NONLINEAR ELASTIC CONSTITUTIVE MODEL FOR PVDF

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Abstract

This paper concerns the development of a constitutive model of Polyvinylidene fluoride (PVDF), a piezoelectric polymer. Suitable assumptions are made based on experimental data available in literature. The model is proposed for Form II of the PVDF material. Mooney-Rivlin and Neo-Hookean models are assumed to predict the finite elastic deformation characteristics of the material and experimental data are fitted to test the range of validity of the model. Predictions based on the Mooney-Rivlin and the Neo-Hookean models show that the Mooney-Rivlin model correlates very well with the experimental data within reasonably finite strain ranges (deviation upto 3-5%) whereas the Neo-Hookean model deviates largely from the experimental (about 50%).

Keywords: Piezoelectric polymer, Nonlinear elasticity, PVDF, Polyvinylidene Fluoride, Smart Materials

Introduction

Polyvinylidene fluoride (PVDF) is a semi-crystalline polymer which is inherently polar and is piezoelectric. A piezoelectric material is a material that is capable of giving an electrical response for a given mechanical input. PVDF was discovered in 1969 by Kawai [1]. PVDF polymer has better piezoelectric properties than any other organic material [1]. PVDF also has certain advantages over other piezoelectric materials like piezoceramics, since it is light weight and compliant. It has better dielectric strength, has high sensitivity to mechanical loads and is robust. Due to these qualities, PVDF has been increasingly used in applications such as sensors and actuators in applications involving lightweight and flexible structures [2].

PVDF is available in four different forms (I, II, IIB and III). Form I is piezoelectric. Form II is non-piezoelectric. Form III and IIB are less piezoelectric than Form I [1]. The stress strain response of PVDF is, in general, strain rate sensitive like other polymeric materials [3,4]. Form I PVDF is shown to exhibit nonlinear elasticity [3,4]. It also exhibits nonlinearity in its electro-mechanical (stress to electric field relationship) response [5]. Form II VDF is non-piezoelectric and its mechanical response is nonlinearly elastic [6].

Since Form II PVDF is used in applications in which it can be subjected to high static and dynamic stresses such as

a) process equipment
b) tank linings
c) pump and valve components
d) pipe flanges and spacers
e) components for wet process stations and
f) food trays for high heat applications,

there is a need for a constitutive model, which would describe the nonlinear elastic and electromechanical properties of PVDF. The main objective of this paper is to propose and develop a constitutive model for nonlinear elasticity for the applications mentioned above. The nonlinear elastic properties of form II PVDF from the experimental data available in the literature is used for the modeling of PVDF. Two of the popular models from rubber elasticity, viz, Neo-Hookean and Mooney-Rivlin model are used to model Form II PVDF. It is found that the Neo-Hookean model characterizes the stress strain of the material with as much as 50% deviation at higher strains, and Mooney Rivlin model characterizes accurately with only 5% deviation at higher strains.

In the first section of the paper, the existing data for PVDF is analyzed. Based on the analysis, in the second section of the paper appropriate observations are made on the material behavior and suitable assumptions have been

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proposed. Using these assumptions, models are proposed and relevant material parameters have been obtained. Correlations have been made to verify the effectiveness of the proposed models. Finally in the last section of the paper, the implications of the proposed model is discussed.

Experimental Data and Observations

Experimental Data Available for Mechanical Response of PVDF

Description of the mechanical properties of PVDF described in this section is based on the experimental program involving compression tests on Form II PVDF (Fig. 1) under various hydrostatic pressures done by K.D. Pae, K.Vijayan, et. al (1984) [6]. In these tests, Form II PVDF is subjected to uniaxial loading under hydrostatic pressure. The rate of loading was 0.000333 cm/cm/sec. The maximum uniaxial stress experienced by the material in the experiments is around 60 Mpa. The maximum strain is around 8%. The stress strain tests show that the relationship is nonlinear for higher stresses. This nonlinear material response cannot be captured by simple material models of linearized isotropic elasticity. Hence, there is a need to develop nonlinear elastic models that can capture this nonlinear response.

Assumptions Made About the Material for Form II

Following are the assumptions made about the behavior of Form II PVDF.

a) PVDF is isotropic : This assumption regarding Form II PVDF is reasonable. Since it is non piezoelectric, it implies that the material has symmetry in mechanical response and is not anisotropic. The advantage of this assumption is that the stress strain curve in a single direction is enough to characterize the material. If this assumption was not true, the stress-strain curve would have to be determined along all the principal directions.

b) PVDF is incompressible : Since PVDF is a polymer showing a rubberlike behavior (large deformation), the assumption for material deformation used in rubber elasticity are assumed to be valid also for PVDF. Most simplified models of rubber elasticity assume that the material is incompressible and hence the same assumptions are used for PVDF. The importance of the second assumption is that it simplifies the model, as no data regarding the compressibility and transverse strains are required to do the modeling. The constants can be interpolated for various pressures for Form II. The pressure sensitivity of the stress-strain curves that are shown in Fig. 1, is the familiar confining effect, that is manifested in the uniaxial response. Since the material is confined to expand laterally under hydrostatic pressure, greater loads are required to produce the same axial displacements, compared to the displacements that are obtained in an unconfined axial stress-strain test. This phenomenon is familiar in testing of granular materials like soils. This behavior is not to be confused with the assumptions of incompressibility, which is an assumption that is valid for any control volume of the material.

c) The elastic limit is the breaking stress : This assumption is reasonable, since PVDF is a polymer which exhibits creep. Since unloading experiments are generally not done to test the existence of yield of thin films, the implication of this assumption is that, the nonlinear elastic curve can be taken up to the breaking stress [7] and this assumption is generally accepted for elastomers.

Constitutive Modelling of PVDF (Form II)

Based on the assumptions made in the previous section, a proper model is chosen to fit the experimental data. The Neo-Hookean model and the Mooney-Rivlin models are chosen for the purpose of fitting the data. Both the models are for incompressible and isotropic materials and are obtained by incorporating the above conditions on the strain energy function, which enables the strain energy function to be expanded as a polynomial function of the strain invariants of the finite strain tensor. The Neo-Hookean model is a one parameter model which is a linear expansion of the first invariant of strain. The Mooney-Rivlin model is the linear expansion of the first and second invariants of strain [8].
Since these two models are the simplest popular models with least number of coefficients, which can be implemented easily, the constants obtained from these models from the data will be useful for engineers for predicting the response of PVDF.

**Neo-Hookean Model**

Since isotropy is assumed, one can postulate the existence of a strain energy density, $\psi$ which can be expressed as a function of the three strain invariants of cauchy finite strain tensor [8]

$$\psi = \psi(I_1, I_2, I_3)$$

where $I_1$, $I_2$ and $I_3$ are the strain invariants. The strain invariants can be defined in terms of the principal strains $\lambda_1$, $\lambda_2$ and $\lambda_3$ of a material and are given by

$$I_1 = \lambda_1^2 + \lambda_2^2 + \lambda_3^2$$
$$I_2 = 1/\lambda_1^2 + 1/\lambda_2^2 + 1/\lambda_3^2$$
$$I_3 = \lambda_1^2 \lambda_2^2 \lambda_3^2$$

Since incompressibility is assumed for Form II, $I_2=1$ therefore, $\psi = \psi(I_1, I_2)$ [7].

The Piola Kirchoff stress, which is the force per unit undeformed cross-section, in the principal directions can be obtained by taking the partial derivative of $\Psi$ with the corresponding principal extensions. Denoting $F_i$ as the Piola Kirchoff stress along the principal direction 'i', we can write

$$F_i = \frac{\partial \psi}{\partial \lambda_i}$$

For a simple extension or compression test on a material that is incompressible and isotropic in nature, the extension is primarily in the direction of the application of the load. Denoting this direction as direction 1, the extension ratios are given by

$$\lambda_1 = \lambda$$
$$\lambda_2 = \lambda_3 = 1/\lambda$$

$$F/(2(\lambda - 1/\lambda^2)) = C_1/\lambda$$

where $\lambda$ is the extension or compression ratio and $F$ is the Piola Kirchoff stress along the direction of principal extension $\lambda$ [10].

A linear interpolation between $F/(2(\lambda - 1/\lambda^2))$ and $1/\lambda$ would help us to determine the constant $C_1$.

The Figs 2, 3, 4 and 5 shows experimental results and the best fit of the model for the compression tests. Each of the above figures represent the mechanical response for a different hydrostatic pressure $P$ and hence would be characterized with a different constant $C_1$. A least square fit can then be obtained between $C_1$ and $P$ for the range of data available.

This fit was found to be:

$$C_1 = -28.1411*P - 104.4075$$

Where $C_1$ is in units of N/sqmm.

Eq.(1) would be useful for doing simplified Neo-Hookean analysis of PVDF at various bias pressures.

The curves clearly show that the model fits the experimental curves only up to strain level of 5-6%. Beyond that, the deviation from the model is very sharp and high (about 40%). To model the higher strain behavior, it will be necessary to use a two parameter like a Mooney Rivlin model that is described in the next section.
Mooney Rivlin Model

The Mooney Rivlin model is given by:

$$\psi = C_1 (I_1 - 3) + C_2 (I_2 - 3)$$

where $C_1$ and $C_2$ are constants to be determined [8].

Following the same procedure as indicated in the earlier section, we get the following expression for the stress as:

$$F/(2*(\lambda - 1/\lambda^2)) = C_1 + C_2/\lambda$$

where $F$ is the Piola Kirchoff stress and $\lambda$ is the extension ratio or compressible ratio.

A linear interpolation between $F/(2*(\lambda - 1/\lambda^2))$ and $1/\lambda$ would help us to determine the constants $C_1$ and $C_2$.

The Figs. 6, 7, 8 and 9 shows experimental results and the best fit of the model for the compression tests.

The least square fit of the constants $C_1$ and $C_2$ in terms of hydrostatic pressure $P$ for compression (upto 8.75% compression) was found to be:

$$C_1 = 926.9 + 158.6P$$

$$C_2 = -1081.3 - 195P$$

Where $C_1$ and $C_2$ are in units of N/mm$^2$. It is found from the figures that the model fits the experimental curves fairly accurately. Eq. (2) would be useful for doing simplified Mooney-Rivlin analysis of PVDF at various bias pressures. Mooney Rivlin model performs better than the Neo-Hookean model since even at higher strain levels, the deviation from the experimental data is only about 4-5% whereas for the Neo-Hookean model, the deviation is about 40-50%.

Results and Discussions

1. When comparison is made between the Mooney-Rivlin model and the Neo-Hookean model, which is a subset of the Mooney-Rivlin model, it is found that the Mooney Rivlin model predicts the response well within 8.75% strain (accuracy of 2-3%), whereas the deviations are large for the Neo-Hookean model (40-50%).
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Fig. 6 Experimental and Mooney rivlin model curve for Form II at p=0 Kbar

Fig. 8 Experimental and Mooney rivlin model curve for Form II at p=2 Kbar

Fig. 7 Experimental and Mooney rivlin model curve for Form II at P=1 Kbar

Fig. 9 Experimental and Mooney rivlin model curve for Form II at P=3 Kbar

2. The mechanical response of PVDF is viscoelastic in nature. The elastic component of the viscoelastic response can be obtained by doing stress-strain characterization at low strain rates. Hence, the mechanical characterization done in this paper will be useful in building a good viscoelastic model for the polymer.

3. The major implication of the model is that it captures the mechanical response of an electro-mechanical model of PVDF. The present work will be useful in predicting the pure mechanical response of Form II when subjected to high stresses as in the case of tank and lining applications.

Conclusions

The time independent material characteristics of PVDF Form II is modeled based on the theory of nonlinear elasticity. Mooney-Rivlin model is adopted for Form II material. The constants for Form II were found for various pressures for both tension and compression. A suitable interpolation is obtained for the pressure vs $C_1$ and $C_2$ constants for Form II PVDF. It is found that the Mooney-Rivlin model predicts the response of PVDF better than the Neo-Hookean model, which is a subset of the Mooney-Rivlin model. It can be concluded that the constants found out can be used for the prediction of stress-strain response at low strain rates like in tank and lining.
applications. Since the molecular structure of the material remains the same between Form I and Form II, we expect no drastic differences between the mechanical responses of Form I and Form II. Hence, it is postulated a similar rubber elasticity model would be valid for a Form I PVDF also. This phenomenon is being investigated by the authors.

References