Available online at www.sciencedirect.com
SCIENCE DIRECT
Polymer 44 (2003) 8195–8199
polymer
www.elsevier.com/locate/polymer

Variational model for ionomeric polymer–metal composite

Ji-Huan He[a,b,*], Hong-Mei Liu[a], Ning Pan[b,c]

[a]Center of Physics of Fibrous Materials, College of Science, Donghua University, P.O. Box 471, 1882 Yan'an Xilu Road, Shanghai 200051, People's Republic of China
[b]Center of Physics of Fibrous Materials, Key Lab of textile Technology, Ministry of Education of China, Donghua University, Shanghai, People's Republic of China
[c]Division of Textiles, Department of Biological and Agricultural Engineering, University of California, Davis, CA 95616, USA

Received 17 September 2003; received in revised form 16 October 2003; accepted 18 October 2003

Abstract

Governing equations for one-dimensional ionic polymer–metal composites are reviewed and then cast into the framework of a variational statement. Starting from a trial-Lagrangian, a generalized functional is derived through a systematic procedure of the semi-inverse method proposed by Ji-Huan He. All field equations and boundary conditions are cast into Euler equations of the obtained functional, leading to much convenience in incorporating analytical and numerical approaches.

Keywords: Variational theory; Electroactive polymer (EAP)

1. Introduction

The growing interest of engineers in ionomeric polymer–metal composites (IPMC) has arisen from the promising perspectives and possibilities provoking drastic phase transitions by inducing small changes in external conditions [1]. For technical applications, electrical actuators made of IPMC can be utilized in various areas. When voltage is applied, the resulting electrostatic forces compress a film in thickness and expand it in area. Additionally, IPMC is of particular interest because of low cost of materials and flexibility of polymers to be tailored to particular applications. Therefore, the mathematical models for IPMC have played and continue to play an important role in enhancing our understanding of actuation mechanism. Partial differential models have been used extensively to study the behaviors, but no variational model, as far as the authors know, exists in open literature. One advantage of variational model is that it provides us with various approximate analytical and numerical approaches to dynamics simulation.

The rapid development of computer science and the finite element applications reveals the importance of searching for a classical variational principle for the discussed problem, which is the theoretical basis of the finite element methods [2]. Furthermore, such variational formulations have served as a basis for development of variety of approximate methods of analysis. The recent research reveals that variational theory is also a powerful tool for meshless method or element-free method [3].

However, IPMC has not been frequently viewed from a variational point of view. In this paper we will apply the semi-inverse method [4] to establish a variational model for the entitled problem, whose stationary conditions satisfy all the field equations and boundary conditions. An advantage of the semi-inverse method is that it can provide a powerful mathematical tool to the search for variational formulations for a rather wide class of physic problems without using the well-known Lagrange multipliers, which can result in variational crisis (the constrains can not eliminated after the identification of the multiplier or the multipliers become zero) [5], furthermore, to use the Lagrange multipliers, we must have a known variational principle at hand, a situation which not always occurs in continuum physics.

* Corresponding author. Address: Center of Physics of Fibrous Materials, College of Science, Donghua University, P.O. Box 471, 1882 Yan'an Xilu Road, Shanghai 200051, People's Republic of China. Tel.: +86-216-237-9917; fax: +86-216-237-3137.
E-mail address: jhhe@dhu.edu.cn (J.H. He).

0032-3861/$ - see front matter © 2003 Elsevier Ltd. All rights reserved.
doi:10.1016/j.polymer.2003.10.043

2. Governing equation

The dynamics of ionic polymer gels in an electric field are investigated by many authors. Details can be found in a recently published book [1], ample references can be found there. Hereby we use an electromechanical model for ionic polymer metal composites proposed by Nemat-Nasser et al. [6].

For better illustration of the basic procedure of searching for a variational model for the discussed problem, making the underlying idea clear and not darkened by the unnecessarily complicated form of mathematical expressions, we consider here only a simple example: one-dimensional case. The governing equations read [1,6]

$$\frac{\partial D}{\partial x} = \rho, \tag{1}$$

$$D = k_e E, \tag{2}$$

$$E = -\frac{\partial \varphi}{\partial x}, \tag{3}$$

$$\frac{\partial C^+}{\partial t} + \frac{\partial J}{\partial x} = 0. \tag{4}$$

Here, D, E, φ, respectively, denote the electric displacement, the electric field, and the electric potential. ρ is the charge density defined by $\rho = F(C^+ - C^-)$, C^+ and C^- are the positive and negative ion densities, respectively, F is Faraday's constant, k_e is the effective electric permittivity of the polymer. J denotes ion flux vector given by

$$J = -D^+\left[\frac{\partial C^+}{\partial x} - \frac{C^+F}{RT}E + \frac{C^+V^{+w}}{RT}\frac{\partial p}{\partial x}\right] + C^+ v. \tag{5}$$

Here v is water flow velocity, defined by Darcy's law

$$v = D_h\left[C^- FE - \frac{\partial p}{\partial x}\right]. \tag{6}$$

In these two equations, D^+ and D_h are the ionic diffusivity and hydraulic permeability coefficients, respectively; R is the gas constant, T is the absolute temperature, p is the fluid pressure, and

$$V^{+w} = M^+(V^+/M^+ - V^w/M^w),$$

in which V^+ and V^w are partial molar volumes of the cation and water, respectively, and M^+ and M^w are the corresponding molar weights.

Boundary conditions

At $x = x_0$ we prescribe $D = \bar{D}_0$, $(\partial p/\partial x) = \bar{p}_{x0}$, and $v = \bar{v}_0$; and at $x = x_1$, we give $D = \bar{D}_1$, $(\partial p/\partial x) = \bar{p}_{x1}$, and $v = \bar{v}_1$.

Though the above one-dimensional problem can with some algebraic difficulty be solved using Fourier series, it becomes an extraordinary tedious work if not possible to obtain a closed-form expression for full three-dimensional problems and even non-linear ones by Fourier series. Variational theory provides us with both analytical (e.g. Ritz method) and numerical (e.g. finite element method) approaches with ease. This paper is a preliminary report in the spirit of applied mechanics (the calculus of variations) applied to a problem in polymer science. In order to allow the readers to follow the basic idea of variational approach, an illustrating example is given in the appendix.

Some of above equations will be rewritten in general forms which are easy to be cast in the framework of some variational statements by the semi-inverse method [4].

Eq. (6) is written in the form

$$E = \frac{1}{D_h C^- F}\left(v + D_h\frac{\partial p}{\partial x}\right). \tag{7}$$

Substituting Eq. (5) into Eq. (4), we have

$$\frac{\partial C^+}{\partial t} - D^+\frac{\partial^2 C^+}{\partial x^2} + \frac{C^+D^+F}{RT}\frac{\partial E}{\partial x} - \frac{C^+D^+V^{+w}}{RT}\frac{\partial^2 p}{\partial x^2} + C^+\frac{\partial v}{\partial x} = 0. \tag{8}$$

Further applying the relation, Eq. (7), the above equation can be cast into a more general form:

$$\frac{\partial C^+}{\partial t} - D^+\frac{\partial^2 C^+}{\partial x^2} + a\frac{C^+D^+F}{RT}\frac{\partial E}{\partial x} + \left(b\frac{C^+D^+}{C^-RT} - \frac{C^+D^+V^{+w}}{RT}\right)\frac{\partial^2 p}{\partial x^2} + \left(C^+ + b\frac{C^+D^+}{D_h C^- RT}\right)\frac{\partial v}{\partial x} = 0, \tag{9}$$

where a and b are constants, and meet the identity $a + b = 1$.

Eq. (2) can also be written in the following general form

$$D = \alpha k_e E + \beta k_e E = \alpha k_e E + \frac{\beta k_e}{D_h C^- F}\left(v + D_h\frac{\partial p}{\partial x}\right), \tag{10}$$

where α and β are constants with relation $\alpha + \beta = 1$.

3. Variational model

The essence of the proposed method is to construct an energy-like functional with a certain unknown function, which can be identified step by step. An energy-like trial-functional with five kinds of independent variations (D, E, φ, p and v) can be constructed as follows

$$\Pi(D, E, \varphi, p, v) = \int_{x_0}^{x_1} L\,dx + \mathrm{BI}, \tag{11}$$

where L is a trial-Lagrangian and BI is the boundary items. There exist many approaches to the construction of trial-Lagrangian, illustrating examples can be found in the author's previous publications [7,8].

We begin with the following trial-Lagrangian:

$$L = -D\frac{\partial \varphi}{\partial x} - \rho\varphi + F(D, E, p, v), \tag{12}$$

where F is an unknown function to be further determined, and it is free from the variable φ.

It is easy to see that the stationary condition with respect to φ is Eq. (1). Now the stationary condition with respect to D reads

$$-\frac{\partial \varphi}{\partial x} + \frac{\delta F}{\delta D} = 0, \tag{13}$$

where $\delta F/\delta D$ is the variational derivative, which is defined as

$$\frac{\delta F}{\delta D} = \frac{\partial F}{\partial D} - \frac{\partial}{\partial x}\left(\frac{\partial F}{\partial D_x}\right), \ D_x = \frac{\partial D}{\partial x}.$$

We search for such an F that the above trial-Euler equation (13) satisfies one of field equations, saying, Eq. (3). Accordingly, we can identify the unknown F in the form

$$F = -DE + F_1. \tag{14}$$

The Lagrangian, Eq. (12), therefore, can be renewed as follows

$$L = -D\frac{\partial \varphi}{\partial x} - \rho\varphi - DE + F_1, \tag{15}$$

where F_1 is a newly introduced unknown function with less variables. It is an unknown function of E, p, v and/or their derivatives.

By the same operation, the Euler equation for δE reads

$$-D + \frac{\delta F_1}{\delta E} = 0. \tag{16}$$

If we set

$$\frac{\delta F_1}{\delta E} = \alpha k_e E + \frac{\beta k_e}{D_h C^- F}\left(v + D_h\frac{\partial p}{\partial x}\right), \tag{17}$$

then the above trial-Euler equation (16) turns out to be the field Eq. (10). From the above relation, we can easily identify F_1 in the form

$$F_1 = \frac{1}{2}\alpha k_e E^2 + \frac{\beta k_e}{D_h C^- F}\left(v + D_h\frac{\partial p}{\partial x}\right)E + F_2, \tag{18}$$

where F_2 is an unknown function of p and v.

The trial-Lagrangian can be further updated as

$$L = -D\frac{\partial \varphi}{\partial x} - \rho\varphi - DE + \frac{1}{2}\alpha k_e E^2 + \frac{\beta k_e}{D_h C^- F} \times\left(v + D_h\frac{\partial p}{\partial x}\right)E + F_2. \tag{19}$$

Now the trial-Euler equation for δp reads

$$-\frac{\beta k_e}{C^- F}\frac{\partial E}{\partial x} + \frac{\delta F_2}{\delta p} = 0. \tag{20}$$

Comparing Eq. (20) with Eq. (9), we set

$$\frac{\beta k_e}{C^- F} = a\frac{C^+ D^+ F}{RT}. \tag{21}$$

Therefore, we have

$$\begin{aligned}\frac{\delta F_2}{\delta p} &= \frac{\beta k_e}{C^- F}\frac{\partial E}{\partial x} = a\frac{C^+ D^+ F}{RT}\frac{\partial E}{\partial x} \\ &= -\frac{\partial C^+}{\partial t} + D^+\frac{\partial^2 C^+}{\partial x^2} \\ &\quad - \left(b\frac{C^+ D^+}{C^- RT} - \frac{C^+ D^+ V^{+\mathrm{w}}}{RT}\right)\frac{\partial^2 p}{\partial x^2} \\ &\quad - \left(C^+ + b\frac{C^+ D^+}{D_h C^- RT}\right)\frac{\partial v}{\partial x},\end{aligned} \tag{22}$$

from which we determine F_2 in the form

$$\begin{aligned}F_2 = &-\frac{\partial C^+}{\partial t}p + D^+\frac{\partial^2 C^+}{\partial x^2}p + \frac{1}{2} \\ &\times\left(b\frac{C^+ D^+}{C^- RT} - \frac{C^+ D^+ V^{+\mathrm{w}}}{RT}\right) \\ &\times\left(\frac{\partial p}{\partial x}\right)^2 + \left(C^+ + b\frac{C^+ D^+}{D_h C^- RT}\right)v\frac{\partial p}{\partial x} + F_3.\end{aligned} \tag{23}$$

We update the Lagrangian in the form

$$\begin{aligned}L = &-D\frac{\partial \varphi}{\partial x} - \rho\varphi - DE + \frac{1}{2}\alpha k_e E^2 + \frac{\beta k_e}{D_h C^- F} \\ &\times\left(v + D_h\frac{\partial p}{\partial x}\right)E - \frac{\partial C^+}{\partial t}p + D^+\frac{\partial^2 C^+}{\partial x^2}p + \frac{1}{2} \\ &\times\left(b\frac{C^+ D^+}{C^- RT} - \frac{C^+ D^+ V^{+\mathrm{w}}}{RT}\right) \\ &\times\left(\frac{\partial p}{\partial x}\right)^2 + \left(C^+ + b\frac{C^+ D^+}{D_h C^- RT}\right)v\frac{\partial p}{\partial x} + F_3.\end{aligned} \tag{24}$$

Here F_3 is an unknown function of v. We obtain the following stationary condition with respect to v :

$$\frac{\beta k_e}{D_h C^- F}E + \left(C^+ + b\frac{C^+ D^+}{D_h C^- RT}\right)\frac{\partial p}{\partial x} + \frac{\delta F_3}{\delta v} = 0. \tag{25}$$

This equation should be Eq. (6). We, therefore, set

$$\frac{\beta k_e}{D_h C^- F} = kD_h C^- F, \tag{26}$$

and

$$C^+ + b\frac{C^+ D^+}{D_h C^- RT} = -kD_h, \tag{27}$$

where k is a non-zero constant. Accordingly, we have

$$\frac{\delta F_3}{\delta v} = -kD_h\left[C^- FE - \frac{\partial p}{\partial x}\right] = -kv, \tag{28}$$

which leads to the result

$$F_3 = -\frac{1}{2}kv^2. \tag{29}$$

The following finial Lagrangian is obtained

$$\begin{aligned} L = {} & -D\frac{\partial \varphi}{\partial x} - \rho\varphi - DE + \frac{1}{2}\alpha k_e E^2 + \frac{\beta k_e}{D_h C^- F} \\ & \times\left(v + D_h\frac{\partial p}{\partial x}\right)E - \frac{\partial C^+}{\partial t}p + D^+\frac{\partial^2 C^+}{\partial x^2}p + \frac{1}{2} \\ & \times\left(b\frac{C^+D^+}{C^-RT} - \frac{C^+D^+V^{+w}}{RT}\right) \\ & \times\left(\frac{\partial p}{\partial x}\right)^2 + \left(C^+ + b\frac{C^+D^+}{D_hC^-RT}\right)v\frac{\partial p}{\partial x} - \frac{1}{2}kv^2. \end{aligned} \tag{30}$$

The constants a, b, α, β and k are determined from the relations $a + b = 1$, $\alpha + \beta = 1$, Eqs. (21), (26) and (27), leading to the results

$$\beta = -\frac{F^2 - C^-C^+(C^-D_hRTF + D^+)}{k_eRT(F^2 - 1)}, \quad \alpha = 1 - \beta,$$

$$k = \frac{k_e}{(D_hC^-F)^2}\beta, a = -\frac{F^2 - C^-C^+(C^-D_hRTF + D^+)}{C^-C^+D^+F^2(F^2 - 1)},$$

$$b = 1 - a.$$

By incorporating boundary conditions, we finally obtained the following variational principle:

$$\begin{aligned} \Pi(D, E, \varphi, p, v) = {} & \int_{x_0}^{x_1} L\,dx + \bar{D}_0\varphi|_{x=x_0} - \bar{D}_1\varphi|_{x=x_1} \\ & -\bar{p}_{x0}\left(b\frac{C^+D^+}{C^-RT} - \frac{C^+D^+V^{+w}}{RT}\right)p\bigg|_{x=x_0} \\ & +\bar{p}_{x1}\left(b\frac{C^+D^+}{C^-RT} - \frac{C^+D^+V^{+w}}{RT}\right)p\bigg|_{x=x_1} \\ & -\bar{v}_0\left(C^+ + b\frac{C^+D^+}{D_hC^-RT}\right)p\bigg|_{x=x_0} \\ & +\bar{v}_1\left(C^+ + b\frac{C^+D^+}{D_hC^-RT}\right)p\bigg|_{x=x_1}, \end{aligned} \tag{31}$$

where L is defined by Eq. (30).

4. Conclusions

We obtain, by the semi-inverse method, a variational formulation for ionic polymer–metal composites in terms of electric displacement, electric field, electric potential, pressure, and water flow velocity. The stationary conditions of the obtained functional satisfy all field equations and boundary conditions. The variational model is the basis for numerical approximation techniques. The result can be readily expanded to three-dimensional case, and it is also easy to take the thermal effect into consideration. From the obtained generalized variational principle, Eq. (31), various constrained variational functionals can be obtained by a systematic procedure of relaxing some admissibility conditions and imposing others [9].

Appendix A

We consider a differential equation in the form:

$$\frac{d^2y}{dx^2} + y + x = 0, \quad y(0) = y(1) = 0. \tag{A1}$$

The equation is simple, and it is easy to obtain the exact solution:

$$y_{ex} = \frac{\sin x}{\sin 1} - x. \tag{A2}$$

By the semi-inverse method, we obtain the following functional

$$J(y) = \int_0^1 \left\{\frac{1}{2}\left(\frac{dy}{dx}\right)^2 - \frac{1}{2}y^2 - xy\right\}dx. \tag{A3}$$

Minimizing the above functional results in the following stationary condition called Euler equation:

$$\frac{\partial L}{\partial y} - \frac{d}{dx}\frac{\partial L}{\partial y'} = 0, \tag{A4}$$

where $y' = dy/dx$ and $L = (1/2)(dy/dx)^2 - (1/2)y^2 - xy$. Substituting the results in Eq. (A4), we obtain

$$-y - x - \frac{d}{dx}\left(\frac{dy}{dx}\right) = 0, \tag{A5}$$

which is equivalent to Eq. (A1).

Now we apply the Ritz method to obtain an explicit analytical solution from Eq. (A3). The basic character of Ritz method is choose a trial-function satisfying the boundary conditions. We choose a simplest one in the form

$$y = cx(1 - x), \tag{A6}$$

where c is an unknown constant to be further determined. It is obvious that Eq. (A6) satisfies the boundary conditions $y(0) = y(1) = 0$.

Substituting Eq. (A6) into Eq. (A3), and integrating the result, we obtain a function of c:

$$J(c)=\int_0^1\left\{\frac{1}{2}c^2(1-2x)^2-\frac{1}{2}c^2x^2(1-x)^2-cx^2(1-x)\right\}\mathrm{d}x$$
$$=\frac{3}{20}c^2-\frac{1}{12}c. \quad \text{(A7)}$$

Minimizing Eq. (A7) to identify the constant c :

$$\frac{3}{10}c-\frac{1}{12}=0. \quad \text{(A8)}$$

So we obtain the following approximate solution:

$$y_{\text{app}}=\frac{5}{18}x(1-x). \quad \text{(A9)}$$

To illustrate its accuracy, we calculate the value at $x=0.5$. The exact value is $y_{\text{ex}}(0.5)=0.06974$, while the approximate one reads $y_{\text{app}}(0.5)=0.069444$. The 0.42% accuracy is remarkable good in view of the crude and simple trial-function.

References

[1] Bar-Cohen Y. Electroactive polymer (EAP), actuators as artificial muscles, reality, potential, and challenges. Washington: SPIE Press; 2001.
[2] Zienkiewicz OC, Taylor RL, 4th ed. The finite element method, vol.1. London: McGraw-Hill; 1989.
[3] He JH. Treatment of shocks in transonic aerodynamics in meshless method. Int J Turbo Jet-Engines 1999;16(1):19–26.
[4] He JH. Semi-inverse method of establishing generalized variational principles for fluid mechanics with emphasis on turbomachinery aerodynamics. Int J Turbo Jet-Engines 1997;14(1):23–8.
[5] He JH. Coupled variational principles of piezoelectricity. Int J Engng Sci 2000;39:323–41.
[6] Nemat-Nasser S, Li JY. Electromechanical response of ionic polymer–metal composites. J Appl Phys 2000;87(7):3321–31.
[7] He JH. Generalized Hellinger–Reissner principle. ASME J Appl Mech 2000;67(2):326–31.
[8] He JH. Variational theory for linear magneto-electro-elasticity. Int J Non-Linear Sci Numer Simul 2001;2(1):309–16.
[9] Felippa CA. Parametrized multifield variational principles in elasticity: I. Mixed functionals. Comm Appl Numer Meth 1989;5:89–98.