

# FY 2008 Project Proposal

Project No. BROU-08

## Novel Antimicrobial Polymers

---

### Project Team:

Leader: Prof. Roy Broughton ([brougrm@auburn.edu](mailto:brougrm@auburn.edu))

Members: Prof. Maria L. Auad ([auad@auburn.edu](mailto:auad@auburn.edu)),  
Prof. S. D. Worley ([worlesd@auburn.edu](mailto:worlesd@auburn.edu))  
Prof. Tung-Shi Huang([huangtu@auburn.edu](mailto:huangtu@auburn.edu))

---

### Objective:

There is substantial demand for antimicrobial coatings, films and fibers in medical and industrial sectors. Bacterial infections are harmful to people and are responsible for expensive repainting jobs caused by fouling of structures like ships, marine construction, etc. Barrier materials and coatings are used for the protection of structures and people. Current deficiencies include lack of antimicrobial effectiveness, lack of durability, and release of the agent into the environment. Environmental concerns stimulate the search for better coatings/films/fibers having low release of the antimicrobial agents into the environment. Currently used materials will not meet the expected future environmental regulations.

In this proposal, we envision a new type of waterborne polyurethane, suitable for the above mentioned applications. The antimicrobial properties will result from incorporation of quaternary ammonium groups covalent bonded to the polymer backbone. The expected features of these polymers are a relatively high stability, and good antimicrobial properties. The work proposes the synthesis of polyurethanes, dispersal into water, formation of films, evaluation of film properties, and testing the antimicrobial performance. If successful, the results will be used as preliminary data for the preparation of a proposal for submission in a nationally competitive grant process.

---

### Relevance to The Polymer and Fiber Engineering Department Mission:

The proposal includes polymer synthesis, fabrication of polymeric film, and testing of a product in a application for which there is significant demonstrated need as well as commercial potential. All of these activities fit within the mission of the Department of Polymer and Fiber Engineering.

---

### State of the Art:

There are specific problems that are addressed in this proposal.

1) There is a consistent need for barrier materials (coatings/films/fibers) that will protect people and materials biological agents, and perhaps some toxic chemicals. These materials find application in the medical field, military, hazardous waste materials, structural applications (paints and coatings), etc. Finding hand-protection materials (elastomeric gloves) that provide protection, while at the same time allowing performance of tasks requiring dexterity and tactile sensing is a particular challenge.

2) Natural rubber latex, precipitated onto hand molds has been the material of choice for both medical worker's gloves and condoms. A growing number of people are becoming allergic to the protein surfactants used by the rubber tree to maintain the latex emulsion, and so newer synthetic elastomers are increasing in use.

3) An elastomeric film with antimicrobial and antiviral properties (and perhaps destructive of some highly reactive chemicals) would be a welcome addition to the arsenal of protective clothing. It would also be of considerable value if the film could be manufactured from a water dispersion of polymer rather than from a solution in a volatile organic solvent (VOC).

4) Elastomeric, environmental safe polyurethanes, suitable for preparing films, fibers, membranes and coatings, that do not contain a high proportion of volatile organic solvents, might be the materials of choice for such applications.

5) Due to environmental concerns, antimicrobial polymers should have agents that cannot be released into the environment. An interesting alternative to the existing systems may be to develop coatings containing polymeric antimicrobial segments which are effective, but which are not easily released into the environment. Such coatings could combine greater efficiency with lower environmental impact in applications ranging from biomedical to painting.

6) The ability to modify the properties of polyurethanes means that they can be tailored to serve in a variety of applications from elastomers, to hard, scratch-resistant coatings and paint. The tailoring of

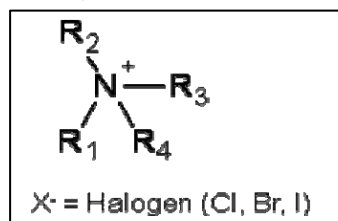
properties is simple in concept, but considerable art must be developed to produce and demonstrate the use of antimicrobial, water-dispersable polyurethanes in these applications..

The proposed work is to synthesize water-dispersable, environmentally-safe polymeric materials (polyurethanes) with biocidal surface-active group bonded to the polymer backbone. Subsequently, the polyurethane emulsion will need to be coated on a mold, or in the case of coatings, painted/sprayed on a surface. Upon drying, a strong, flexible elastomeric film is expected, but not guaranteed. Initially, the antimicrobial functionality will be a polymeric quaternary amine, which will be a part of the polyurethane structure. The quat functionality will also likely increase the water dispersability of the polymer. Subsequently, we would propose to incorporate a nitrogen heterocycle which could be converted to a halamine, which will insure a faster kill and would add activity against viruses and chemicals. The halamines have been shown to inactivate viruses, as well as some of the reactive, easily-oxidized compounds that have been used in chemical warfare.

### Significance of the proposed research: challenges

**Why Waterborne polyurethanes?** PUs have been used in many industrial applications such as: coatings biomedical applications, glass fiber sizing, textile adhesives, automotive and marine paints, films for packaging, gloves, etc. [1]. Conventional PU resin systems are diluted in volatile organic solvents (approximately 40-60% by weight). The wide property range available in PU's allows multiple uses, but there is considerable pressure from the coatings industry and environmental legislation for low organic solvent content. The use of waterborne resin systems is used to meet the increasing concern for health, safety and the environment [1-2]. Central to the utilization of polymers in aqueous media is the fact that certain polar functional groups (usually carboxylic acids or tertiary amine groups) can confer water solubility or water dispersibility to a water insoluble PU. The concentration of such functional groups in the polymer is important in determining the solubility or dispersibility in an aqueous environment. Thus, at high concentrations of quat, the polymer may be water soluble, and at low concentrations the polymer may be water dispersible. As a result, aqueous polymer systems with a wide range of different morphological and physical characteristics can be obtained, depending on the synthetic routes used for preparation. During the past years, both Dr. Broughton, and Dr. Auad's research groups have examined the synthesis and properties of solvent based PU systems [3-5].

### Why Quaternary ammonium compounds (QACs)? How does QAC destroy microorganisms?



Quaternary ammonium compounds consist of a nitrogen cation with four covalently-bound alkyl groups and a halogen counter ion (Figure 1).

Figure 1 - Chemical Structure of Quaternary ammonium compounds.

Two molecular groups are needed for QACs' activity: a cationic group and a nonpolar alkyl chain with at least 8-16 carbons [5]. These two groups are responsible for the bactericidal activity of QACs, which is based on disruption of bacterial cell membranes. This causes the cytoplasm to leak from the cell, and disrupts the cell metabolism. There is some indication that recurring quaternary groups along a polymer chain may function well, even with smaller alkyl chains attached.

Two main approaches have been developed to make antimicrobial coatings: a) a molecular biocide is simply added to a classical binder. It becomes active by migrating out of the polymer matrix, b) a biocidal compound is grafted to a polymer by a bond sensitive to hydrolysis [5-6]. In both cases, the biocidal activity depends on the liberation of the biocide in the environment, resulting in a progressive loss of the activity with time, and an environment hazard (biocides are frequently toxic). The proposed approach is a covalent attachment between the biocidal group and polymer that will not be cleaved by environmental conditions and which will show consistent antimicrobial activity with time (Figure 2).

During the past years, Dr. R. Broughton, Dr. S.D. Worley and Dr. T. S. Huang have been involved in the development of N-Hamine based protective materials. They have strong background in antimicrobial compounds, antimicrobial testing and protective materials [7-9]. Dr. Auad has been active in the synthesis and property measurement of polyurethanes.

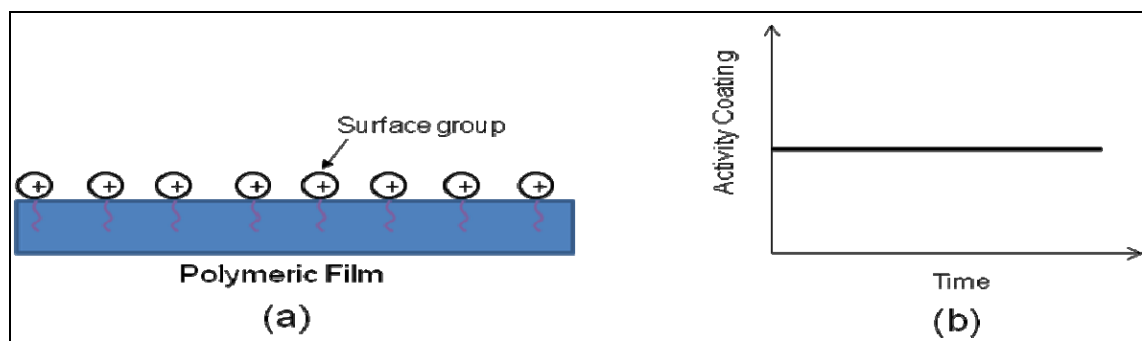


Figure 2: Functioning of the PU coatings/films (a) and the antimicrobial activity of the coating (b).

### Approach and Mid-Project Review Goals:

During the one year of this effort, we will conduct the necessary research needed to design and synthesize a new waterborne PU/antimicrobial coating. During this period we will produce at least one research grant proposal to be submitted to NSF, NIH, etc. The project will involve three tasks:

**1 - Synthesis of waterborne polyurethane.** Waterborne segmented PU consisting of soft amorphous segments and hard crystalline segments will be synthesized. The hard segments will be formed by reacting 1,4-butanediol and 4,4'-methylenebis (phenyl isocyanate) and the soft segments from poly(oxytetramethylene glycol). Polar functional groups (carboxylic acids or tertiary amine groups) will be incorporated into the PU structure, conferring water solubility or dispersibility. The procedure will allow the manipulation of the thermal and mechanical performance of the PU via altering: a) the molecular weight of the soft segments, b) the mole ratio between hard and soft segments, and c) the nature of the soft and hard domains, d) the nature and amount of the polar group. This will allow selection of formulations with desirable properties (flexibility, barrier properties, tear strength, etc). [1<sup>st</sup>. Period – 4 months]

**2 – Synthesis of quaternary ammonium (QAC) based PU.** This task is the synthesis of PU with quaternary ammonium compounds incorporated in the PU. We will replace all/part of the hard crystalline segment of the PU by di-hydroxyl terminated amide (i.e. N,N-bis(2-hydroxyethyl) isonicotinamide). This chemical will provide both biocidal activity and the polar functional groups in order to conferring the PU water solubility. The variables will be studied systematically: a) concentration of QACs (important parameter controlling the bioactivity and water solubility), b) influence of the PU chemistry (aliphatic chain length and type of isocyanate, c) ability to form a film. [2<sup>nd</sup>. Period – 4 months]

**3- Test the antimicrobial properties in the final material.** This task is to study the efficacy of the final materials in disrupting the cell membrane of bacterial cells. The antibacterial properties against Gram-positive (*Staphylococcus aureus*) and Gram-negative (*Pseudomonas aeruginosa*, and *E. coli*) bacteria will be evaluated using recoverability from the surface and serial dilution on agar plates. Different contact times and temperatures will be evaluated. Scanning electron microscopy will be used to assess damage to the cell wall of bacteria. [3<sup>rd</sup>. Period – 4 months]

---

### Outreach to Industry:

Results will be disseminated to industry through normal scientific meetings and through direct contact with individual companies that are already active in the development and sale of antimicrobial products.

---

### New Resources Required:

We expect to spend part of the money of this proposal in the following equipment: 2 inch melt blowing attachment to extruder, FTIR microscope, contribution to chaotic mixer, vacuum oven, precision balance, pH meter.

# BIBLIOGRAPHY SECTION

## FY 2008 Project Proposal

Project No. BROU-08

---

- 1- Michael Szyche, "Handbook of Polyurethanes", CRC Press, 1990
- 2- X. Jiang, J. Li, M. Ding, H. Tan, Q. Ling, Y. Zhong, Q. Fu, "Synthesis and degradation of Nontoxic Biodegradable waterborne polyurethanes elastomers with PCL and PEG as soft segments", *European Polymer Journal*, 43 (2007) 1838-1846
- 3- M L Auad, VS Contos, S Nutt, M I Aranguren, NE Marcovich, -"Characterization of nanocellulose reinforced shape memory polyurethanes", *Polym Int* **57**:651-659 (2008)
- 4- Marcovich NE, Auad ML, Bellesi NE, Nutt, S.R., Aranguren, M.I., -"Cellulose micro/nanocrystals reinforced polyurethanes" *J. Materials Research* 21 (4): 870-881 APR 2006
- 5- C.P. Gerba, G.E. Janauer, M. Costello, "Removal of polyvirus and rotavirus from Tap water by a Quaternary Ammonium Resin", *Water Res.* Vol 18, N1, 17-19, 1984.
- 6- N. Nurdin, G. Helary, G. Sauvet, "Bocidal polymers active by contact: Synthesis of Polybutadiene with pendant quaternary ammonium groups", *Journal of applied Polymer Science*, Vol 50, 651-662 (1993)
- 7- Hasan Kocer, Fatma Kilinc-Balci, Maria Auad, Mirna Mosiewicki Roy M. Broughton, Jr., S. D. Worley<sup>2</sup>, and T.S. Huang "Antimicrobial, Elastomeric Fibers and Films via Halamines" *The Fiber Society*, UC Davis, October 9 - 12, 2007.
- 8- Jaewoong Lee, R. M. Broughton, J. Liang, S. D. Worley and T. S. Huang, "Antimicrobial Acrylic Fiber", accepted for publication in *Research Journal of Textile and Apparel*.
- 9- Jaewoong Lee, R. M. Broughton, S. D. Worley, T. S. Huang, Xiuling Fan, "Antimicrobial Polymeric Materials: Cellulose and m-Aramid Composite Fibers", ACS National Meeting, San Francisco, September 10, 2006.

# BIOGRAPHY SECTION

## FY 2008 Project Proposal

Project No. BROU-08

---

### ROY M. BROUGHTON, JR.

Auburn University,

Auburn, AL, 36849

Polymer and Fiber Eng. Department

(334) 844-5460

Fax:(334) 844-4068

[brougrm@auburn.edu](mailto:brougrm@auburn.edu)

---

#### a. Professional Preparation

|   |      |
|---|------|
| North Carolina State University Ph.D. Fiber and Polymer Science         | 1970 |
| North Carolina State University M. S. Wood and Paper Science; Chemistry | 1967 |
| North Carolina State University B. S. Pulp and Paper Technology         | 1964 |

#### b. Appointments

September, 1976 - present: Professor of Textile Engineering, Auburn University, Auburn, Alabama (Tenure: 1982, Graduate faculty: 1985, Full Professor: 1993)

January, 1970 - September, 1976: Senior Research Chemist, Polyester Research and Development Division, The Goodyear Tire and Rubber Company, Akron, Ohio

#### c. Publications (from among more than 50)

1-Jaewoong Lee, Xuehong Ren, R. M. Broughton, Jie Liang, S. D. Worley, and T. S. Huang, Electro-spun Antimicrobial Acrylic Fiber, *Journal of the Korean Society of Dyers and Finishers* **19**, (2) 44-49 (2007)

2-J. Lee, R. M. Broughton, A. Akdag, S. D. Worley\*, Tung S. Huang "Preparation and Application of *s*-Triazine-Based *N*-Halamine Biocide for Antimicrobial Fibers", *Fibers and Poly.*, **8** (2) 148-154 (2007)

3-"Light-Controlled Generation of Palladium Crystallite Structures in Polyimide Films", G. A. Gaddy, Edward P. Locke, G. Mills, R. Broughton, R. Albrecht-Schmitt, M. E. Miller, Diane M. Stoakley, Catharine C Faye, And Gilda Miner, *J. Phys. Chem.*, 2004, 108, 45, 17378-17383.

4-"Quasistatic Behavior of Polymer Composite Flywheels" Jianmin Chen, Yasser Gowayed, R. M. Broughton, *Polymer Composites*, **25** (5) 2004.

5-"Analysis of Circular Braiding Process, Part 1: Theoretical Investigation of Kinematics of the Circular Braiding Process", Q. Zhang, D. Beale, R.M. Broughton, 1999, *ASME J of Manufacturing Science and Engineering*, v121(3), p.345-350.

---

**MARIA L. AUAD**

Auburn University,  
Polymer and Fiber Eng. Department

Auburn, AL, 36849  
(334) 844-5459 Fax:(334) 844-4068

[auad@auburn.edu](mailto:auad@auburn.edu)

---

**Professional Preparation**

|   |                                |           |
|---|--------------------------------|-----------|
| University of Mar del Plata, Argentina      | B.Sc. in Chemical Engineering, | 1989-1995 |
| University of Mar del Plata, Argentina      | Ph.D. in Material Science,     | 1995-2000 |
| California Institute of Technology, CALTECH | Chemical Engineering Dep.      | 2000-2002 |

**Appointments**

|  |                      |
|--|----------------------|
| Assistant Professor, <i>Auburn University</i>  | August, 2006-present |
| Polymer and Fiber Engineering Department,<br>Research Assistant, <i>University of Southern California, USC</i> | 2002-2006            |
| Department of Materials Science,   |                      |

**Publications: (from among more than 25)**

- 1-“Characterization of nanocellulose reinforced shape memory polyurethanes”, M L Auad, VS Contos, S Nutt, M I Aranguren, NE Marcovich, *Polym Int* **57**:651–659 (2008)
- 2-“Shear-Induced Alignment of Smectic Side Group Liquid Crystalline Polymers”, Stanley Rendon and Wesley R. Burghardt, Maria L. Auad and Julia A. Kornfield, *Macromolecules* **2007**, *40*, 6624-6630.
- 3-“Synthesis and characterization of organically modified attapulgite/polyurethane nanocomposites”, Chia-Hao Wang, Maria L. Auad, Norma E Marcovich, Steven Nutt, accepted to be published in *Journal of Applied Polymer Science*, 2007
- 4-“Synthesis and Properties of Epoxy-Phenolic clay Nanocomposites”, M. L. Auad, S. R. Nutt, V. Pettarin, P.M. Frontini, *Express Polymer Letter*, *Vol.1, No.9 (2007)* 629–639.
- 5- “Nano-cellulose Reinforced Shape Memory Polyurethanes”, M. L. Auad, V. S. Contos, S. R. Nutt, M. I. Aranguren, N. E. Marcovich, accepted, *Polymer International*, 2007.
- 6-“*Temperature, Conversion and Phase Separation Profiles during Mold Cure of a Modified Vinylester Resin*”, *Walter F. Schroeder, María L. Auad and Ezequiel R. Soulé, accepted, Polymer Engineering and Science* **2007**.
- 7-“Mechanical Behaviors of Hybrid Composite Phenolic Foam”, A. Desai, M. L. Auad, H. Shen, S. R. Nutt, Accepted, *Journal of Cellular Plastics*, 2007.
- 8-“Flammability Properties and Mechanical Performance of Epoxy modified Phenolic Foams”, M.L. Auad, L. Zhao, HB Shen, S. Nutt, U. Soratia, *Journal of Applied Polymer Science* **104** (3): 1399-1407 MAY 5 2007
- 9-“Short-Fiber-Reinforced Epoxy Foams” Alonso MV, Auad ML, Nutt S, *Composites Part A- Applied Science and Manufacturing* **37** (11): 1952-1960, 2006.

**S. D. WORLEY**

Auburn University,  
Department of Chemistry and Biochemistry

Auburn, AL 36849  
(334) 844-6980,

[worlesd@auburn.edu](mailto:worlesd@auburn.edu)

---

**a. Professional Preparation**

Ph.D. 1969

Postdoctoral Research Chemist, 1969-1972

University of Texas, Ph. D., 1969

NASA

**b. Appointments**

Present

Professor, Department of Chemistry and Biochemistry, Auburn University

**c. Publications-selected refereed publications in past 3 years**

- (1) Akdag, A.; McKee, M.L.; Worley, S.D., "Mechanism of Formation of Biocidal Imidazolidin-4-one Derivatives: An ab initio DFT Study", *J. Phys. Chem. A.* 2006, 110, 7621-7627.
- (2) Akdag, A.; Okur, S.; McKee, M.L.; Worley, S.D., "The Stabilities of N-Cl Bonds in Biocidal Materials", *J. Chem. Theory & Comp.* 2006, 2, 879-884.
- (3) Akdag, A.; Webb, T.; Worley, S.D., "Oxidation of Thiols to Disulfides with Monochloro Poly(styrenehydantoin) Beads", *Tett. Lett.* 2006, 47, 3509-3510.
- (4) Liang, J.; Owens, J.R.; Huang, T.S.; Worley, S.D., "Biocidal Hydantoinylsiloxane Polymers. IV. N-Halamine-Functionalized Silica Gel", *J. Appl. Polym. Sci.* 2006, 101, 3448-3454.
- (5) Liang, J.; Chen, Y.; Barnes, K.; Wu, R.; Worley, S.D.; Huang, T.S., "N-Halamine/Quat Siloxane Copolymers for Use in Biocidal Coatings", *Biomaterials* 2006, 27, 2495-2501.
- (6) Barnes, K.; Liang, J.; Wu, R.; Worley, S.D.; Lee, J.; Broughton, R.M.; Huang, T.S., "Synthesis and Antimicrobial Applications of 5,5'-ethylenebis[5-methyl-3-(3-triethoxysilylpropyl)hydantoin]", *Biomaterials* ,2006, 27, 4825-4830.

---

**TUNG-SHI HUANG**

Auburn University,

Auburn, AL 36849

Department of Nutrition and Food Science

(334) 844-3290, Fax: (334) 844-3268

[huangtu@auburn.edu](mailto:huangtu@auburn.edu)

---

**a. Professional Preparation**

Ph.D. 1993      University of Florida-Food Science and Human Nutrition Department  
M.S. 1981      National Chung-Hsing University, Taiwan-Plant Pathology  
B.S. 1978      National Chung-Hsing University, Taiwan-Plant pathology

**b. Appointments**

08/07 - present      Associate Professor, Nutrition and Food Science, Auburn University  
08/02 - 08/07      Assistant Professor, Nutrition and Food Science, Auburn University  
10/01 - 08/02      Research Associate Fellow, Nutrition and Food Science, Auburn  
University  
09/99 - 09/01      Postdoctoral Associate, Nutrition and Food Science, Auburn University

**c. Publications-selected refereed publications in past 3 years**

- 1-Ren, X., L. Kou, H. B. Kocer, C. Zhu, S. D. Worley, R. M. Broughton, T. S. Huang. 2008. Antimicrobial coating of an *N*-halamine biocidal monomer on cotton fibers via admicellar polymerization. *Physicochem. Eng. Aspects* 317: 711-716.
- 2-Lee, J., R. M. Broughton, S. D. Worley, and T. S. Huang. 2007. Antimicrobial polymeric materials; cellulose and m-aramid composite fibers. *Journal of Eng. Fibers and Fabrics* 2(4): 25-32.
- 3-Lee, J., R. M. Broughton, A. Akdag, S. D. Worley, and **T. S. Huang**. 2007. Antimicrobial fibers created via polycarboxylic acid durable press finishing. *Textile Research Journal* 77(8)604-611.