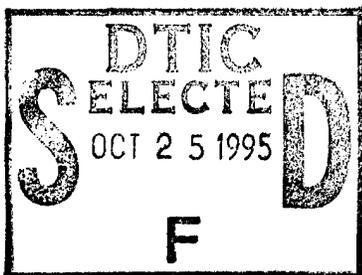


OFFICE OF NAVAL RESEARCH



GRANT Number N00014-92-J-1047

R & T Code 413m008

Cognizant Scientific Officer
Dr. Kenneth Wynne

FINAL REPORT

"Polymerization of Poly(p-Phenylene Sulfide) from Cyclic Precursor"

by

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October 18, 1995

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**Final Report for the Grant
under Contract Number N00014-92-J-1047**

Following are the description based on the unified ONR Final Report Format.

The objective, approach and scientific conclusions derived from the research effort

The objective of this project is to understand the effect of carbon fibers and other high performance reinforcing fibers on the structure of high performance resins such as poly(phenylene sulfide) and epoxies. Of particular interest is the molecular structure/property relationships. Our approach for this project utilized molecular vibrational technique for the understanding of the structure of polymers. Significant scientific conclusions are that we have investigated detailed structural aspects of a cyclic poly(phenylene sulfide) for its crystal structure and polymerization characteristics. As the interest in cyclic compounds as precursors for polymers became strong in recent several years, the conclusion obtained in this study will help evaluate feasibility of using cyclic poly(phenylene sulfide) as potential raw materials for advanced composite materials.

We have also studied the state of cure of epoxy resin around an organic fiber using infrared microscopy. With a site specific information on curing, we were able to map the state of cure around a single reinforcing filament, thus enabling the study of the fiber surface on the curing reaction of the matric resin.

A list of all undergraduate, graduate and post-doctoral associates funded through the grant

Graduate students

- Robert Shick, Ph.D. student (full support)
- Dean Zimmermann, Ph.D. student (full support, after R. Shick's graduation)
- Angela M. Mavric, M.S. student (full support)
- Marcos Labronici, Ph.D. student (partial support)

A list of all the publications, presentations, patents, and reports associated with the grant

A. *Published*

1. "Theoretical Development for Depth Profiling of Stratified Layers Using Variable-angle ATR," R. Shick, J.L. Koenig and H. Ishida, *Appl. Spectrosc.*, **47**., 1237 (1993).
2. "The Study of Fiber-Matrix Interactions Via FT-IR Microscopy and NMR Imaging," A. Maverich, F. Fondeaur, H. Ishida, J.L. Koenig, and H.D. Wagner, *J. Adhesion*., **41**., 649 (1993).
3. "Application of Optical Theory to Quantitative Surface FT-IR with Emphasis on Molecular Depth Profiling," H. Ishida, in "Comemoration of the Sixtieth Anniversary of

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Professor T. Takenaka," *Bull. Inst. Chem. Res.*, Kyoto University, Kyoto, **71**, 198 (1993).

4. "Elastic and Viscoelastic Behavior of Composites," R. Shick and H. Ishida, in "*Characterization of Composite Materials*," H. Ishida, Ed., Butterworth-Heinemann, London (1994) p.148.
5. "Toughening Composites by Fiber Coating: A Review," M. Labronici and H. Ishida, *Comp. Interfaces*, **2**, 199 (1994).
6. "The Study of Fiber-Matrix Interactions via FT-IR Microscopy and NMR Imaging," A. Mavrich, F. Fondeur, H. Ishida, J.L. Koenig and H.D. Wagner, *J. Adhesion*, **46**, 91 (1994).
7. "Infrared Mapping of Surface-Modified Kevlar Fiber-Reinforced Epoxy Systems," A.M. Mavrich, H. Ishida and J.L. Koenig, *Appl. Spectrosc.*, **49**, 149 (1995).

B. Papers In Press

8. "Infrared Spectroscopic Analysis of Poly(p-phenylene sulfide)," D.A. Zimmerman, J.L. Koenig and H. Ishida, *Spectrochim. Acta* (in press).

C. Accepted Papers

9. "Depth Profiling of Stratified Layers using Variable Angle ATR," R.A. Shick, J.L. Koenig and H. Ishida, *Appl. Spectrosc.*, (accepted).

D. Submitted Papers.

10. "Polymerization of Poly(p-Phenylene Sulfide) from a Cyclic Precursor," D.A. Zimmerman, J.L. Koenig and H. Ishida, *Polymer*, (submitted).
11. "Effect of the Degree of Cure of the Matrix Resin and Fiber Content of the Composite on Mechanical and Dynamic Mechanical Properties of Carbon Fiber Reinforced PMR-15 Polyimide," M. Labronici and H. Ishida, *Polymer Composites* (submitted).

Presentation

1. "Interphases in Advanced Composite Materials," Fourth SPSJ International Polymer Conference (IPC 92), Yokohama, Japan, November (1992).
2. "Morphology Control of Polypropylene/Polystyrene Immiscible Blend by Ultra-small Particles," International Conference on Interphases, Williamsburg, Virginia, February (1993).
3. "The Role of Interphase in Mesophase Composites," Symposium on Mesophase Composites, Kyoto University, Kyoto, Japan, June (1993).
4. "Effect of Surface Treatment on the Interphase Structure of Advanced Composites," International Symposium on Advanced Materials, Osaka Municipal Research Institute, Osaka, Japan, December (1993).

5. "Dynamic Mechanical Analysis of Carbon Fiber Reinforced PMR-15 Polyimides with Silicone Innerlayers," International SAMPE Symposium, Chiba, Japan, December (1993).
6. "Application of Optical Theory to Thin Film Analyses," Symposium on Surface Characterization of Adsorption and Interfacial Reactions, Kona, Hawaii, January (1994).
7. "Application of Silane-treated Fillers to the Compatibilization of Immiscible Polymer Blends," 28th Silicone Symposium, Albany, New York, March (1994).
8. "Structure and Thermodynamics of Transcrystal Formation," The Fifth International Conference on Composite Interfaces, Gothenburg, Sweden, June (1994).

A list of transitions that resulted from your research under the ONR grant

None

Highlight three papers and significance of the paper

1. *"Theoretical Development for Depth Profiling of Stratified Layers Using Variable-angle ATR," R. Shick, J.L. Koenig and H. Ishida, Appl. Spectrosc., 47,, 1237 (1993).*

Inverse Laplace transform was used to depth profile concentration gradient of materials near a substrate surface. The significance of the paper is that for the first time the depth resolution of less than 100 nm has been achieved and information from the each slice of such depth resolution was obtained.

2. *"Infrared Mapping of Surface-Modified Kevlar Fiber-Reinforced Epoxy Systems," A.M. Mavrich, H. Ishida and J.L. Koenig, Appl. Spectrosc., 49, 149 (1995).*

Infrared microscopy was used to obtain molecular structural information on the curing of epoxy resin near the reinforcing fiber was obtained. For the first time, the mapping of the degree of cure of an epoxy resin was done around a single filament of an ultra-high modulus organic fiber.

3. *"Polymerization of Poly(p-Phenylene Sulfide) from a Cyclic Precursor," D.A. Zimmerman, J.L. Koenig and H. Ishida, Polymer, (submitted).*

Detailed study of the possibility of polymerization of a cyclic poly(phenylene sulfide) compound was done. With recent strong interest in using cyclized precursors for polymerization without forming byproducts the demonstrated ability to polymerize the compound lead the way toward future development of high performance carbon fiber reinforced composites.

Award

Jack L. Koenig has been honored as honorary member of the Society of Applied Spectroscopy.

Hatsuo Ishida has been honored as Eminent Scientist from the Institute for Chemical and Physical Research (RIKEN), Tokyo, Japan.

Hatsuo Ishida is also chosen as Editor-in-Chief of a Journal, *Composite Interfaces*. He is also chosen as Associate Editor of a journal, *Polymers and Polymer Composites*. He is also Vice President of the Society of Interface Science in Composite Materials.