. Gregory, School of Materials Science and Engineering and NSF/ERC Center for Advanced Fibers and Films, Clemson University, Clemson, SC.

The electronic and optical properties of conjugated polymeric fibers and films have been shown to be highly dependent on the orientation, microstructure, and morphology of the film/fiber-forming polymer. These effects will need to be quantified and fully characterized prior to use in composite structures or as coatings on other materials to impart a desired electronic or optical effect. Changes in the electronic, optical and/or photonic properties, due to morphological changes induced by orientation of the polymeric films and electroactive fibers prepared from these materials, are related in this study to the polymer morphology. The developed microstructure is discussed and related to the optical and molecular chain axis and finally to the formed film or fiber morphological structure. The potential for tuning the morphological structure to specific end uses by selectively changing the polymer microstructure during processing will also be discussed. In addition we will briefly discuss studies and

characterization of the visco-elastic properties of wet-spun polyaniline fibers and highly oriented films. This work has shed light on the interaction of the polymer chains in this important conductive polymer, which lead to a more complete understanding of the observed electronic and electrical properties.

**2:00 PM \*U6.2**

**POLYMERIC ELECTROLYTE MEMBRANE NANOCOMPOSITES.** James E. McGrath, Department of Chemistry and Materials Research Institute, Virginia Tech, Blacksburg, VA.

Polymeric electrolyte membrane (PEM) based systems for automobiles, homes, and portable power fuel cells are already an important strategy for high density and very good environmentally benign energy sources. Currently, fluorinated sulfonic acid containing copolymers are utilized primarily at 80 degrees C or lower. An increase in the fuel cell utilization temperature is desired for a number of reasons, including better efficiency and to improve the tolerance of impurities, such as carbon monoxide, in hydrogen or other fuels. New and improved mechanisms for conductivity above the boiling point of water are needed, which operate with little or no water vapor present. We have been interested in the direct copolymerization of homopolymers based upon poly (arylene ethers) and naphthalene based polyimides. Both random (statistical) copolymers and block copolymers based on these two major classes of materials are being investigated. Several of these systems are surprisingly highly compatible with important additives, such as nanosilica and heteropoly acids (HPA), such as phosphotungstic acid. The high degree of dispersion is related to specific interactions between the inorganic additive and the host polymer, including hydrogen bonding in the case of silanol functional nanosilicas, and dipolar interactions between the HPA and the sulfonic acid groups and/or the phosphine oxide groups. The highly dispersed HPA systems allow conductivity values of greater than 0.1 S/cm at temperatures approaching 150 degrees C. Excellent adhesion to the matrix affords transparent ductile films. In contrast, the fluorocopolymers under identical conditions produce opaque films in which the HPA is readily re-extracted. The synthesis and characterization of the polymer matrix systems, as well as the development of the nanocomposites and their thermal, mechanical, and conductivity characterization, will be presented with a particular orientation toward proton exchange membranes for fuel cells.

**3:00 PM U6.3**

**BULK MICROSTRUCTURE AND LOCAL ELASTIC PROPERTIES OF LAMINATE COMPOSITES STUDIED BY THE MICRO-ACOUSTICAL TECHNIQUE.** V.M. Levin, Laboratory of Acoustic Microscopy, Institute of Biochemical Physics, Russian Academy of Sciences, Moscow, RUSSIA; Songping Liu, Beijing Aeronautical Manufacturing Technology Research Institute, Beijing, PR CHINA.

The focused ultrasonic beam technique has been employed for imaging of bulk microstructure of fiber-reinforced composites, measuring local elastic properties and mapping their distribution over the composite body. Fairly high ultrasonic frequency of 50 MHz and ultrashort probing pulses provide lateral resolution of 60  $\mu\text{m}$  and depth resolution of 40  $\mu\text{m}$ . We have used this technique for nondestructive layer-by-layer acoustic imaging of internal microstructure of the laminate composites. Series of sequential acoustic images in planes parallel to fiber plies *C - scans* or across fibers *B - scans* enable to perform pseudo-3D reconstruction of the specimen microstructure. The method makes it possible to measure velocities of longitudinal and transverse elastic waves and obtain local values of elastic moduli within area of 50 - 100  $\mu\text{m}$  diameter. The regime of mapping elastic properties distribution over a specimen is available. The technique has been applied to diverse types of carbon fiber laminates - unidirectional and cross-ply carbon fiber-epoxy laminates, textile composites with plane and serge weaving of fabrics and through-the-thickness stitched woven composites. Topology of internal microstructure - packing of fiber bundles and threads, stacks of bundles and plies, etc.; and different bulk defects - inclusions, voids, inhomogeneity of resin matrix, resin pockets, buckling and so on; has been observed. Quality of acoustic images depends on kind and density of fiber packing and on depth of an imaging plane position. Experience shows that specimens 4-6 mm thick are still available for acoustic visualization of their bulk microstructure. Measurement of local values of sonic velocities and elastic moduli were performed. In particular the method has been applied to studying elastic anisotropy of a single fiber ply. Values of longitudinal wave velocities along fiber direction and across fibers have been measured for a single ply 120  $\mu\text{m}$  thick incorporated into a cross-ply composite. The technique is promising for NDE of different composites, not only for carbon-based ones.

**3:15 PM U6.4**

**INFLUENCE OF PROCESSING PARAMETERS ON THE NANOSTRUCTURED MORPHOLOGY OF ELECTROSPUN POLYMER FIBERS.** Silke Megelski, Jeannie Stephens, Mei Wei Tsao,

John F. Rabolt, Univ of Delaware, Dept of Material Science and Engg., Newark, DE; D. Bruce Chase, Central Research and Development Dept, DuPont Experimental Station, Wilmington, DE.

Uniform polymer fibers with sub-micrometer diameters can be produced by electrospinning. Within this electrospinning process, fibers are formed by accelerating a jet of a polymer solution using high electric fields and collected as a mat on a grounded electrode plate. Electrospun polymeric fibers are of considerable interest because of their porosity, their large specific surface area and their uniformity. The morphology of the fibers is strongly dependent on the processing parameters (e.g. spinning voltage, solution viscosity, polymer molecular weight). The understanding of the electrospinning process as well as the correlation between the processing parameters and the resulting fiber morphology is still unclear. This work presents the results obtained from systematic investigations of variations of the solution concentration, the spinning voltage and the working distance on the morphology of Polystyrene (PS) fibers. Using optical microscopy, SEM and AFM measurements we were able to look at the influence of these parameters on the morphology and surface morphology of the fibers. This work has provided further understanding of the formation of nanostructures during the electrospinning process.

### 3:30 PM U6.5

**TENSILE AND FATIGUE BEHAVIOR OF RENEWABLE AND NONRENEWABLE HIGH PERFORMANCE FIBERS.** M. Kerr, J.J. Williams, and N. Chawla, Arizona State Univ., Department of Chemical and Materials Engineering, Tempe, AZ; K.K. Chawla, Univ. of Alabama at Birmingham, Department of Materials Science & Engineering, Birmingham, AL.

Characterizing the behavior of fibers is of great importance, regardless of whether the fiber is used in woven form or as a continuous fibrous reinforcement in a composite. In a composite, it is the fiber, of course, that typically imparts high strength and stiffness to the composite. Testing of single fibers, however, is quite problematic, particularly when the fibers are brittle and exhibit poor handling characteristics. A sophisticated microforce testing system was used to conduct single fiber testing. In addition to tensile testing, reproducible and stable cyclic loads were applied to study the cyclic fatigue behavior of single fibers. The elastic modulus, fiber strength (characterized by a Weibull distribution), and stress versus cycles behavior of several high performance ceramic fibers were determined. Natural, renewable fibers, with relatively lower modulus, were also examined and the tensile and fatigue behavior compared to that of their synthetic counterparts. The effect of processing-induced flaws and the effect of fiber microstructure on mechanical behavior will be discussed.

### 3:45 PM U6.6

**NOVEL TEMPLATED POLYPHENOL FOR IONIC CONDUCTIVITY.** Ferdinando F. Bruno, Lynne Samuelson, Materials Science Team, Natick Soldier Center, U.S. Army Soldier and Biological, Chemical Command, Natick, MA; Ramaswamy Nagarajan, Jayant Kumar, Departments of Physics and Chemistry, Center for Advanced Materials, University of Massachusetts Lowell, Lowell, MA.

Phenolic polymers and phenol formaldehyde resins are of great interest for a number of electronic and industrial applications. Unfortunately, the toxic nature of the starting materials (formaldehyde) and harsh reaction conditions required for the synthesis of these polymers have severely limited their use in today's markets. We present here an alternative, biocatalytic approach where the enzyme horseradish peroxidase is used to polymerize phenol in the presence of a template such as polyethylene oxide. Here the template serves as a surfactant that can both emulsify the phenol and polyphenol chains during polymerization and maintain water/solvent solubility of the final polyphenol/template complex. The reactants and the reaction conditions of this approach are mild and results in high molecular weight, electrically and optically active, environmentally friendly water-soluble complexes of polyphenol/template. Water-soluble polyphenol/polyethylene oxide complexes were formed with high molecular weights. The ionic conductivity will be reported and the possible application of these polymers as polyelectrolyte will be discussed. Thermal, UV-Vis, NMR, FTIR, light scattering and conductivity studies of the polymer complexes will also be presented.

### 4:00 PM U6.7

**ELECTROSPINNING OF POLYCARBONATES AND THEIR SURFACE CHARACTERIZATION USING THE SEM AND TEM.** Ravi V.N. Krishnapppa, Changmo Sung, University of Massachusetts, Center for Advanced Materials, Dept of Chemical Engineering, Lowell, MA; Heidi Gibson, US Army Soldier Center, Natick, MA.

Electrospinning is a process of forming a polymer fiber from a polymer solution under the influence of an electric field. The repulsive forces between the charges on the liquid surface, 'draws out' fibers

with diameters in the sub-micron range. The high aspect ratio of such fibers results in large specific surface areas, that tremendously enhances the rate of evaporation of the solvent from the polymer solution jet, forming solid polymer fibers, even as 'the drawing process' is still occurring. The charged polymer fibers are collected onto a grounded metal plate, to obtain a fiber mat. The aim of this study is to electrospin a polycarbonate and to study the nature of the fiber surface. Results have indicated that electrospun polycarbonate fibers have a 'raisin like', wrinkled structure. The appearance of such a surface is linked to the relative rates of evaporation of the solvent from the surface of the wet polymer fiber and the rate of evaporation at the core. Rapid evaporation of the solvent on the surface of the polymer fiber could result in formation of a dry polymer skin, while at the core, evaporation is incomplete. Thus, the polymer fiber possesses a fixed surface area even before it has completely lost its solvent content. Further loss of the solvent from the inside of the fiber by diffusion causes the polymer fiber to 'deflate', thus warping into a 'raisin' like structure. The same effect is also believed to cause the cylindrical fibers to warp into flat bands. More work on this aspect is expected to reveal answers, which would enable us to control the surface area by varying the process parameters such as the solvent used, viscosity, applied voltage, spin distance etc. Such a polymer fiber, whose surface area could be controlled, would find good use in separation processes.

### 4:15 PM U6.8

**DIFFERENT MORPHOLOGIES INDUCED BY NANOPARTICLES.** Junrong Zheng, Rensselaer Polytechnic Institute, Department of Chemistry, Troy, NY; Linda Schadler, Richard W. Siegel, Rensselaer Polytechnic Institute, Department of MS&E, Troy, NY.

Interfacial Morphology plays an important role in polymer nanocomposite. This paper is mainly focused on the morphology change of nanocomposite of nylon 6 and ceramic nanoparticles. Different kind and size of nanoparticles with different surface chemistry were used to make the composites. The crystalline forms of nylon 6 changed with the difference of the particles and the chemistry of the surface. DSC, XRD and SEM were used to study the composite.

### 4:30 PM U6.9

**PROCESSING, MICROSTRUCTURES AND MECHANICAL PROPERTIES OF INJECTION MOLDED SHORT FIBER-REINFORCED THERMOPLASTICS.** Guo-Xin Sui, Chee-Yoon Yue, Nanyang Technological University, School of Mechanical and Production Engineering, SINGAPORE; Shing-Chung Wong, Nanyang Technological University, School of Materials Engineering, SINGAPORE.

Short glass fiber-reinforced, rubber-toughened nylon 6,6 hybrid composites were manufactured using both the one-step processing of injection molding and the two-step processing of extrusion pre-compounding followed by injection molding. The microstructures of the injection molded bars from both of the processing procedures were therefore carefully studied and the mechanical properties were interpreted accordingly. The fracture toughness was assessed using the Essential Work of Fracture (EWF) technique. It was found that the two-step processing caused severely fiber breakage but a better dispersion of the fibers in the polymer matrix. The fibers from the one-step processing presented a longer average fiber length but a less dispersion. It has been well known that the fiber length and orientation are two elementary factors to determine the final mechanical properties of the injection-molded products, provided a same fiber/matrix interfacial bonding property. Different microstructures lead to differences in the fracture mechanisms and the toughening mechanisms, which determined the mechanical properties and the mechanical behaviors of the injection molded bars. An assessment was made on the two processing methods, based on the micro-structural and mechanical analysis results. Key words: Processing, hybrid composites, fracture, toughening.

### 4:45 PM U6.10

**CHARACTERIZING THE THERMOMECHANICAL DEGRADATION OF A FILLED ELASTOMER BY X-RAY PHOTOELECTRON SPECTROSCOPY AND MORPHOLOGY.** Marina C. Camatini, Univ of MI-Bicocca, Dept. of Environmental Sci., Milan, ITALY; A.J. Nelson, Lawrence Livermore National Laboratory, Chemistry and Materials Science Directorate, Livermore, CA; Giovanni F. Crosta, Univ of MI-Bicocca, Dept of Environmental Sci., Milan, ITALY.

In many applications filled, vulcanized elastomers are subject to wear under conditions, which differ by the applied forces and torques, heat exchange rate and exposure to reactive gases. The dynamics of the fracture process is known to affect the size distribution and shape of both the worn material surface and of the debris particles at the micrometer and submicrometer scale. Some related results about morphology have been described in the table below. X ray

photoelectron spectroscopy (XPS) is being used to probe the chemical environment of some elements, among which C, O, and S. XPS is providing essential information about the chemical alteration of wear particle surfaces. The morphology and microstructure of the same particles are obtained by optical and transmission electron microscopy. The correlation between these two sets of data originated from some types of wear particles is investigated herewith. The morphology of the particle perimeter is described by the estimated structural (coarse scale) and textural (fine scale) fractal dimensions,  $D_{FS}$  and  $D_{FT}$ . A preliminary result pertains to wear particles of types R and H (samples  $H_1$  and  $H_2$ ), produced at room temperature and, respectively at 120 Celsius. The materials exhibit the following values of  $D_{FS}$ ,  $D_{FT}$  ( $\pm 0.05$ ) and of the peak binding energies (eV) for Carbon and Sulfur.

Type	$D_{FS}$	$D_{FT}$	c (ls)	S (2p)
R	1.42	1.18	284.6	163.3
H1	1.39	1.11	285.6	162.6
H2	1.39	1.11	285.6	163.2

Further results will be presented as well as their interpretation by thermodynamic process analysis. The goal is to simultaneously describe fracture dynamics and elastomer degradation. {99}{C} M.C. Camatini *et al.*, 2001, "Fractal Shape Analysis of Tire Debris Particles: Preliminary Results and Applications", to appear in A.J. Nakatani *et al.*, Eds., *Filled and Nanocomposite Polymer Materials* MRS Proc. vol. **661**, MRS: Warrendale, PA.

#### SESSION U7: POLYMER AND CERAMIC MATRIX COMPOSITES

Chair: James E. McGrath  
Thursday Morning, November 29, 2001  
Liberty (Sheraton)

##### 8:30 AM U7.1

##### CHARACTERIZATION OF RENEWABLE COMPOSITES.

A. Emekalam, X. Gu, and D. Raghavan, Polymer Division, Dept of Chemistry, Howard Univ, Washington. DC.

An approach for mapping chemical heterogeneity of corn starch filled plastic using chemical modification and tapping mode atomic force microscopy (TMAFM) is demonstrated. This approach is based on selective degradation of one or more phase(s) in a multi-phase polymer blend system and the ability of TMAFM to provide nanoscale lateral information about the different phases in the polymer system. Polymer composite films containing different percentage of renewable additive were melt processed and exposed to a hydrolytic acidic environment and analyzed using TMAFM. Pits were observed to form in the blend films. The progressive hydrolysis of the degradable component in the composite was studied by mass loss measurement and FTIR analyses. TMAFM phase imaging was also used to follow pit growth of the blend as a function of exposure time. The usefulness of the chemical modification in the design of degradable membranes with controlled porosity is discussed.

##### 8:45 AM U7.2

NEW INSIGHTS INTO TOUGHENING PARTICULATE BRITTLE COMPOSITES. Ian J. Merchant, Howard W. Chandler, Robin J. Henderson, Dept of Engr, Univ of Aberdeen, Aberdeen, SCOTLAND; Donald E. Macphee, Terry F. Stebbings, Dept of Chemistry, Univ of Aberdeen, Aberdeen, SCOTLAND.

This paper presents a new interpretation of crack behaviour in quasi-brittle composites and from this, develops a variety of approaches to toughening. The key insight is that the time at which particle debonding takes place is critical to how the crack behaves in the vicinity of the particle. It is vital that for toughening to be maximised, debonding occurs before the main crack arrives. This ensures that a flat fracture path in the matrix is followed and the particle can act so as to pin the crack faces. This generic method centres on the ability not only to encourage bridging, but also to make it very difficult for a crack to avoid a path that will result in bridging. The paper highlights two approaches to ensuring timely de-bonding of particulates. These are:  $\Sigma$  coating the particles to discourage particle-matrix bonding and;  $\Sigma$  designing residual stresses to promote debonding by either heat treatment or use of expansive matrices at room temperature. These ideas have been confirmed by detailed experiments on a variety of particulate composites: refractory ceramics; cement-based composites, both pressed and conventionally cast; dental cements; thermosetting polymers and dual-phase glass composites. The improved bridging in these composites is demonstrated and the implications are discussed.

##### 9:00 AM \*U7.3

##### LAYER ORDERING EFFECTS ON THE IMPACT RESISTANCE OF GLASS / POLYCARBONATE LAMINATE PANELS.

R.C. Bradt, M.E. Stevenson and S.E. Jones, College of Engineering, The University of Alabama, Tuscaloosa, AL.

The impact resistant of SLS glass / polycarbonate laminates is addressed theoretically and experimentally for glass / polycarbonate laminate panels. The much lower elastic modulus of the polycarbonate relative to the SLS glass allows for the macrostructural design of the laminate panels to have different elastic compliances. The compliance depends on the thicknesses of the glass and polycarbonate layers and also on the sequencing, or order of the two materials in the overall panel laminate.

Following the examination of these considerations, two series of different SLS glass / polycarbonate layer ordered panels with significantly different compliances were tested in ballistic impact with copper cylinders. The damage resistance to the panels is correlated with the design of the panel laminates and their compliances. Velocity and energy criteria are applied to complete perforation. Implications for the resistance of laminate panel designs for impact events are discussed and compared with the experimental results.

##### 9:30 AM \*U7.4

##### DESIGN OF SANDWICH COMPOSITES WITH MULTI-FUNCTIONAL FACESHEETS.

Uday Vaidya, Chad Ulven, Department of Mechanical Engineering and Applied Mechanics, North Dakota State University, Fargo, ND.

Sandwich composites find increasing use as flexural load bearing lightweight sub-elements in air and space vehicles as well as other commercial structure. Typically, a sandwich construction stiffens a structure without substantially increasing its weight. The commercial applications (aerospace, marine and rail/ground transportation) of sandwich structures primarily utilize foam, balsa and honeycomb as core materials. These cores exhibit lightweight advantages, energy absorption and good damage resistance. However, the space in the core becomes inaccessible once the facesheets are bonded in place. Significant multi-functional benefits can be obtained by making either the facesheets or the core space accessible. Multi-functionality is generally referred to as value added to the structure in terms of advantages that the design has to offer (in comparison to a conventional sandwich structure). In addition to conventional load bearing, the structure has integrated design capabilities. Such designs would include enhanced vibration damping, increased damage resistance, improved transverse stiffness, acoustical transmission/absorption, noise control, ability to route electrical wires, store fuel, provide fire retardant capability, enable self-healing, and embed electronics/sensors etc. These benefits are derived in addition conventional load bearing, lightweight and high flexural strength / stiffness requirements. In this work traditional core materials of nomex honeycomb, aluminum honeycomb and metal foam have been bonded to functional space accessible facesheets. The facesheets offer functional benefits in terms of ability to route wires, enhance vibration damping and store sensors, electronics etc. This paper will present the processing and dynamic response studies of these innovative core designs with example applications for various structures.

##### 10:30 AM \*U7.5

INJECTION MOLDING A POLYOLEFIN-BASED NANOCOMPOSIT VERSUS A TALC-FILLED TPO. D.A. Okonski, Materials and Processes Laboratory, GM R&D Center, Warren, MI.

General Motors Research and Development and Basell Polyolefins have jointly developed a family of polyolefin-based nanocomposites for use in the injection molding of body-side claddings. Basell Polyolefins commercialized one of these materials as HiFax DX277A in September of 2000, and General Motors has exclusive use of this material. Confidence in the ability of DX277A to perform as intended is being reinforced by molding trials at various Tier 1 locations. In addition to mass savings, the nanocomposite material is proving to have a much wider processing window than a conventional talc-filled TPO allowing Tier 1 molders the opportunity to process away problems rather than initiating a tooling change. This paper will describe the processing advantages associated with the injection molding of a polyolefin-based nanocomposite over a more conventional talc-filled TPO.

##### 11:00 AM \*U7.6

GLASS AND GLASS-CERAMIC MATRIX COMPOSITES: FROM MODEL SYSTEMS TO USEFUL MATERIALS. Aldo R. Boccaccini, Imperial College, London, UNITED KINGDOM.

By reinforcing glass and glass-ceramic matrices with a second constituent in the form of whiskers, particles or fibres, advanced composite materials with improved mechanical properties can be fabricated. These composites were originally developed as model

systems for laboratory-scale experiments. Due to their remarkable properties and relative ease of fabrication, however, the materials are candidate for a variety of technical applications. The present contribution is based on an extensive review of the available literature on these materials and on our own work, focussing on their potential for thermostructural applications. It will be shown that there is currently a fairly deep understanding of the mechanical behaviour of the materials at room and high-temperatures, as well as substantial knowledge on the material behaviour under fatigue and thermal shock conditions. Our work will show that a number of challenges remain, however, for future developments. These include the need for a further understanding of the thermomechanical behaviour of the composites under in-service conditions, i.e. mainly at high temperatures and in oxidative or corrosive atmospheres. Moreover, it will be emphasised that relative limited R&D work has been carried out so far in the area of manufacturing of engineering components and structures having complex geometry and large dimensions, including the development of machining and joining techniques. It will be shown that the addition of a functional property to traditional glass matrix composites, for example an electrical, thermal or optical function, may open new, until now not considered, applications. Optomechanical composites and glass matrix composites reinforced by piezoelectric phases represent novel developments in this area to be discussed here. The final goal of this presentation is to generate a broader interest in glass and glass-ceramic matrix composites both in the scientific and industrial communities, so that the high technological potential of these materials can be wider exploited.

#### 11:30 AM \*U7.7

EBC-PROTECTED OXIDE FIBER/POROUS MULLITE MATRIX COMPOSITES (WHIPOX). H. Schneider, J. Goring, B. Kanka, M. Schmucker, Inst for Materials Research, German Aerospace Center (DLR), Koeln, GERMANY.

The new developments in the field of oxide/oxide composites with highly porous matrices (Wound Highly Porous Oxide CMCs, i.e. WHIPOX) presented in this paper focus in two areas:

1. Fabrication of oxide/oxide (WHIPOX) composites: Room temperature and high temperature strength, Youngs modulus, deformation behavior and cyclic fatigue of components are tailored using specific fibers (Nextel 610, 650, 720) and applying different fiber bundle winding angles.
2. Development of high temperature and environmental barrier coatings (EBCs) for WHIPOX-CMCs: High temperature and environmental stability and lifetime of EBCs are controlled by the materials used, and by variation of the deposition-induced microstructure. The EBCs must, moreover, survive the severe conditions of a gas turbine engine combustor.

### SESSION U8: CERAMIC AND METAL MATRIX COMPOSITES

Chair: Richard C. Bradt  
Thursday Afternoon, November 29, 2001  
Liberty (Sheraton)

#### 1:30 PM \*U8.1

RAMAN SPECTROSCOPIC STUDY OF GADOLINIUM IN SODIUM-ALUMINOBOROSILICATE GLASSES. H. Li<sup>a,b</sup>, Y. Su<sup>a</sup>, L. Li<sup>a</sup>, and D.M. Strachan<sup>a</sup>. <sup>a</sup>Pacific Northwest National Laboratory, Richland, WA. <sup>b</sup>Currently with Fiber Science and Technology, PPG Industries, Inc., Pittsburgh, PA.

Understanding of rare earth oxide dissolution in borosilicate-based glass systems is important for special technical glass applications such as optical communication and immobilization of radioactive materials as examples of two extreme applications. A Raman spectroscopic study was recently performed on a series of sodium-alumino-borosilicate glasses with Gd<sub>2</sub>O<sub>3</sub> up to its solubility limit. Experimentally measured spectra were fitted to a Gaussian function for each individual band without any restrictions of the band position, width, and intensity. The evolution of the derived bands was discussed in terms of rare earth element partitioning in the borate-rich and silicate-rich environments as potential dissolution mechanism in the system.

#### 2:00 PM \*U8.2

DIRECTIONALLY SOLIDIFIED SINGLE CRYSTAL AND POLYPHASE OXIDE FIBERS. Ali Sayir, NASA Glenn Research Center, Cleveland, OH.

Directionally solidified single crystal and polyphase oxide fibers are attractive for functional ceramic applications as active devices and important for structural ceramic components as load bearing applications. The fracture characteristics of single crystal fibers from a variety of crystal systems and directionally solidified eutectic

systems will be described. The moderate tensile strength of single crystal <111> Y<sub>3</sub>Al<sub>5</sub>O<sub>12</sub>, was controlled by the facet forming tendency of the cubic garnet structure and in some cases by the precipitation of cubic perovskite phase YAlO<sub>3</sub>. Tensile strength of single crystal Y<sub>2</sub>O<sub>3</sub> and single crystal mullite were controlled by the facet formation of tendency of specific planes. In contrary, single crystal sapphire can be produced with very high strength. Yet, single crystal <0001> Al<sub>2</sub>O<sub>3</sub> fibers do not retain their strength at elevated temperatures. The data suggest that single crystal <0001> Al<sub>2</sub>O<sub>3</sub> failure is dependent on slow crack growth at elevated temperatures. The high temperature tensile strength of Al<sub>2</sub>O<sub>3</sub>/Y<sub>3</sub>Al<sub>5</sub>O<sub>12</sub> eutectic fibers is superior to sapphire (1.3 GPa at 1100°C) and demonstrably less prone to slow crack propagation. Affects of composition on morphology and on crystallographic orientation are currently topics of investigation in several two-phase systems. The effects of varying volume percent of the two constituents and the addition of dopants have been examined. Critical to this effort is the correlation of mechanical properties with eutectic growth data.

#### 2:30 PM \*U8.3

CRYSTALLIZATION AND TEM MICROSTRUCTURE OF OXIDE FIBERS. Waltraud M. Kriven, Bradley R. Johnson, Wonki Yoon, University of Illinois at Urbana-Champaign, Dept. of Materials Science and Engineering, Urbana, IL.

A new fiber crystallizing apparatus, capable of 2400°C in air and various traverse rates over individual fibers, has been developed in our laboratory. Amorphous, alumino-silicate fibers (Nextel 550 - from 3M Inc.) of 15 microns in diameter, have been crystallized by heat treatment at 1600°C. Doped and pure YAG fibers are also crystallizable with this furnace. The microstructures were analyzed by TEM techniques (SAD, BF, DF, EDS). Textured growth of mullite needles along [001] by re-melting and recrystallization of fibers was investigated. Mechanical tensile testing as a function of temperature up to 1400°C is performed to correlated heat treatment with microstructure and properties.

#### 3:30 PM \*U8.4

WOOD-CERAMIC COMPOSITES. D.M. Dabbs, D.R. Treadwell, and I.A. Aksay, Princeton University, Department of Chemical Engineering and Princeton Materials Institute, Princeton, NJ.

We have improved the physical properties of wood by converting it to a wood-ceramic composite. Studies were performed to demonstrate (i) that wood cells could be stiffened by the addition of a ceramic phase and (ii) that the ceramic could be added to the wood through in-situ hydrolysis of metal alkoxides. Several wood samples were impregnated with solutions of either tetraethoxysilane (TEOS) or aluminum alkoxides. Methods for the *in-situ* conversion of the precursors to ceramics were developed. Wood treated in this way was found to have improved hardness, workability, and dimensional stability. Resistance to charring was enhanced as shown by thermal analysis of the treated wood. The structure of the TEOS-treated wood was found to be entirely replicated by silica after the organic component was completely burned off. SEM and TEM analyses confirmed that the cell walls had been penetrated by the precursor and, further, that conversion had occurred within the cell walls. Work with silica particle suspensions (Ludox<sup>®</sup>) and aluminum sec-butoxide demonstrated that techniques for controlling the site of hydrolysis could be developed.

#### 4:00 PM U8.5

MICROSTRUCTURE AND MECHANICAL PROPERTIES OF SILICON NITRIDE REINFORCED ALUMINIUM MATRIX COMPOSITES FABRICATED BY PRESSURE INFILTRATION. L.M. Peng, K. Noda and H. Kawamoto, Japan Fine Ceramics Center, Nagoya, JAPAN.

The present study aims to investigate the microstructure and mechanical properties of aluminium matrix composites reinforced with high volume fraction of Si<sub>3</sub>N<sub>4</sub> fabricated by the pressure casting technique, with variations in the composition of matrix alloy and microstructure of preforms. Characterization was carried out by a combination of metallography, flexural and tensile tests and thermal cycling to study the flexural strength, fatigue and creep behavior in the composites. The findings indicated that increasing matrix strength resulted in an increase in flexural strength, fatigue and creep resistance of composites. The fatigue strength exponent for composites decreases with testing temperatures and is higher than that for the aluminium matrix alloy. The fatigue ratio, taken as the ratio of fatigue strength at 10<sup>7</sup> cycles to corresponding flexural strength, varied between 0.4 and 0.6 depending on the matrix and testing temperatures. By contrast, this ratio for the aluminium matrix alloy was about 0.25. The improvement in mechanical properties of composites is associated with the load transfer effect from matrix to the stiffer reinforcement. Thermal cycling between 25 and 300°C in air for 200 cycles produced a significant decrease (about 38%)

in residual strength ratio for the composites, while a smaller loss of strength (about 17%) was noted for the matrix alloy.

#### 4:15 PM U8.6

INFILTRATION OF Al-Mg ALLOY INTO SiC PREFORM IN THE PRODUCTION OF METAL MATRIX COMPOSITES BY PRESSURELESS INFILTRATION. A. Zulfia, Department of Metallurgy, The University of Indonesia, Jakarta, INDONESIA; R.J. Hand, Department of Engineering Materials, The University of Sheffield, Sheffield, UNITED KINGDOM.

Metal matrix composites have been produced by pressureless infiltration of Al-Mg alloys into SiC preforms at 900°C under nitrogen atmosphere for different infiltration times. The wettability of the ceramic reinforcement by the Al-Mg alloy is crucial in determining whether an Al/SiC metal matrix composite can be produced by pressureless infiltration. Sessile drop results show that Al alloys with Mg content greater than 8-wt% had a contact angle lower than 90° after 5 minutes contact time, this was associated with the pressureless infiltration results as metal matrix composites have been produced after 30 minutes with these alloys. Sessile drop experiment also shows that Al-Mg alloys under nitrogen and argon similarly wet SiC. It is concluded that the infiltration process does not involve the intermediate nitride phase suggested by others authors.

#### 4:30 PM U8.7

HIGH TOUGHNESS CERAMIC LAMINATES BY DESIGN OF RESIDUAL STRESSES. Nina Orlovskaya, Drexel University, Department of Materials Engineering, Philadelphia, PA; Jakob Kuebler, EMPA, Duebendorf, SWITZERLAND; Vladimir Subotin, Institute for Problems of Materials Science, Kiev, UKRAINE.

Multilayered ceramic composites are very promising materials for different engineering applications. Laminates with strong interfaces can provide high apparent fracture toughness and damage tolerance along with the high strength and reliability. The control over the mechanical behavior of laminates can be obtained through design of residual stresses in separate layers. Here we report a development of tough silicon nitride based layered ceramics with controlled compressive and tensile stresses in separate layers. We design the laminates in a way to achieve high compressive residual stresses in thin (100 micron) Si<sub>3</sub>N<sub>4</sub> layers and low tensile residual stresses in thick (600-700 micron) Si<sub>3</sub>N<sub>4</sub>-TiN layers. The residual stresses are controlled by the amount of TiN in layers with residual tensile stresses and the layers thickness. The fracture toughness of pure Si<sub>3</sub>N<sub>4</sub> ceramics was measured to be 5 MPa m<sup>1/2</sup>, while the apparent fracture toughness of Si<sub>3</sub>N<sub>4</sub>/Si<sub>3</sub>N<sub>4</sub>-TiN laminates was in the range of 10-17 MPa m<sup>1/2</sup> depending on the thickness of the top layer. The work is in the progress to measure the surface residual stresses by Raman spectroscopy and instrumented sharp indentation.

#### 4:45 PM U8.8

REACTIVITY OF BORON CARBIDE WITH MULLITE AND ZIRCONIA. Hailei Zhao, Keisuke Hiragushi, Yasuo Mizota, Okayama Ceramic Research Foundation, Okayama, JAPAN.

Boron Carbide (B<sub>4</sub>C) has attracted many attentions due to its having interesting properties such as high hardness, low density and high melting point. As a reinforcement for ceramic matrix composites, it is presently considered a potential candidate in improving the fracture toughness and strength of material. However, its active reactivity with other oxides and low sinterability due to its rigid covalent bonds and corresponding low ions diffusion mobility have restricted its wide application in practice. And up to now, there have been a limit number of reports concerning the reactivity of B<sub>4</sub>C with other inorganic materials. In present work the reactivity of B<sub>4</sub>C with mullite and ZrO<sub>2</sub> at different temperatures and under different atmospheres were investigated. The results indicate that B<sub>4</sub>C can coexist stably with mullite under Ar atmosphere below 1400°C, above which some reaction will occur with the generation of Al<sub>2</sub>O<sub>3</sub> and Al<sub>3</sub>SiB<sub>48</sub> phases. Under reductive atmosphere, they exhibit a much higher co-existing temperature of 1600°C. As to ZrO<sub>2</sub>, B<sub>4</sub>C is stable with it up to 1500°C under reductive atmosphere, but easily reacts with it under Ar atmosphere even at low temperature of 1300°C. The three components of B<sub>4</sub>C, ZrO<sub>2</sub> and mullite can coexist steady up to 1600° under reductive atmosphere, indicating that the presence of mullite is favorable to the co-existence of B<sub>4</sub>C with ZrO<sub>2</sub>. The reaction mechanisms for each case are discussed respectively, based on the XRD and DTA results. Spinning coating technique was employed in this study to produce a thin coating layer on the surface of B<sub>4</sub>C particles to inhibit the reaction between B<sub>4</sub>C and other oxides.

## SESSION U9: POSTER SESSION ADVANCED COMPOSITE STRUCTURES

Thursday Evening, November 29, 2001

8:00 PM

Exhibition Hall D (Hynes)

#### U9.1

OXYGEN STORAGE CAPACITY AND HIGH TEMPERATURE STABILITY OF COMPOSITE CERIA-ZIRCONIA FOR CATALYST PREPARATION. Zhenhua Wang, Jiexiao Jia, Shixin Lu, Longmei Zhao, Yue Long, NFM Ltd., Shanghai, CHINA.

A series of composite ceria-zirconia and lanthana-ceria-zirconia were prepared by special process and aged under air at 600°C, 900°C and 1100°C for 12 hr. The samples before and after aging were characterized by BET, XRD and oxygen storage capacity (OSC) measurement, crystal lattice parameters measurement, as well as its light-off temperature measurement for the conversion of CO, C<sub>3</sub>H<sub>6</sub> and NO<sub>x</sub>. Phase purity of the lanthana-ceria-zirconia after 1100°C aging is still high. Precious metals catalysts with ceria-zirconia showed higher OSC characteristics after aging than precious metals catalysts with ceria. With respect to light-off temperature for the conversion of CO, C<sub>3</sub>H<sub>6</sub> and NO<sub>x</sub>, the ceria-zirconia catalysts have been shown to be lower than the ceria catalyst. Keywords: catalyst, ceria, zirconia, composite.

#### U9.2

SOLIDIFICATION HISTORY IN AlZnMg ALLOY, TO BE APPLIED AS SACRIFICIAL ANODES. S. Valdez, J.A. Juarez Islas, Instituto de Investigaciones en Materiales (IIM)-UNAM DF, MEXICO; J. Genesca, Fac. De Qca. Depto. De Metalurgia-UNAM DF, MEXICO.

In the majority of commercial Al alloys, solidification takes place by the formation of primary solid solution ( $\alpha$ -Al), followed by secondary eutectic and particles in interdendritic regions. The solidification curve is the most important characteristics in solidification processing. The solidification sequence in the AlMgZn alloy, was observed using cooling curves. The study of AlMgZn alloy is due to its use as sacrificial anodes. Nowadays, AlZn alloys with In and Hg additions, have worldwide use in cathodic protection due to its high electrochemical efficiency. However, this encouraging results clash with the increased sensitivity to environmental protection. In order to promote the use of sacrificial anodes free of In and Hg, the AlZnMg system has been proposed. This work present results on the solidification history of several AlZnMg alloys with a chemical composition close to Al-5.3at%Zn-5.8at%Mg, in order to promote and uniform dendritic structure in as-cast condition and the presence of intermetallics of the  $\gamma$ -type. Results of solidification history, microstructure and electrochemical efficiency of this new Al-sacrificial anode were discussed, with a special attention to the good correlation between sequence solidification and microstructure with the anodic efficiency.

#### U9.3

OPTIMIZATION OF THE IN-SITU Al-Si BASE FUNCTIONALLY GRADIENT MATERIAL FABRICATED BY CENTRIFUGAL CASTING. Yoshihiro Oya-Seimiya, Tetsumori Shinoda, Meisei Univ, Advance Materials R&D Center, Tokyo, Yoshimi Watanabe, Shinshu Univ., Ueda, JAPAN.

The fabricating conditions for the in-situ Al-Si base composite by the centrifugal casting method have been examined. Light Si particles precipitated concentrate on the inner side of the cylinder composite wall, and more strengthened the inner than the outer side of the wall. Synthetically, the 25mol%Si composite is recommended for the application like, for instance, the engine liner.

#### U9.4

NICALON/C AND NICALON/SiC COMPOSITES WITH ALUMINUM OXIDE INTERPHASE. J. Nable, M. Gulbinska, S.L. Suib, F.S. Galasso, Univ of Connecticut, Dept of Chemistry, Storrs, CT; M.A. Kmetz, Pratt & Whitney, East Hartford, CT.

Thin coatings containing aluminum oxide were deposited on Nicalon fibers using metal-organic chemical vapor deposition (MOCVD) methods. The protective aluminum oxide coatings were applied on carbon coated silicon carbide fibers prior to chemical vapor infiltration (CVI) with silicon carbide matrix. Tensile strength measurements of prepared Nicalon/C and Nicalon/SiC composites were carried out. The effects of process temperature and the MOCVD aluminum oxide precursor on the degree of fiber degradation were studied.

#### U9.5

A NOVEL POLYAMIDE 12/Al-Cu-Fe QUASICRYSTAL COMPOSITE. Yuejian Liu, Iowa State Univ, Dept of MS&E, Ames, IA; Paul D. Bloom, Valerie V. Sheares, Iowa State Univ, Dept of

Chemistry, Ames, IA; Joshua U. Otaigbe, Iowa State Univ, Dept of Materials Science and Engineering, Ames, IA.

The tribological and mechanical properties of a novel polyamide 12/Al-Cu-Fe quasicrystal composite were systematically studied to accelerate efforts to develop a useful, melt-processable, and wear-resistant polymer composite. The wear and friction properties were characterized using a pin-on-disk configuration and the static and dynamic mechanical properties were investigated using dynamical mechanical analyzer, tensile tester, and an impact tester. Further, the melt processability of the composite was studied using a Haake torque rheometer and a dynamic rotational rheometer. The results suggest that polyamide 12/Al-Cu-Fe quasicrystal composite can be melt-processed into a wear-resistant material with enhanced mechanical properties for applications where combinations of wear resistance and good mechanical properties are required. The static mechanical properties of the composite were found to be consistent with the Halpin-Tsai equation and agreement was observed between the measured viscoelastic properties and theoretical predictions of Burgers' and Eilers' models.

**U9.6**  
EFFECTS OF SHEET ELECTRON BEAM IRRADIATION ON TENSILE STRENGTH OF CARBON FIBER. Akihiro Mizutani, Kazuya Oguri, Akira Tonegawa, Keisuke Satho, Osamu Izumi, Yoshitake Nishi, Tokai Univ, Dept of Matls Sci, Kanagawa JAPAN.

Using sheet electron beam (EB) irradiation, reinforcement for carbon fiber was succeeded. The carbon fiber was cut into pieces 50 mm in length. The sheet electron beam irradiation was homogeneously performed using an electron-curtain processor the acceleration potential and the irradiating current densities were 170 kV and  $0.89 \times 10^{-2}$  mA/cm<sup>2</sup>, respectively. The sheet electron beam irradiation treatment was applied intermittently. The conveyer speed was 10 m/min. Irradiation time was kept constant at 0.23 s in order to control the temperature in each of the samples. The temperature of the sample was below 323 K just after the irradiation. The irradiation dose was controlled by the integrated irradiation time in each of the samples. Here, the total amount of absorbed dose value was converted by the absorbed dose of the distillation water. Although the EB generation was in vacuum, the irradiated specimen was kept under protective nitrogen at atmospheric pressure in the apparatus. Namely, specimen was irradiated by electron beam through the titanium thin film window attached to vacuum chamber. The distance between sample and window is 35 mm. The oxygen concentration was less than 400 ppm in this atmosphere. To evaluate tensile strength on fracture, a tensile test was performed. The stress rate was 0.3 N/s. Since the slope ( $d\sigma/dimpulsion$ ) of stress-strain curve was constant without small strain, the strain rate was approximately constant. The EB treatment increased the fracture stress of fracture at different fracture probabilities (P). The EB treatment enhanced Weibull modulus and also enhanced design tensile strength when the fracture probability (P) is  $10^{-8}$  for aircraft materials. Using electron spin resonance (ESR) spectrometer at low temperature, density of dangling bonds was precisely obtained by dangling bond signals in 10 GPa class carbon fibers.

**U9.7**  
ANHYDRIDE/EPOXY FUNCTIONALIZED BLENDS: MECHANICAL, RHEOLOGICAL AND THERMAL PROPERTIES. Goknur Bayram, Ulku Yilmazer, Middle East Technical University, Department of Chemical Engineering, Ankara, TURKEY.

Blends of styrene maleic anhydride (SMAH) and polyethylene-methyl acrylate-glycidyl methacrylate (E-MA-GMA) were produced in a twin screw extruder. Extruded blends were characterized in terms of mechanical, rheological and thermal properties. E-MA-GMA concentration was varied from 0% to 50%. Thermal properties were not significantly affected by the change in epoxy concentration. As epoxy concentration of E-MA-GMA increases, tensile strength and modulus of elasticity decrease, but percent strain at break increases. Rheological properties such as storage modulus, loss modulus and complex viscosity exhibited maxima at 25% E-MA-GMA content. This may be due to chain extension / branching reactions occur in the system.

SESSION U10: CARBON NANOTUBES, CARBON FIBERS, AND COMPOSITES

Chair: Ali Sayir  
Friday Morning, November 30, 2001  
Liberty (Sheraton)

**8:30 AM U10.1**  
COMPOSITES OF CARBON FILAMENTS MADE FROM

METHANE. Xiaoping Shui, Xuli Fu, Martin Segiet, D.D.L. Chung, Composite Materials Research Laboratory, University at Buffalo, The State University of New York, Buffalo, NY.

Polymer-matrix and cement-matrix structural composites containing discontinuous carbon filaments (diameter = 0.1  $\mu$ m) that were made from methane were developed for structural and electromagnetic functions. The composites were particularly attractive for electromagnetic shielding and radio wave reflection, due to the skin effect and the small diameter of the filaments. Coating the filaments with nickel by electroplating further enhanced the electromagnetic performance. However, the composites were not attractive for structural functions other than vibration damping, due to the large amount of interface between the filaments and the matrix. An effective configuration for the damping function involved using the filaments as an additive between the laminae of continuous conventional carbon fibers in a polymer-matrix structural composite.

**8:45 AM U10.2**  
ELECTROSTATIC DEPOSITION OF ALIGNED NANOSCOPIC BaCO<sub>3</sub>, BaTiO<sub>3</sub> AND PZT GRAINS FROM ORGANOMETALLIC COMPOUNDS. Yu Wang, Santiago Serrano and Jorge J. Santiago-Aviles, University of Pennsylvania, Department of Electrical Engineering, Philadelphia, PA.

We have utilized the technique of electrostatic deposition/ electrospinning to deposit organometallic ceramic precursor fibers. From these micro diameter fibers, nanoscopic ceramic grains are generated after heat treatment in the air. Alkoxides precursors for the formation of BaCO<sub>3</sub>, BaTiO<sub>3</sub> and PZT were utilized after mixing to achieve near stoichiometry. The precursor microfibers were sintered/fired at different typical temperatures indicated by the thermal analysis on the starting solutions. Optical microscope, X-ray diffraction, micro Raman scattering and Auger spectroscopy were used to characterize the sintered fibers. The results indicate that nano-grained BaCO<sub>3</sub>, BaTiO<sub>3</sub> and PZT ceramics can be obtained from organometallic compounds using electrospinning. Keywords: BaCO<sub>3</sub>, BaTiO<sub>3</sub>, PZT, microfibers, metalloorganic compounds, electrospinning

**9:00 AM U10.3**  
ACOUSTIC IMAGING OF MICROSTRUCTURES OF CARBON FIBER-REINFORCED POLYMER COMPOSITE LAMINATES. Songping Liu, Vadim M. Levin, The Center for NDT&E for Composites, Beijing Aeronautical Manufacturing Technology Research Institute, Beijing, CHINA.

Carbon fiber-reinforced polymer composite laminates, which decide the bulk properties of the composite structures, are the fundamental structure cells in industrial applications. Usually the investigation, design and application are based on such assumption that the constituents of the composites are mixed up uniformly, i.e., homogeneous inside the composites. However, the real experiences are not always in the desired situation. For examples, an unconscious mistake included during the manufacturing process or preparations of the laminates, some defects induced, will make the composites tend to be inhomogeneous. It is very important to make the microstructures of inside composites to be visualized, because the microstructures are very relative to the bulk properties of the composite laminates. Optical microscopy and scanning electronic microscopy are two well-known methods to be used to observe the structures of inside composites. Both methods are of destructive method, and only a very limited cross-section or surface information about the structures of the composites can be obtained. Our update investigations have shown that the inside microstructures of carbon fiber-reinforced polymer composite laminates can be visualized by means of acoustic imaging techniques. This paper will be focused on representation of investigation of inside microstructures of different carbon fiber-reinforced polymer composite laminates by means of acoustic imaging techniques. The frequency to be used is up to 50MHz. The composite laminates to be investigated include unidirectional carbon fiber-reinforced polymer composite laminates, bi-directional carbon fiber-reinforced polymer composite laminates, carbon fiber woven composite laminates and carbon fiber-reinforced polymer composite laminates with another fiber threads. Very useful information about inside structures of the composites can be visualized not only in the cross-section of the laminates, but also in the different plan-section of the laminates in the directions of depth by T-scan and three-dimension (3D) B-scan imaging techniques. Typical results have been represented in this article.

**9:15 AM U10.4**  
DESIGN OF FUNCTIONALLY GRADED FIBER REINFORCED STRUCTURES FOR MAXIMUM STRENGTH AND STIFFNESS. Robert Lipton, Louisiana State Univ, Dept of Mathematics, Baton Rouge, LA; Ani Velo, Army Research Labs, Aberdeen, MD.

The control of stress concentrations inside load bearing structural components is of central importance in the design against failure. In this work a method for the design of functionally graded composite materials (FGMs) with optimal structural properties subject to stress constraints is developed. Fiber reinforced materials are considered and a robust numerical method is provided for finding optimal fiber configurations for maximum rigidity subject to constraints on the stress.