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13. ABSTRACT (Maximum 200 words) The research projects covered in this grant developed techniques for improving the properties of three classes of high-temperature polymers of particular interest to the US Air Force, specifically some polyamides, polyimides, and polybenzoxazoles and polybenzobisthiazoles. Mechanical properties were of primary interest, and were improved by precipitating ceramic-type fillers such as silica and titania into them <i>in-situ</i> , using sol-gel hydrolysis and condensation reactions. There was also an important bonus in forming hybrid organic-inorganic composites obtained in this way, specifically decreased water absorption. Such suppression of water absorption is important for maintaining mechanical properties such as dimensional stability, and for control of some dielectric properties as well. The improvements obtained were found to be greatest when a bonding agent was used to improve the interfacial bonding between the organic polymer phases and the inorganic ceramic phases. These bonding agents also have the advantage of improving the transparencies of these materials.				
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Institution: University of Cincinnati

Grant: F49620-92-J-0322

A. Publications (Cumulative)

1. A Polyamide-Silica Composite Prepared by the Sol-Gel Process, S. Wang, Z. Ahmad, and J. E. Mark, Polym. Bulletin, **31**, 323 (1993).
2. Biomimetic, Hybrid, and In-Situ Composites, J. E. Mark and P. D. Calvert, Mats. Sci. Eng. C: Biomim. Mats., Sens., Syst., **1**, 159 (1994).
3. 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).
4. Polyimide-Silica Hybrid Materials Modified by Incorporation of an Organically-Substituted Alkoxysilane, S. Wang, Z. Ahmad, and J. E. Mark, Chem. Mater., **6**, 943 (1994).
5. 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.
6. 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, C. Y-C Lee, and P. A. Bianconi, American Chemical Society, Washington.
7. 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, C. Y-C Lee, and P. A. Bianconi, American Chemical Society, Washington.
8. Inorganic-Organic Composites Containing Mixed Oxides, J. E. Mark and J. Wen, Macromol. Symp., **93**, 89 (1995).
9. Inorganic-Organic Composites, Including Some Examples Involving Polyamides and Polyimides, J. E. Mark, S. Wang, and Z. Ahmad, Macromol. Symp., **98**, 731 (1995).

10. Some Organic-Inorganic Nanocomposites, J. E. Mark, in "Diversity into the Next Century", ed. by R. J. Martinez, H. Arris, J. A. Emerson, and G. Pike, SAMPE Publications, Volume 27, Covina, CA, 1995.
11. Polymer-Silica Hybrid Materials Prepared from Some Functionalized Polybenzoxazoles and Polybenzobisthiazoles, J. Premachandra, C. Kumudinie, W. Zhao, J. E. Mark, T. D. Dang, J. P. Chen, and F. E. Arnold, in press for special Klein issue of J. Sol-Gel Sci. Technol.
12. Hybrid Organic-Inorganic Composites Containing Mixed-Oxide Ceramics and High-Temperature Polymers, J. E. Mark, in press for special Hanoi issue of Macromol. Chem. Phys.
13. The Sol-Gel Route to Inorganic-Organic Composites, J. E. Mark, Heterogeneous Chemistry Reviews, **3**, 000 (1996).
14. Ceramic-Reinforced Polymers and Polymer-Modified Ceramics, J. E. Mark, in press for special "POLYCHAR-4" issue of Polym. Eng. Sci.
15. The Use of Functionalized Polybenzoxazoles and Polybenzobisthiazoles in Polymer-Silica Hybrid Materials, J. E. Mark, J. Premachandra, C. Kumudinie, W. Zhao, T. D. Dang, J. P. Chen, and F. E. Arnold, in press for MRS Proceedings Volume, "Better Ceramics Through Chemistry VII. Organic/Inorganic Hybrid Materials", Materials Research Society, Pittsburgh.
16. Chemically-Bonded Silica-Polymer Composites from Linear and Branched Polyamides in a Sol-Gel Process, Z. Ahmad, M. I. Sarwar, and J. E. Mark, submitted to J. Mats. Chem.
17. Preparation and Properties of Hybrid Organic-Inorganic Composites Prepared from Poly(phenyleneterephthalamide) and Titania, Z. Ahmad, M. I. Sarwar, S. Wang, and J. E. Mark, submitted to Polymer.

The contents of these papers are described, using these reference numbers, in Section E.

In addition to publications in refereed journals and books, as cited above, the results are typically presented at one or more of the following international meetings:

American Chemical Society (Polymer Division and Polymeric Materials Division)

American Physical Society (Division of High-Polymer Physics)

Materials Research Society

SAMPE (Society for the Advancement of Material and Process Engineering)

B. Researchers

Faculty

J. E. Mark (Principal Investigator)

Visiting Scientists

M. A. Sharaf

A. Ahmad

Graduate Students

C. Kumudinie

A. B. R. Mayer

J. Premachandra

Z. Pu

Q. Yuan

W. Zhao

C. Inventions

None

D. 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, American Chemical Society

Rubber Division (1978, '75, '77)

Cincinnati Chemist of the Year, American Chemical Society (1984)

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

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

George Stafford Whitby Award, American Chemical Society Rubber
Division (1991)

American Chemical Society 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
Hans H. Jaffe Chemistry Faculty Award for Excellence, University of
Cincinnati, 1995
McMicken Dean's Award for Distinguished Scholarship, University of
Cincinnati, 1996

E. Report on Research Accomplishments

In two studies 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.^{1,5} 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.^{1,5} 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.

New hybrid materials were also synthesized by incorporating silica in poly(trimethylhexamethylene terephthalamide) using the sol-gel process, and were found to have high transparency and flexibility.⁶ 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 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.

A related study focused on chemically-bonded silica-polymer composites from linear and branched polyamides.¹⁶ In it, new types of polymer-silica composite based on aramids of either linear or non-linear structure were successfully prepared by the sol-gel process. The linear polyamide chains were prepared by the reaction of a mixture of *m*-phenylene and *p*-phenylene diamines and terephthaloyl chloride in dimethylacetamide. The non-linear (branched) polyamide chains (having an increased number of reactive ends) were synthesized using 1,3,5-benzenetricarbonyl chloride and terephthaloyl chloride so as to increase the weight-average functionality of the monomer. A slight excess of acid chloride was added in both cases to produce amide chains with carbonyl chloride end groups, which permitted the chains to be end-capped with aminophenyl-trimethoxysilane. Addition of tetramethoxysilane to a solution of the polymer, and its subsequent hydrolysis and condensation produced a silica network phase chemically bonded to the aramid chains. Films thus produced were yellow, and transparent for concentrations of silica of up to 25 wt %. Tensile strengths gradually increased with increase in silica up to this same concentration, but then decreased significantly. Overall values of the strength were found to be smaller for the non-linear aramid chains, relative to those of the linear, possibly because of the branching interfering with interchain interactions.¹⁶ Nonetheless, the increases in the tensile strength with increase in the inorganic network phase were larger for the non-linear polymer, consistent with the goal of increasing the bonding between the organic and inorganic phases by increasing the number of aminophenyltrimethoxysilane chain ends. Increasing these strengths to values greater than those for the linear chains can probably be achieved by having the branched regions only near the ends of the chains. Since these transparent ceramers were found to withstand tensile stresses the order of 175 MPa and had thermal decomposition temperature around 460 - 475 °C, they could be very useful as matrices for fiber-reinforced composites.

The same sol-gel process was used to prepare poly(phenylene-terephthalamide)-based composites containing in-situ generated titania.¹⁷ As before, the polymer was synthesized by reacting a mixture of *p*- and *m*-phenylene diamines with terephthaloyl chloride in dimethylacetamide, using a stoichiometry yielding chains with carbonyl chloride end groups. These chain ends were then replaced with methoxy groups using aminophenyl-

trimethoxysilane, and a titania network generated and chemically bonded to the polymer matrix by hydrolyzing appropriate proportions of tetrapropylorthotitanate and water. The resulting composite films had amounts of titania ranging from 2.5 to 40 wt %, and were characterized with regard to their mechanical and thermal properties. The films containing relatively small amounts of titania were transparent and tough, and able to withstand tensile strengths the order of 193 MPa. Thermal decomposition temperatures were in the range 350 – 450 °C, and the weights of the samples remaining after heating to 800 °C were found to be roughly proportional to the titania contents.¹⁷ Water absorption of the films consisting of pure Aramid was rather high (12.8 wt %), but decreased with increased amounts of titania. Dynamic mechanical thermal analysis showed a systematic increase in the glass transition temperature with increase in titania content. Increased amounts of titania also caused the tan δ peaks to shift to higher temperatures and to become broader and weaker, indicating the extent to which the mobility of the polymer chains was diminished by the titania phase.

Similar experiments were carried out with polyimides as the organic phase.^{3,4} 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)phenylethane. 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 was found to improve the moduli and strengths of these hybrid materials, with the aminophenyltrimethoxysilane giving the largest improvements.^{3,4} Additional experiments showed that relatively small amounts of APT MOS significantly

improve the moduli and strengths, and the transparencies were 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.

Additional studies during this period were carried out in collaboration with Wright-Patterson Air Force Base (WPAFB).^{7,11,15} 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.⁷ 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. Very recent work on new WPAFB polymers includes new polymers such as some benzoxazoles prepared with structural changes to improve tractibility, and alternative functional groups to improve bonding to ceramic phases.^{11,15}

Some of these results are also described in several recent review articles.^{2,8-10,12-14}

New processing techniques were also explored, including supercritically drying some of the hybrid composites from the gel state, to obtain organic-inorganic aerogels. It was hoped that such aerogels would have greatly reduced brittleness relative to the usual totally-inorganic, ceramic-type materials. Such experiments are being pursued in the present grant, F49620-96-1-0052.

9/16/96