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Polyelectrolyte Gels

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Prepared by
Sandia National Laboratories
Albuquerque, New Mexico 87185 and Livermore, California 94550
for the United States Department of Energy
under Contract DE-AC04-94AL85000

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Polyelectrolyte Gels

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Abstract

Polyelectrolyte (PE) gels are swollen polymer/solvent networks that undergo a reversible volume collapse/expansion through various types of stimulation. Applications that could exploit this large deformation and solvent expulsion/absorption characteristics include robotic "fingers" and drug delivery systems. The goals of the research were to first explore the feasibility of using the PE gels as "smart materials"- materials whose response can be controlled by an external stimulus through a feedback mechanism. Then develop a predictive capability to simulate the dynamic behavior of these gels. This involved experimentally characterizing the response of well-characterized gels to an applied electric field and other stimuli to develop an understanding of the underlying mechanisms which cause the volume collapse. Lastly, the numerical analysis tool was used to simulate various potential engineering devices based on PE gels. This report discusses the pursuit of those goals through experimental and computational means.

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1 Introduction

Polyelectrolyte (PE) gels are swollen polymer/solvent networks that undergo a reversible volume collapse/expansion through various types of stimulation. Applications that could exploit this large deformation and solvent expulsion/absorption characteristics include robotic “fingers” and drug delivery systems. The primary goal of this research was to explore the feasibility of using PE gels as “smart materials”- materials whose response can be controlled by an external stimulus through a feedback mechanism. This goal involved many different issues including:

- identifying potential engineering applications
- experimentally investigating the response of well-characterized gels to an applied electric field and other stimuli in order to develop an understanding of the underlying mechanisms which cause the volume collapse
- formulating a set of mathematical expressions that model the dynamic behavior of polymeric gels
- developing a numerical analysis tool to solve the theoretical set of equations
- evaluating theoretical gel-based devices using the numerical analysis tool
- experimentally developing different gel devices

The first challenge was developing a constitutive model for the gel-solvent systems and assessing that model against experiment. This phase of the work was taken to engineering level during the first two years of this LDRD. Also during this time, we developed some very primitive computational models of basic properties. (1) We have since completed the software development of numerical simulation techniques to predict the coupled chemo-mechanical response of PE gels in one and two dimensions for several simple sorts of stimuli. We have refined and verified a finite element code, including the capability for graphical animation of results to predict the 2D dynamic behavior of one phase PE gels with solvent or pH stimulation. (2) We have experimentally characterized the dependence of the modulus and osmotic pressure of our model PE gel (polyacrylamide - PAM) with respect to various parameters. (3) We have developed a theory describing the coupled chemo-mechanical response for the bending behavior of PE gels in an electric field. The computational simulations are in excellent agreement with experimental observations. (4) We have synthesized amphoteric and heterogeneous gels for use in proposed devices. (5) We have established and developed stand alone prototyping capabilities in two “Smart Materials Laboratories”, at Sandia and UNM, and have started developing and fabricating engineering devices using high performance (HP) gels (such as polyacrylonitrile fibers - PAN). (6) We have developed an experimental capability to characterize the mechanical properties of these HP gels as functions of different manufacturing variables.

In the past three years, we have become recognized in the international technical community as being leaders in the characterization and computer simulation of polyelectrolyte gels. Several parties - including research facilities at MIT, University of Miami School of Medicine, and the University of Utah Center for Controlled Chemical Delivery, the University of Pisa, Italy and the Graduate School of Science at Hokkaido University, Sapporo, Japan - have expressed interest in performing collaborative research with us. The most productive direction for this work to continue in the near future would be in computational modeling and design of controlled release systems. LDRD funding was not awarded for this new endeavor, but other sources are being explored. This

report gives a brief discussion of each of the different aspects of the work explored in this LDRD. Chapter 2 presents the theoretical formulations of the mass transport and structural mechanics equations. Chapter 3 introduces the finite element formulation used to solve the system of equations presented in Chapter 2. Experimental investigations are briefly described in Chapter 4. Potential engineering applications are given in Chapter 5. Two theoretical devices were simulated using the numerical analysis tool GELLO and are presented in Chapter 6. More detailed explanations of each of these topics are given in the included papers. These papers were presented at various conferences and published in various journals and conference proceedings. A complete list of publications is given in Section 7 of this report. A list of important contacts made during the period of the LDRD is given in Appendix A. Individual papers published in journals or presented at conferences are given in Appendices B-1 through B-7. An LDRD summary is presented in Appendix C.

2 Theory

The original research team, D. Adolf, B. Hance, D. Segalman, M. Shahinpoor, and W. R. Witkowski developed the first consistent set of governing equations for the macroscopic behavior of polyelectrolyte gels. This theory addressed the gel as a single phase material through which solvent diffuses.

The governing equations consist of:

- transport equations for the solvent
- transport equations for the activating agent (pH in our applications)
- hyper-elastic constitutive equations for the gel
- an incompressibility condition on the gel
- and equations for static equilibrium.

The incompressibility condition asserts that the gel does not change volume in response to changes in isotropic pressure, but the system of equations does permit the change in volume due to the absorption or desorption of solvent.

The governing equations (referred to in the following as the SWAS equations) are capable of predicting swell, anisotropic deformation, cyclic deformation, and relaxation and constraint forces.

Further refinement of the theory would reproduce the phenomenon of nonuniform swelling in reaction to nonuniform surface tractions or internal pressure gradients. (see Appendix B)

3 Numerical Analysis

A finite element code for simulating the two-dimensional, plane strain deformation of gel was devised. This code, operationally referred to as GELLO, accommodated:

- transport equations for the solvent
- hyper-elastic (neo-Hookean) constitutive equations for the gel
- an incompressibility condition on the gel
- and equations for static equilibrium.

In the above, the pH field is specified, usually as a boundary condition. The incompressibility condition is accommodated by the introduction of a field of hydrostatic pressures as Lagrange multipliers to accompany the explicit enforcement of incompressibility.

Because of the nonlinear dependence of diffusivity on solvent concentration and because of the nonlinear elasticity incorporated into the model, the equations are exceedingly nonlinear. Numerical solution of those equations is achieved through Newton iteration.

Special capabilities have been built into the code to address specific gel applications. The most significant of these is that of “killing” elements that swell beyond some threshold limit. This optional capability has utility in simulating the use of polyelectrolyte gels in controlled drug release where the drug transport medium erodes away thereby dispersing dopant. Details of the finite element technique used in GELLO are given in the paper included in Appendix B-2.

4 Experimental Studies

Our experimental studies have concentrated on primarily two different areas. The first dealt with investigating a model gel system to fully understand the physics of the swell/contraction problem. This information was used to estimate material properties and verify our theoretical predictions. The second area focused on investigation of gel-based devices.

Most of the experimental work concerned with characterization of PE gels was performed by Doug Adolf and Brad Hance in Department 1812 at Sandia. They experimentally characterized the dependence of the modulus and osmotic pressure of our model PE gel (polyacrylamide - PAM) with respect to various parameters. They have developed a theory describing the coupled chemo-mechanical response for the bending behavior of PE gels in an electric field. The computational simulations are in excellent agreement with experimental observations. We have synthesized amphoteric and heterogeneous gels for use in proposed devices. Detailed results of the experimental characterization are presented in the paper "Electric Field-Induced Deformation of Polyelectrolyte Gels" which is included in Appendix B-7.

We have established and developed stand-alone prototyping capabilities in two "Smart Materials Laboratories", at Sandia and UNM, and have developed and fabricated a few engineering devices using high performance (HP) gels (such as polyacrylonitrile fibers - PAN).

Dr. M. Shahinpoor has worked directly with us from the start of the project and is responsible for the UNM facility. He and his graduate students have made several gel-based devices including a pH meter and several different actuators. They have also studied fabric weaved from PAN fibers. They have developed an experimental capability to characterize the mechanical properties of these HP gels as functions of different manufacturing variables.

We have also worked with Dr. D. Brock from the Artificial Intelligence Laboratory at the Massachusetts Institute of Technology. His work has also concentrated on actuator development. Results of this work were published in a paper entitled "A Dynamic Model of a Linear Actuator Based on Polymer Hydrogel" (see Appendix B-5). Brock and his co-workers have also endeavored into changing the chemistry of the PAN so that the gel can be stimulated with weaker acid and base. This work is still being investigated.

5 Applications

Several applications have been proposed that are based on a gel engine. The appeal of such devices is the potential for large-deflection, low energy actuation. Much development remains to be done in this area, particularly in addressing speed limitations due to the diffusive process of the solvent. (The computer codes were developed to understand some of these limitations and how to mitigate them.)

Designs for a large class of gel driven actuators were developed and a U.S. patent (No. 5,250,167) was issued to D. Adolf, M. Shahinpoor, D. Segalman and W. Witkowski on October 5, 1993. This patent was entitled "Electrically Controlled Polymeric Gel Actuators" and dealt with exploiting the electrical stimulation characteristics of some gel/solvent systems to produce actuators.

More near term are gel-based controlled drug release systems. Some such systems are already in use, though a systematic method of design is still to be presented. This is probably the most immediate application of the computational tools developed in this LDRD.

6 Theoretical Examples

The numerical code discussed above was used to explore several gel applications. A broad class of gel actuators is discussed in the paper "Electrically-Controlled Polymeric Gels as Active Materials in Adaptive Structures," reproduced in Appendix B-1, and the initial purpose of the computational tool was to explore and predict the properties of such devices. Because polyelectrolyte gels are currently being used in controlled drug release, the code was extended to explore those applications with the intent of making their design more systematic.

Actuator Example

The first exploration of gel actuators using the Sandia code is outlined in "Finite Element Simulation of the 2D Collapse of a Polyelectrolyte Gel Disk" (SPIE Vol. 1916 pp. 14-21, Feb., 1993) and reproduced in Appendix B-4. Additional studies involving more realistic geometries were done, including that published in the paper by Brock, D., W. Lee, D. Segalman and W. Witkowski, "A Dynamic Model of a Linear Actuator Based on Polymer Hydrogel," Proc. of the Second International Conference on Intelligent Materials, Williamsburg VA, June 1994.

Drug Delivery System Example

Polyelectrolyte gels are currently used in "smart" controlled drug release strategies. In general such strategies and devices are created on a "cut and try" basis. In order to see if our tools could be used to make that development more systematic, the code was extended to simulate one such release process. That work is reported in Segalman, D. and W. Witkowski, "Two-Dimensional Finite Element Analysis of a Polymer Gel Drug Delivery System," (accepted in Materials Science and Engineering Journal.) and reproduced in Appendix B-6.

7 Conclusions

1. Though the polyelectrolyte gels have near term applications as smart materials in such things as smart filters and drug delivery devices, their role in large displacement actuators is more long term. The longer term expectations for gel-based actuators are due to the need for advances in material science. Materials of greater strength and stiffness as well as greater sensitivity to environment are required.
2. More research needs to be done in gel actuation techniques.
3. Our work in finite element modelling places Sandia at the forefront of numerical simulation of polyelectrolyte gel mechanics and of computer aided design of gel applications.

8 List of Publications

- 1) Segalman, D., W. Witkowski, D. Adolf, and M. Shahinpoor, "Electrically-Controlled Polymeric Gels as Active Materials in Adaptive Structures," Proceedings of ADPA/ASME Conference of Smart Materials and Adaptive Structures, Alexandria, Virginia, 1991.
- 2) Segalman, D., W. Witkowski, D. Adolf, and M. Shahinpoor, "Numerical Simulation of the Dynamic Behavior of Polymeric Gels," In the Proceedings of the 1st International Conference of Intelligent Materials, Oiso, Japan, 1992
- 3) Witkowski, W. R., D. Segalman, D. Adolf, and B. Hance, "Simulation of the Dynamic Behavior of Polymeric Gels," In the Proceeding of the First European Conference on Smart Materials, Glasgow, Scotland, 1992.
- 4) Segalman, D., W. Witkowski, D. Adolf, and M. Shahinpoor, "Theory and Application of Electrically-Controlled Polymeric Gels," Smart Materials and Structures, Vol. 1, No. 1, pp.95-100, 1992.
- 5) Rao, Rekha R., Walter R. Witkowski, Daniel J. Segalman, Doug Adolf and Moshen Shahinpoor, "Finite Element Analysis of Chemomechanical Gels," Presented at AIChE, Miami, 1992.
- 6) Daniel J. Segalman, Walter R. Witkowski, Rekha Rao, Doug Adolf and Mo Shahinpoor, "Finite Element Simulation of the 2D Collapse of a Polyelectrolyte Gel Disk," SPIE Vol. 1916 pp. 14-21, Feb., 1993.
- 7) Daniel J. Segalman and Walter R. Witkowski, "Two-Dimensional Finite Element Analysis of a Polymer Gel Drug Delivery System," Proc. of the Second International Conference on Intelligent Materials, Williamsbury, VA, June, 1994.
- 8) Brock, D., W. Lee, D. Segalman and W. Witkowski, "A Dynamic Model of a Linear Actuator Based on Polymer Hydrogel," Proc. of the Second International Conference on Intelligent Materials, Williamsburg VA, June 1994.
- 9) Brock, D., W. Lee, D. Segalman and W. Witkowski, "A Dynamic Model of a Linear Actuator Based on Polymer Hydrogel," Journal of Intelligent Materials Systems and Structures, Nov./Dec. 1994.
- 10) Segalman, D. and W. Witkowski, "Two-Dimensional Finite Element Analysis of a Polymer Gel Drug Delivery System," accepted in Materials Science and Engineering Journal.

9 Appendix A - Contacts

During the duration of the LDRD project we made many different contacts with researchers in several different areas of expertise which are very influential in the gel community. We have visited several of these researchers and their facilities. Many of these have showed an interest in joint collaboration in future research. Following is a list of some of these contacts.

Dr. Sun Wan Kim
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Salt Lake City, UT 84108

Dr. Teruo Okano
Tokyo Women's Medical College
Tokyo, Japan

Dr. Yoshito Osada
Hokkaido University
Sapporo, Japan

Dr. Danilo DeRossi
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Dr. Dejan Popovic
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Purdue University
Department of Chemical Engineering
West Lafayette, IN 47954

Dr. J. Gong
Division of Biological Sciences
Hokkaido University
Sapporo 060, Japan

10 Appendix B - 1

This paper entitled "Electrically-controlled polymeric gels as active materials in adaptive structures" was our first paper dealing with potential gel applications and our first effort in formulating the gel transport dynamics. This paper was first presented at the Active Materials and Adaptive Structures Conference and then published in the Smart Materials and Structures Journal (Vol. 1, pp. 95-100 (1992)) under the title "Theory and application of electrically controlled polymeric gels".

*conference papers
cycled separately*

17 Appendix C - LDRD Summary

LDRD Summary:

Number of patent disclosures resulting from this project:	4
Number of patent applications resulting from this project:	1
Number of patents:	1
Number of Copyrights resulting from the project:	0
Number of students supported by the project:	3
Number of technical staff hired as result of the project:	0
Number of awards received by the staff as a result of the project:	1 television interview

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