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13. ABSTRACT (Maximum 200 words) Some final studies during this period were carried out in collaboration with Wright-Patterson AFB. They were based on some benzoxazole copolymers of good thermo-oxidative stability and solubility in tetrahydrofuran. The hydroxypolybenzoxazoles employed were reacted with an isocyanatosilane coupling agent and the hybrid consequently with in-situ produced silica. The resulting hybrid films containing one third silica were transparent. The mechanical properties of the hybrid materials were highly dependent on the nature of the organic polymers. In general, the tensile modulus of the hybrid materials increased with addition of silica but, as in the case of the polyamides, the elongation at break decreased at higher silica contents. Future work will focus on new polymers, additional physical properties, and new processing techniques. The new polymers will include benzoxazole polymers being prepared at Wright-Patterson AFB with structural changes to improve tractibility, and alternative functional groups to improve bonding to ceramic phases. Examples of new physical properties of importance are thermal expansion coefficients and impact strengths. New processing techniques to be sought include methods for densifying ceramers prepared from glassy polymers such as poly(methyl methacrylate).				
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and preparing organic-inorganic aerogels by supercritically drying some of the hybrid composites from the gel state.

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Institution: University of **nnati**
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A. Publications

Polyimide-Silica Hybrid Materials Having Interfacial Bonding Through Use of a Sol-Gel Technique, S. Wang, Z. Ahmad, and J. E. Mark, Macromol. Sci., Macromol. Reports, A31, 411 (1994).

Preparation and Properties of Poly(phenyleneterephthalamide)-Silica Ceramers with Interphase Bonding from Aminophenyltrimethoxysilane, Z. Ahmad, S. Wang, and J. E. Mark, in "Better Ceramics Through Chemistry, Part VI", ed. by C. Sanchez, C. J. Brinker, M. L. Mecartney, and A. Cheetham, Materials Research Society, Pittsburgh, PA, 1994.

Polyimide-Silica Hybrid Materials Modified by Incorporation of an Organically-Substituted Alkoxysilane, S. Wang, Z. Ahmad, and J. E. Mark, Chem. Mater., 6, 000 (1994).

Inorganic-Organic Composites, Including Some Examples Involving Polyamides and Polyimides, J. E. Mark, S. Wang, and Z. Ahmad, submitted to the Akron-IUPAC issue of Makromol. Chemie.

Preparation and Properties of High-Clarity Polyamide-Silica Hybrid Materials, J. E. Mark, S. Wang, and Z. Ahmad, submitted to "Hybrid Organic-Inorganic Composites", Ed. by J. E. Mark, P. A. Bianconi, and C. Y-C Lee, American Chemical Society, Washington.

Preparation and Mechanical Properties of Polybenzoxazoles-Silica Hybrid Materials, J. P. Chen, Z. Ahmad, S. Wang, J. E. Mark, and F. E. Arnold submitted to "Hybrid Organic-Inorganic Composites", Ed. by J. E. Mark, P. A. Bianconi, and C. Y-C Lee, American Chemical Society, Washington.

JUL 1994

B. Researchers

Faculty: 1 (Including the Principal Investigator)

Postdocs: 1

Graduate Students: 3

Visiting Scientists: 1

C. Professional Honors, J. E. Mark

Special Research Fellow, National Institutes of Health

Massachusetts Institute of Technology (Fall Term of 1975)

Stanford University (Spring Term of 1976)

Best Paper and Honorable Mention Awards, ACS Rubber Division (1978, '75, '77)

Cincinnati Chemist of the Year (1984)

Distinguished Scientist Award, Technical Societies Council of Cincinnati (1985)

Rieveschl Award for Distinguished Scientific Research, University of Cincinnati, (1986)

George Stafford Whitby Award, ACS Rubber Division (1991)

ACS Award in Applied Polymer Science (1994)

Fellow of American Physical Society, New York Academy of Sciences, Graduate School of the University of Cincinnati, and American Association for the Advancement of Science

PROGRESS REPORT

New hybrid materials were synthesized by incorporating silica in poly(trimethylhexamethylene terephthalamide) using the sol-gel process, and were found to have high transparency and flexibility. They showed an increase in tensile strength at the yield point of up to 25 %, but the elongation at rupture was found to decrease sharply upon the addition of the silica. Water uptake under saturated conditions was reduced from 8 wt % for the pure polymer, to approximately 3 wt % for the hybrid material containing 15 % silica. Since there is nearly a 20 % drop in the value of the yield stress reported for the pure polymer upon long storage in water, the present class of ceramers could be particularly useful in polyamide applications requiring dimensional stability under high-humidity conditions.

In another study on polyamides, poly(phenyleneterephthalamide) chains having carbonyl chloride end groups were prepared by reacting a mixture of *m*- and *p*-phenylene diamines with terephthaloyl chloride, and were then end capped with aminophenyl-trimethoxysilane. The polymer thus prepared was used to synthesize a hybrid material in which it was chemically bonded to the silica network produced *in-situ* by hydrolyzing tetramethoxysilane. Films prepared from this hybrid material were yellow but transparent, and quite tough. The transparency of the films and their mechanical strength were considerably improved relative to the corresponding systems in which the inorganic network was not bonded to the organic phase. A systematic increase in the tensile modulus and hardness with increase in silica content, and a decrease in water absorption were observed. These transparent ceramers were found to withstand tensile stresses the order of 175 MPa and had thermal decomposition temperatures around 460 - 475 °C, and could thus be very useful in engineering applications at high temperatures.

Similar experiments were carried out with polyimides as the organic phase. In this way, hybrid materials having a bonded polyimide-active silica structure were prepared using the *in-situ* polymerization of tetramethoxysilane and several other silicon alkoxides which had been suitably modified so as to act as bonding agents between the ceramic and polymer phases. The reactions were carried out in the polyimide precursor, polyamic acid, which was then cyclized at high temperatures. The bonding between the polymer and the silica phases was achieved using aminophenyltrimethoxysilane (APT MOS), (aminoethylaminomethyl)phenethyltrimethoxysilane, and 1-trimethoxysilyl-2-(*m,p*-chloromethyl)phenyl-ethane. These bonding agents can undergo hydrolysis and polycondensation along with the

tetramethoxysilane to form silica or polymeric silicates, while the groups at their other ends (such as the amino and chloro groups) provide good bonding with the polyimide. These specific aromatic compounds were chosen for their high thermal stability, which is comparable to that of the polyimide. Adding small amount of these bonding agents were found to improve the moduli and strengths of these hybrid materials, with the aminophenyltrimethoxysilane giving the largest improvements. Additional experiments showed that relatively small amounts of APTMOS significantly improve the modulus and strength of these hybrid materials, and their transparency was found to increase with increase in amount of APTMOS. The thermal decomposition temperatures they exhibited were approximately 570 °C, and their residual weights after exposure to 800 °C were directly proportional to their inorganic contents.

Some final studies during this period were carried out in collaboration with Wright-Patterson Air Force Base. They were based on some benzoxazole copolymers of good thermo-oxidative stability and solubility in tetrahydrofuran. The hydroxypolybenzoxazoles employed were reacted with an isocyanatosilane coupling agent and the hybrid consequently with in-situ produced silica. The resulting hybrid films containing one third silica were transparent. The mechanical properties of the hybrid materials were highly dependent on the nature of the organic polymers. In general, the tensile modulus of the hybrid materials increased with addition of silica but, as in the case of the polyamides, the elongation at break decreased at higher silica contents.

Future work will focus on new polymers, additional physical properties, and new processing techniques. The new polymers will include benzoxazole polymers being prepared at Wright-Patterson Air Force Base with structural changes to improve tractibility, and alternative functional groups to improve bonding to ceramic phases. Examples of new physical propertyies of importance are thermal expansion coefficients and impact strengths. New processing techniques to be sought include methods for densifying ceramers prepared from glassy polymers such as poly(methyl methacrylate), and preparing organic-inorganic aerogels by supercritically drying some of the hybrid composites from the gel state.

7/12/94