

FINAL PROGRESS REPORT

ARO Grant # W911NF-04-1-0155

Project Title:

**STIR: IONOMERIC CARBON NANOTUBE COMPOSITES FOR ADAPTIVE SKINS
AND STRUCTURAL CONTROL**

BAA Research Area:

Research Area 7: Mechanical Sciences

ARO Technical Point of Contact:

Dr. Gary Anderson

Program Relevance:

The proposed STIR program will focus on the development of new active polymeric materials for use in shape changing vehicles and structural control. The research is relevant to Topic 7.3.3 in the ARO BAA on the development of new structural materials for shape change and vibration suppression.

Principal Investigator:

Donald J. Leo
Associate Professor
CIMSS / Mechanical Engineering Department
307 Durham Hall
Virginia Polytechnic Institute and State University
Blacksburg, VA 24061-0261

Tel: (540) 231-2917
Fax: (540) 231-2903
email: donleo@vt.edu
URL: <http://filebox.vt.edu/users/donleo/>

DISTRIBUTION STATEMENT A
Approved for Public Release
Distribution Unlimited

20050425 032

REPORT DOCUMENTATION PAGE

Form Approved
OMB NO. 0704-0188

Public Reporting burden for this collection of information is estimated to average 1 hour per response, including the time for reviewing instructions, searching existing data sources, gathering and maintaining the data needed, and completing and reviewing the collection of information. Send comment regarding this burden estimate or any other aspect of this collection of information, including suggestions for reducing this burden, to Washington Headquarters Services, Directorate for Information Operations and Reports, 1215 Jefferson Davis Highway, Suite 1204, Arlington, VA 22202-4302, and to the Office of Management and Budget, Paperwork Reduction Project (0704-0188), Washington, DC 20503.

1. AGENCY USE ONLY (Leave Blank)		2. REPORT DATE 03-29-05	3. REPORT TYPE AND DATES COVERED Final Progress 6/1/04 to 2/28/05	
4. TITLE AND SUBTITLE STIR: Ionomeric Carbon Nanotube Composites for Adaptive Skins and Structural Control			5. FUNDING NUMBERS W911NF-04-1-0155	
6. AUTHOR(S) Donald J. Leo				
7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES) Virginia Polytechnic Institute and State University 301 Burruss Hall Blacksburg, VA 24061-0249			8. PERFORMING ORGANIZATION REPORT NUMBER	
9. SPONSORING / MONITORING AGENCY NAME(S) AND ADDRESS(ES) U. S. Army Research Office ATTN: AMSRD-ARL-RO-OI (TR) P.O. Box 12211 Research Triangle Park, NC 27709-2211			10. SPONSORING / MONITORING AGENCY REPORT NUMBER 47056.1-EG- II	
11. SUPPLEMENTARY NOTES The views, opinions and/or findings contained in this report are those of the author(s) and should not be construed as an official Department of the Army position, policy or decision, unless so designated by other documentation.				
12 a. DISTRIBUTION / AVAILABILITY STATEMENT Approved for public release; distribution unlimited.			12 b. DISTRIBUTION CODE	
13. ABSTRACT (Maximum 200 words) A class of polymer-metal composites was developed for applications in shape-changing vehicles and vibration suppression. The polymer-metal composites considered in this work exhibited real-time control of the elastic modulus through variation of the hydration state of the material. These materials, called ionomers, were combined with precious metals and carbon nanotubes using a previously-developed fabrication technique. The elastic properties of the composite materials were tested, and it was determined that modulus variations on the order of 3X to ~10X were achievable with different solvents. The loss properties of the material could not be measured as a function of hydration level, precluding the use of carbon nanotubes as a metal particulate in the composite. An experiment in switched-state vibration control illustrated the use of these materials as a variable-modulus isolation mount for suppressing resonant vibration. The time constants of the modulus change were determined to be approximately 10 seconds for the softening and on the order of minutes for the stiffening. The rate of stiffening could be controlled by application of an external electric field to de-solvate the material more rapidly. These results demonstrate the feasibility of using ionomeric-metal composites in applications which require large strains (>10%) and do not require rapid changes in the elastic properties.				
14. SUBJECT TERMS polymer-metal composites, shape-changing structures, vibration control, controllable modulus			15. NUMBER OF PAGES 12	
			16. PRICE CODE	
17. SECURITY CLASSIFICATION OR REPORT UNCLASSIFIED	18. SECURITY CLASSIFICATION ON THIS PAGE UNCLASSIFIED	19. SECURITY CLASSIFICATION OF ABSTRACT UNCLASSIFIED	20. LIMITATION OF ABSTRACT UL	

Foreward

Materials that exhibit controllable modulus variations will enable new developments in applications in vibration suppression and shape change. In this project we analyzed a class of materials that exhibit reversible modulus variations due to solvent incorporation or removal. These materials, known as ionomeric polymers, have been shown previously to exhibit 20X changes in modulus depending on the hydration state of the material. A test fixture that allows a ionomeric polymer sample to be placed in a hydration controlled environment was developed. The Young's modulus of virgin materials and materials plated with metal was measured as a function of hydration level. A change of 2.55 and 3.89 times in modulus was obtained for the unplated and plated material, respectively, when using water as a solvent. Experiments on carbon nanotube-plated ionomers illustrated that the composite materials were too brittle for large-strain loading, therefore conventional plating materials such as platinum and ruthenium dioxide were used for the remaining experiments.

Experiments were performed to determine the ability to increase the stiffening rate of the polymer using applied electrical energy. Square input signals were applied to increase the elastic modulus of these materials. The rate of modulus change was higher or lower depending on the voltage amplitude and the forcing frequency of the input signal. Different kinds of solvents were used to control the modulus of the ionomer plated with platinum. Glycerol was the solvent with the highest modulus reduction (88.87%) and water was the smallest (67.71%). In addition, a test fixture consisting of a mass on a plate was built and modeled as moving-base. The change in stiffness was explored as a method to reduce unwanted vibration. The displacement transmissibility versus frequency was measured for water and acetonitrile solvents. The stiffness of Nafion 117 was computed when the solvents were applied and after they dried. The steady state response of the system was measured by applying a sinusoidal input signal. A forcing frequency of 94 Hz near the natural frequency is selected to produce a high amplitude. The displacement amplitude is reduced 5 times in 10 seconds after the application of the acetonitrile to the ionomeric polymer. These results demonstrate the basic feasibility of controlling the modulus in real time and quantify the time constants associated with hydration and dehydration of the material.

Table of Contents

Problem Statement	1
Summary of Results	1
Elongation Experiments	2
Modulus Measurements	3
Real-Time Modulus Control	4
Switched-State Vibration Control Experiments	5
Project Summary	8
Listing of Publications and Reports	9

Problem Statement

This STIR program focused on developing a new class of polymer composites that could be used in shape changing structures and for vibration suppression applications which require materials that undergo large strain. The specific goals of the project were to develop a polymer material that could

1. The ability to undergo 10% reversible strain without failure.
2. Controllable modulus variations that range over an order of magnitude (10X).
3. Controllable loss factor variations that range from 0.1 to 0.5.
4. The ability to be integrated into a polymer or ceramic composite.

Summary of Results

The first task of the effort was to build a test fixture that enables measurement of elastic properties as a function of hydration level. The fixture that is developed allows the mechanical properties of a sample to be tested in a hydration controlled environment. Figure 1 shows a front and top view of the test fixture. The fixture consists of two plates in which the ionomer sample is clamped. The plates are supported to ensure that they exhibit uniaxial motion. The plates are placed inside a transparent plastic box and sealed so that humidity could be controlled. A shaker is attached to the moving plate and a laser vibrometer measures the motion of the sample. A

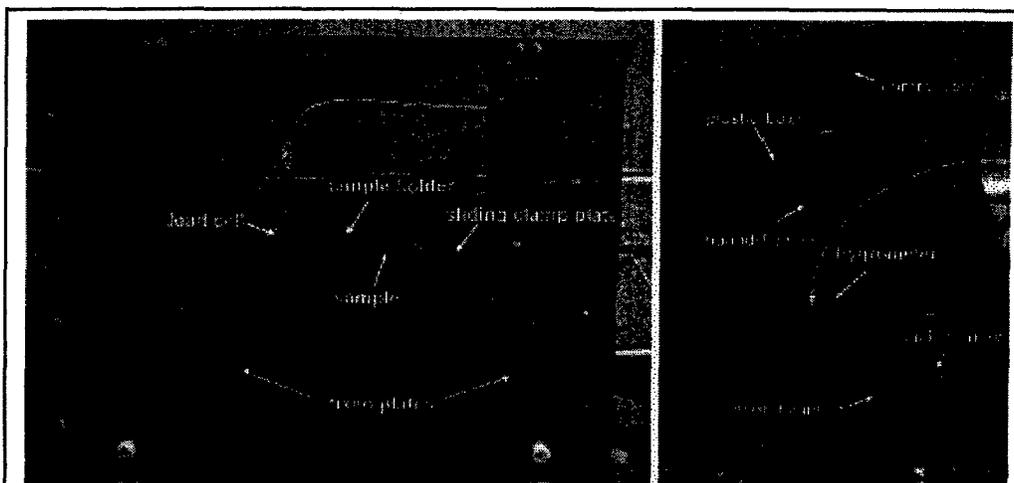


Figure 1: Humidity-controlled environment for measurement of elastic properties.

load cell attached to the rigid plate measures the force applied to the sample. A hygrometer is placed in the interior of the fixture to measure the

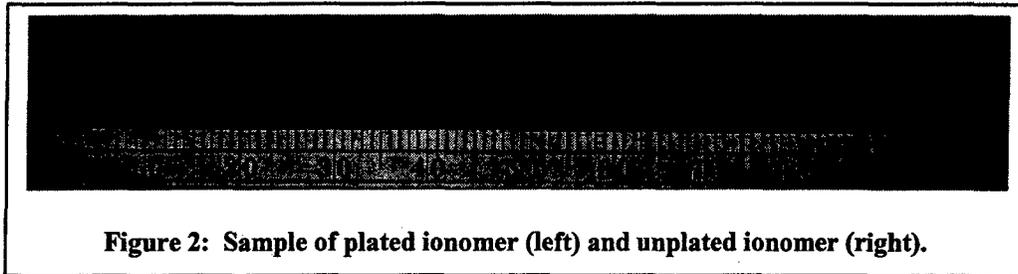


Figure 2: Sample of plated ionomer (left) and unplated ionomer (right).

hydration level of the polymer sample. The initial hydration percent of Nafion is the

same as the room relative humidity. Room relative humidity can range from 20% to 50% depending on the weather. However, during a day the relative humidity only varies approximately by 5%. In order to reach low levels of hydration, the polymer sample is placed in a vacuum oven for two hours and a desiccant bed is placed on the bottom of the fixture to control the humidity level of the interior space. Instead of a desiccant bed, humidified air is pumped in to reach high humidity levels. Figure 2 displays a commercially-available ionomer, Nafion 117, plated with 5 layers of platinum using the impregnation reduction method and a thin layer of gold electroplated on top of the platinum at the left, and Nafion 117 perfluorosulfonic acid polymer in hydrogen form at the right.

Elongation Experiments

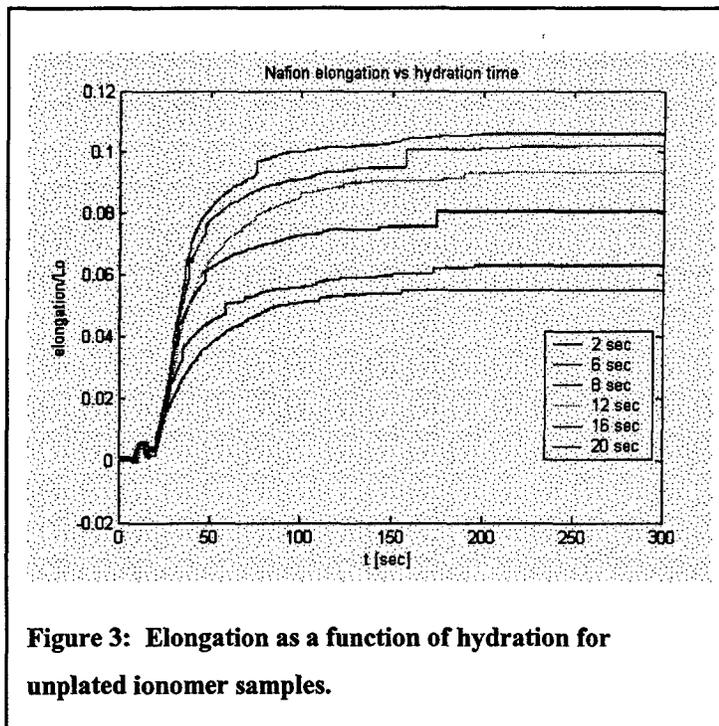


Figure 3: Elongation as a function of hydration for unplated ionomer samples.

The first set of experiments tested the elongation properties of unplated ionomer to determine the percent elongation that could be induced by hydrating the material. In this set of tests an unplated ionomer sample was loaded with a weight to induce strain. The material was then hydrated for a specified period of time by spraying water on the material to soften the ionomer. The sample was then allowed to dry without the weight applied and the process was repeated. The results shown in Figure 3 illustrate

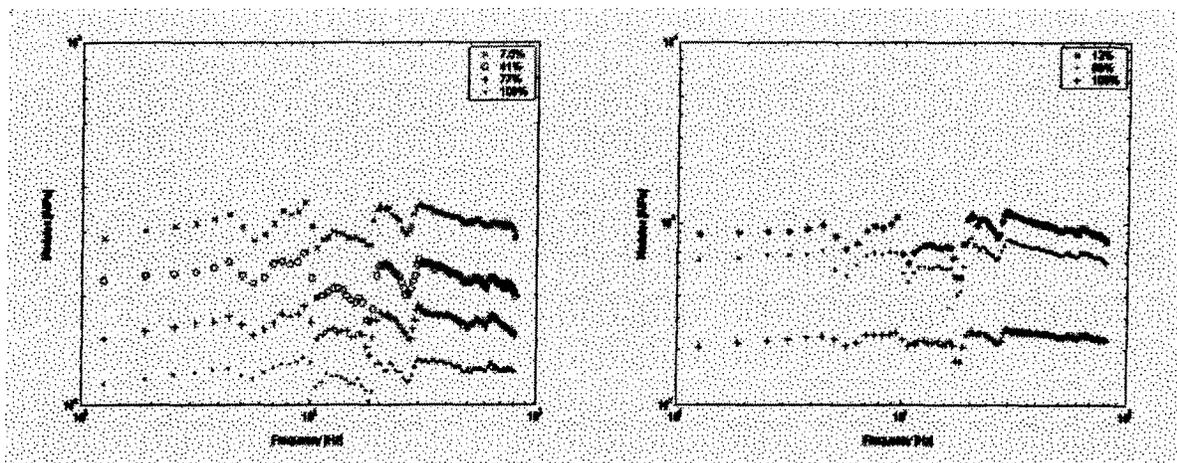


Figure 4: Modulus measurements for unplated (left) and plated (right) ionomers.

that the samples are able to withstand reversible elongation on the order of 6% to 10% of the original length.

Modulus Measurements

Experiments were performed on unplated and plated ionomer samples to determine the modulus as a function of hydration level using water as a solvent. For each measurement the frequency response between applied force and measured displacement was obtained. The elastic modulus of Nafion 117 with platinum versus frequency is presented in Figure 4 for several hydration levels. The initial dimensions are (26.5 mm x 13.5 mm x 0.18 mm) for 12% hydration and the final dimensions are (28 mm x 14 mm x 0.19 mm) for 100% hydration. A single elastic modulus value is obtained by calculating the mean of the modulus value over the frequency range. The modulus changes approximately from 924.62 MPa to 237.84 MPa for 12% and 100% hydration levels, respectively. The same behavior for the modulus of Nafion 117 as hydration changes is followed by Nafion 117 with platinum. The modulus variation of Nafion (194.51 MPa) as hydration change from 7.5% to 100% is less than the modulus variation of Nafion with platinum (686.78 MPa) as hydration change from 12% to 100%, see Figure 4.

Table 1: Modulus reduction for various solvents.

Solvents	glycerol	acetonitrile	butyl acetate	water
modulus reduction [%]	89	79	83	68
Density [g cm ⁻³]	1.261	0.786	0.882	1.00

Another series of experiments was performed to test the ability of different solvents to vary the modulus of the plated ionomer. Table 1 lists the modulus reduction associated with several different solvents. The results demonstrate that approximately 10X reductions are obtained using glycerol as the solvent.

One difficulty with the modulus measurements was the inability to measure loss factors as a function of hydration level. The data shown in Figure 4 illustrates that the modulus frequency response was approximately flat over the range tested. Initially we had hoped to measure the viscoelastic properties of the material as a function of hydration but this was not possible with the humidity-controlled environment developed in this project. This precluded the measurement of material loss as a function of solvent, particulate type, or hydration.

Real-Time Modulus Control

The use of ionomeric composites for shape change and vibration suppression requires knowledge of the time constants associated with the modulus variations. A series of experiments were performed to analyze the time required to reduce or increase the modulus of unplated and plated ionomers. In these experiments the test fixture described previous was used to measure the modulus before and hydration hydrating the polymer. Frequency response tests were obtained periodically to determine the modulus change as a function of time. In all tests the softening effect occurred in less than 1 minute as shown in Figure 5.

Real-time control of elastic modulus is demonstrated by applying different square input signals to the polymer. First, the modulus versus frequency is measured at room hydration for Nafion with platinum. Next, water is applied with a small brush on both sides of the sample and the modulus versus frequency is measured once again for 100% hydration. Then, a square-wave input signal is applied to the polymer for a specified time and the modulus versus frequency is measured approximately each 5 minutes until the modulus versus frequency data reaches steady-

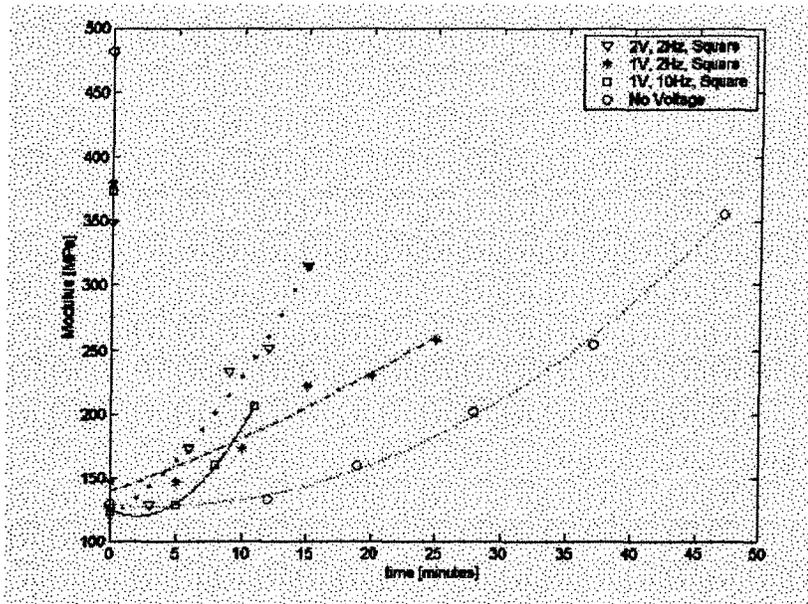


Figure 5: Modulus variation as a function of time for various methods of exciting the material.

state.
This
full
process
is
repeated
for
each
input
signal.
A single
modulus
value
is

obtained by calculating the mean from the modulus versus frequency data. The single elastic modulus value of Nafion with platinum versus time for several square input signals is shown in Figure 5. The hydration percent was controlled by applying voltage within the material. The time that the polymer hydration took to change from 100% to 20% was around 50 minutes without applying voltage. The time was reduced between 10 to 25 minutes depending on the voltage amplitude and forcing frequency of the square input signal.

The results shown in Figure 5 illustrate two important attributes of the materials developed in this program. First, the results demonstrate that the modulus change is reversible. Secondly, the results demonstrate that the time constant associated with the reversibility is on the order of minutes even in the case in which the polymer is excited with an external voltage to speed up the stiffening process.

Switched-State Vibration Control Experiments

The final aspect of the project is to demonstrate the use of the modulus variation in a vibration control experiment. Due to the fact that we were unable to measure variations in the loss factor of the polymer it was decided to perform an experiment that would utilize the softening and

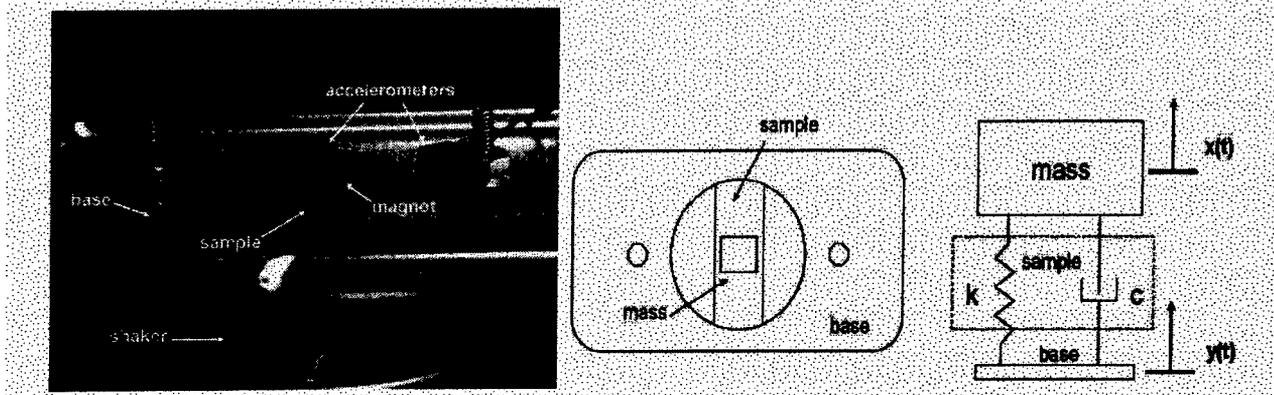


Figure 6: SDOF vibration experiment for switched-state control.

stiffening effect of the polymer composite. An experiment was developed that represented a single-degree-of-freedom vibration model in which the elastic support was the unplated ionomer. A picture and schematic of the setup is shown in Figure 6. A small mass is supported by an ionomer strip which can be hydrated by spaying it with solvent.

The effect of hydration on the resonance of the mass is measured by measuring the frequency response between the base motion, $y(t)$, and the motion of the mass, $x(t)$. The measurement is a measure of the transmissibility. Figure 7 illustrates that the measurement is an excellent representation of a single-degree-of-freedom (SDOF) system. In the case of softening of the material, the resonance peak decreases from approximately 108 Hz to 56 Hz in approximately 3

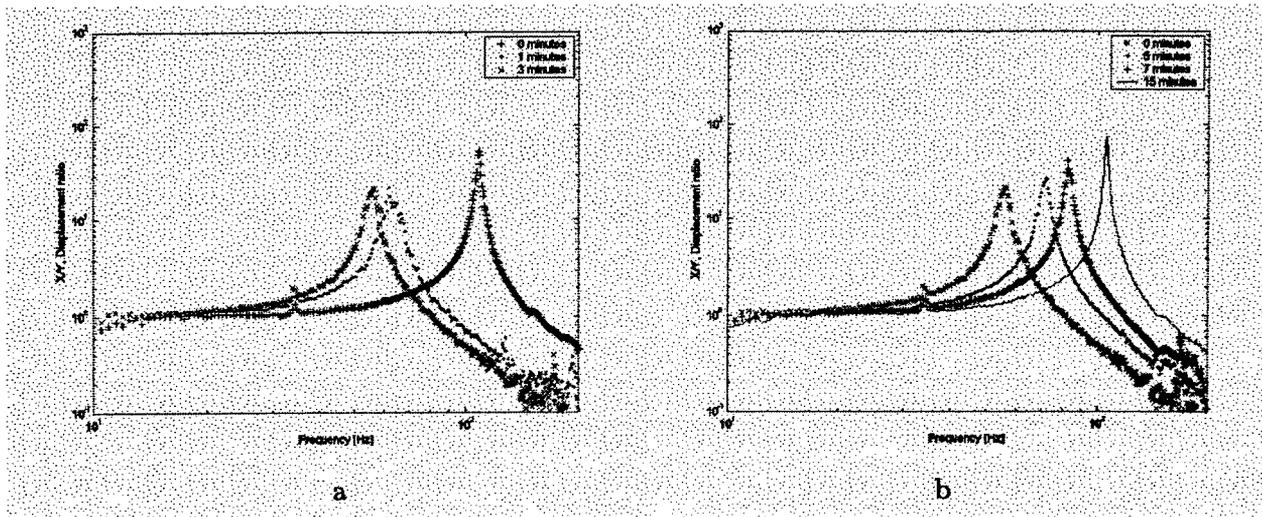


Figure 7: (a) Frequency response measurements during the softening of the polymer; (b) frequency response measurements during the stiffening of the polymer.

minutes when solvated with water (see Figure 7a). The stiffening effect as shown in see Figure 7b demonstrates that the resonance peak will approach the 'dry' resonance peak after approximately 15 minutes. This confirms the reversibility of the modulus variation.

The ability of the modulus variation to assist with switched-state vibration control was also demonstrated on the SDOF test setup. Switched-state control is the real-time variation of the physical parameters for the purpose of reducing undesirable vibration. In our experiment we utilize the modulus variation property of the ionomer to switch the state from stiff to soft to reduce unwanted resonance vibration. This is demonstrated using the test setup shown in Figure 6 by exciting the base at a frequency near the resonance of the 'dry' polymer and measuring the motion of the mass. The support is then hydrated to soften the polymer thus moving the forcing frequency to a frequency greater than the resonance of the system. As shown in the transmissibility plots this will cause a substantial reduction in the vibration.

The ability to use the polymer for state-switched control is shown in Figure 8. The results

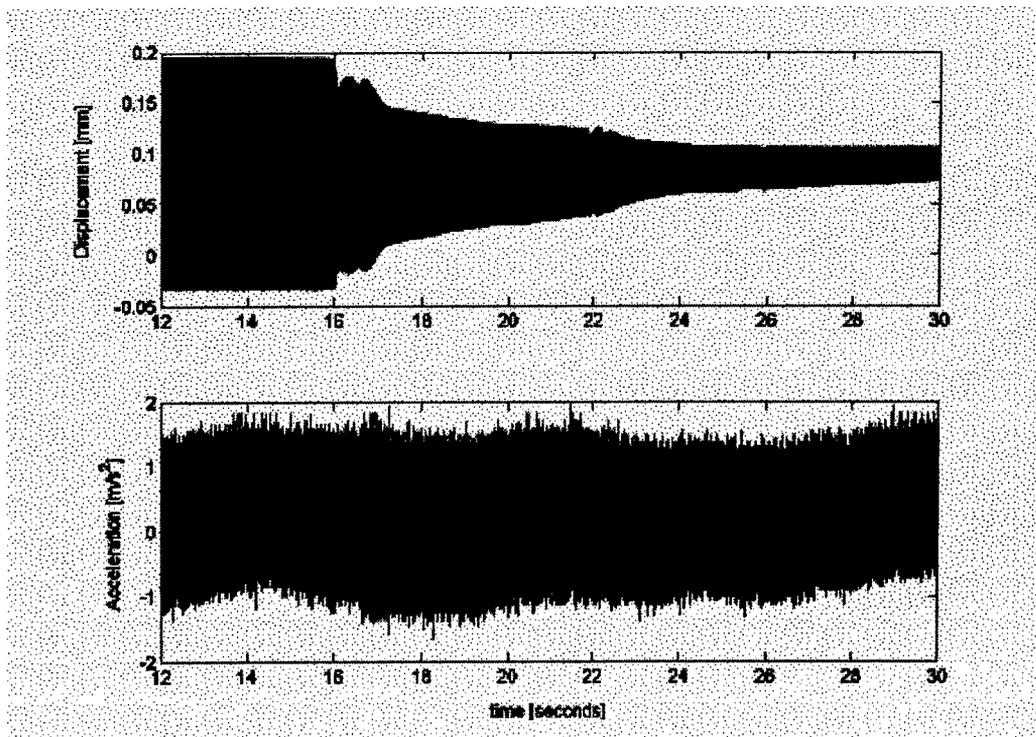


Figure 8: Measurement of the mass motion as a function of time after the support polymer has been hydrated. The results illustrate the use of the ionomer for state-switched control.

illustrate that the motion of the head mass in the SDOF experiment decreases by approximately 80% (5X) when the support polymer is hydrated. The vibration reduction is directly related to the softening of the polymer due to addition of the solvent (water). More importantly, this result also demonstrates that the time constant associated with this motion is only on the order of 10 to 15 seconds.

Project Summary

Three of the four goals of this project were achieved. Polymer composites were fabricated that exhibited greater than 10% elongation and reversible behavior as a function of hydration level. The modulus variation was demonstrated to be on the order of 10X for certain types of solvents, although the common solvent, water, only produced a 3X variation in the modulus over realistic changes in hydration level. Finally, these polymer composites were integrated with a structure to demonstrate real-time vibration control through modulus variation. The only goal that was not obtained was a demonstration of real-time control of loss factor. This was inhibited due to the inability of our test setup to measure appreciable changes in loss factor as a function of hydration.

This project did demonstrate the feasibility of using ionomeric composites as materials that require controllable modulus variations. The use of carbon nanotubes did not produce appreciable benefits due to the fact that the loading of the nanotubes produced a brittle composite which was introduced problems at high strains. More conventional particulates such as platinum and ruthenium dioxide were more useful for this project. Most important was that this project demonstrated that the time constants associated with softening the material were only on the order of 10 to 15 seconds to 1 minute.

Listing of Publications and Reports

Mejia-Ariza, J., Leo, D.J., 2005, "Switched-state control of a vibration isolation mount using ionomeric materials," Proceedings of the SPIE, volume 5760, Paper Number 5760-01.