Material characterization of poly (vinylidene fluoride) : a thin film piezoelectric polymer

by Frank Conly Holloway

A thesis submitted in partial fulfillment of the requirements for the degree Of Master of Science in Mechanical Engineering
Montana State University

Abstract:
Material properties of polyvinylidene fluoride are determined. It is shown that these properties are anisotropic and time dependent. The instantaneous elastic properties are found and compared to published results. A model describing the time dependent behavior of the material is then developed. It is shown that the theory of viscoelasticity can successfully accomplish this task, and the parameters describing this theory in the separate material directions are determined from dynamic mechanical testing and analysis. The results of these tests are then compared to results obtained from traditional creep tests. The piezoelectric coupling properties are also examined. It is shown that these coefficients are independent of studied parameters within measured ranges. The values of these coefficients are determined and compared to published results.

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APPROVAL

of a thesis submitted by

Frank Conly Holloway

This thesis has been read by each member of the thesis committee and has been found to be satisfactory regarding content, English usage, format, citations, bibliographic style, and consistency, and is ready for submission to the College of Graduate Studies.

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TABLE OF CONTENTS

TABLE OF CONTENTS - Continued

LIST OF TABLES

LIST OF FIGURES

LIST OF FIGURES - Continued

Figure Page

LIST OF FIGURES - Continued

Figure Page

NOMENCLATURE

Symbol	Description	Units
σ	Stress	Nm^{-2}
σ^o	Maximum stress amplitude	Nm^{-2}
σ_Y	Yield stress	Nm^{-2}
$\sigma_{U.}$	Ultimate stress	Nm^{-2}
Y	Young's modulus	Nm^{-2}
ε	Strain	mm^{-1}
ε^o	Maximum strain amplitude	mm^{-1}
ε_Y	Yield strain	mm^{-1}
ε_U	Ultimate strain	mm^{-1}
η	Viscosity of dashpot	Pa sec
T_o	Reference temperature	C
a_T	Temperature dependent shift factor	
D(t)	Creep compliance	Pa^{-1}
$D'(\omega)$	Extension storage compliance	Pa^{-1}
$D''(\omega)$	Extension loss compliance	Pa^{-1}
$D^*(\omega)$	Extension complex compliance	Pa^{-1}
E(t)	Relaxation modulus	Pa
$E'(\omega)$	Extension storage modulus	Pa

NOMENCLATURE- Continued

Symbol	Description	Units
$E''(\omega)$	Extension loss modulus	Pa
$E^*(\omega)$	Extension complex modulus	Pa
δ	Phase angle between stress and strain	Degrees
$\Delta(t)$	Unit step function	
$\overline{D}$	Electric flux density	Cm^{-2}
e	Dielectric constant	Fm^{-1}
$\overline{E}$	Electric Field	Vm^{-1}
d	Piezoelectric coefficient	CN^{-1}
s	Elastic compliance coefficient	m^2N^{-1}
G	Shear modulus	m^2N^{-1}
ν	Poisson's ratio	
V_{act}	Actual voltage produced by sample	V
V_{osc}	Measured voltage produced by sample	V
$\overline{E}^{o}$	Maximum electric field amplitude	Vm^{-1}
ϕ	Phase angle between E_{act} and strain	degrees
z	Thickness	m

ABSTRACT

Material properties of polyvinylidene fluoride are determined. It is shown that these properties are anisotropic and time dependent. The instantaneous elastic properties are found and compared to published results. A model describing the time dependent behavior of the material is then developed. It is shown that the theory of viscoelasticity can successfully accomplish this task, and the parameters describing this theory in the separate material directions are determined from dynamic mechanical testing and analysis. The results of these tests are then compared to results obtained from traditional creep tests. The piezoelectric coupling properties are also examined. It is shown that these coefficients are independent of studied parameters within measured ranges. The values of these coefficients are determined and compared to published results.

CHAPTER 1

INTRODUCTION

The development of an active vibration suppression system specifically targeted for vibration control for experimental payloads aboard space vehicles has been underway at Montana State University since 1994. The project aims at using a low force, high displacement actuators in conjunction with sensors and control circuitry to minimize 3-D vibration accelerations from spacecraft mechanisms that can adversely affect sensitive experimental payloads.

Contributions to the project have been made by more than 16 individuals from both the physics and mechanical engineering departments. The efforts made toward this end can be divided into four main areas consisting of actuator design and development, feedback system analysis and optimization, accelerometer development, and electro-mechanical characterization.

The first area, actuator design and development, has focused on producing a low force, high displacement actuator capable of providing precise position control for the payload. The actuators have been constructed of piezoelectric polyvinylidene fluoride (PVDF or PVF_2) thin films (28μm thick) in a bellows configuration, as shown in Figure 1-1. This design has utilized two piezoelectric bimorphs glued together, creating the final form. Strategic application of electric fields to the electrodes of the bimorphs results in

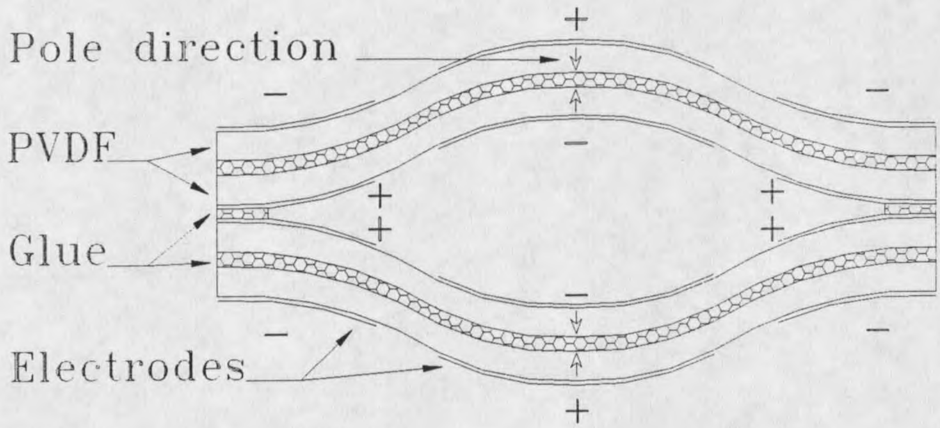

Figure 1-1. PVDF double bimorph actuator.

vertical displacement of the actuator in a known direction. Current actuator designs use voltages near 1000V and achieve vertical displacements of 1-3 mm over a range of frequencies from 0 to 25 Hz.

The next two areas of design effort focus on the electronic control of the actuators using feedback and feedforward signals from sensors. The control circuitry uses information from sensors perceiving the motion of the space vehicle and the payload as well as knowledge of actuator characteristics to produce an output signal which would then be used to control the actuators. Optimization of this system involves minimizing accelerations without allowing the payload to contact the walls of the payload enclosure. The objective thus involves providing minimal payload movement while ensuring that the payload properly "tracks" the space vehicle.

Design and development of both the actuator and the control system depends heavily on precise knowledge of the actuator's electro-mechanical properties. Without accurate description of the material response to a given set of conditions, the control system would be incapable of providing the corrective steps necessary to minimize accelerations. Also, the mechanical properties are critical in terms of describing the passive vibration response of the actuator. In addition, material properties are required to predict the usable conditions for the actuators, such as the operating temperature, load, and frequency range. Material characterization could also lead to future improvements of the actuator by tailoring it's design to the specific strengths of the material. For these reasons, the material properties of PVDF are necessary for the effective design of active control devices. The accurate characterization of these properties is the subject of this thesis.

Chapter 2 of this thesis provides a background into PVDF. This includes a description of the manufacturing processes that affects the microstructural form of the material. This is necessary for understanding the methodology behind the experimental program. Also, the known physical properties of PVDF are listed and discussed.

The third chapter contains a theoretical background of the constitutive laws describing the phenomena of piezoelectricity. A background is also given for the theory of viscoelasticity, which will be used to model the time dependent effects of the mechanical material response. The basis of an experimental technique developed to characterize these effects will then be given as a special case of this theory.

The fourth chapter describes the objectives and the components of the experimental program dedicated to determining the mechanical and electro-mechanical coupling properties of PVDF. Each of the separate tests conducted will be considered individually in chapters 5 to 8. This includes a list of the parameters that each test is aimed at characterizing, a description of each experimental setup, and the data reduction steps, and the results of the experiment.

Chapter 5 describes the testing methods used to determine the instantaneous elastic properties of PVDF. The sixth chapter outlines the tests aimed at determining the significance of time dependent effects on the mechanical response of the material. The characterization of the viscoelastic functions describing this time dependence from dynamic mechanical testing and analysis is described in chapter 7. The eighth chapter then illustrates the testing techniques used to determine the properties of the piezoelectric strain coefficients.

The final chapter is dedicated to a discussion of the experimental results and the conclusions that can be drawn from them.

CHAPTER 2

MICROSTRUCTURE AND PHYSICAL PROPERTIES OF PVDF

The material being characterized in this study is polyvinylidene fluoride (PVDF or PVF_2). The strong piezoelectric effect in PVDF was discovered in 1969 by Kawai [1]. Piezoelectric materials are those which exhibit a linear coupling between strain and electric field. Electric polarization of a material subjected to mechanical stress is known as the direct piezoelectric effect. Conversely, the straining of a material produced under the presence of an electric field is known as the converse piezoelectric effect. Some other materials that exhibit these characteristics include crystals such as $LiNbO_3$ and $LiTaO_3$, ceramics such as $BaTiO_3$, and polymers like PVF.

The piezoelectric response found in PVDF and its copolymers are among the largest of all polymers known [2]. This, combined with other beneficial characteristics of PVDF, such as its ease of shaping, low density, mechanical strength and flexibility, wide frequency response, high stability, and its availability in large dimensions at a relatively low cost, has generated considerable interest in the material. PVDF has been used in an ever increasing range of applications, including microphones, ultrasonic transducers, and strain gages [3].

PVDF is a semicrystalline polymer, $(-CH_2-CF_2-)_n$ as shown in Figure 2-1, that has crystallinity of 40-50%. From melt temperatures, PVDF forms lamellar crystals embedded

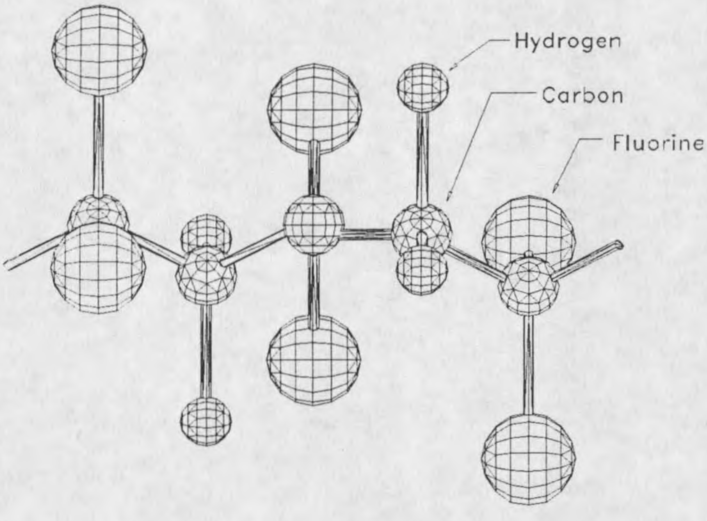

Figure 2-1. Molecular structure of PVDF polymer before poling.

in an amorphous background. The amorphous phase exhibits the behavior of a supercooled liquid having a liquid-glass transition at about -50 °C [1]. The polymer molecules are known to form four possible crystal structures termed α, α_p, β, and γ phases. The piezoelectric properties are believed to be mainly attributable to the β and α_p phases [1]. These crystal structures form from melt into spherulitic structures composed of crystalline lamella radiating from the center. These lamellae are made up of molecular chains that fold back upon themselves many times to form surfaces normal to the radii of the spherulites [4].

Because the hydrogen atoms are positively charged and the fluorine atoms are negatively charged with respect to the carbon atoms, PVDF is inherently polar. However, the molecular chains pack to form a polar cell in only two of the four possible crystal phases, β and α_p. These two forms therefore result in crystal lamellae that can have a net polarization. However, even the presence of polar crystallites does not yield piezoelectricity in PVDF. This is due to the fact that the net polar moment of a region of the material is zero because of the random orientation of the individual crystallites [2]. For this reason, extruded sheets of PVDF are stretched and poled, thereby altering the molecular structure. Stretching serves to break up the spherulitic structures and orient the individual lamella so that the molecular axes are parallel to the stretch direction [2]. Poling of the stretched sheets is then achieved by holding them at temperatures above the glass transition so that the molecules are free to rotate as shown in Figure 2-2. In this process, PVDF is typically held at 130°C for up to 2 hours under an electric field of up to 100 kV mm^{-1} [5]. This field causes a rotation of molecular segments within the individual lamellae, thereby causing a net polarization. The material is then cooled to room temperature while maintaining the electric field, which permanently aligns the molecular dipoles thus giving the film piezoelectric properties. The orientation of the crystal

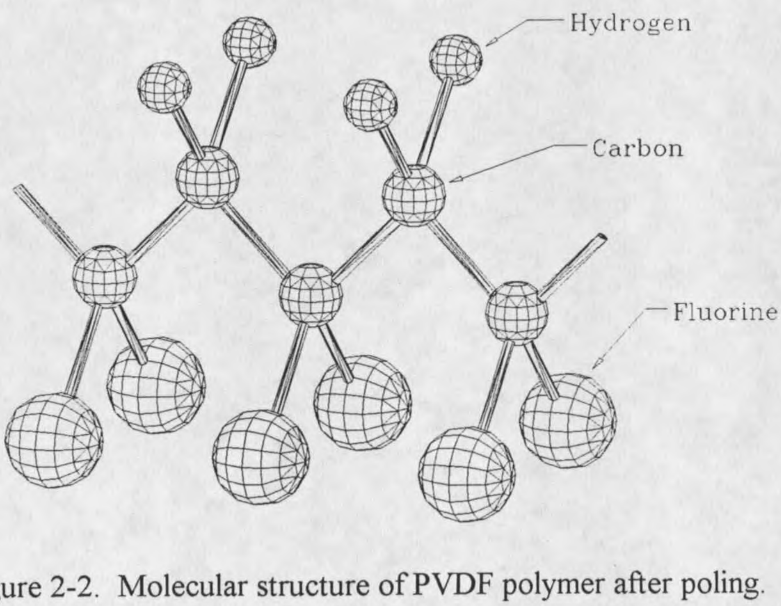

Figure 2-2. Molecular structure of PVDF polymer after poling.