JOURNAL OF APPLIED POLYMER SCIENCE VOL. 8, PP. 1129–1146 (1964)

# A Continuum Theory of Nonlinear Viscoelastic Deformation with Application to Polymer Processing

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## Synopsis

A continuum theory of nonlinear viscoelastic behavior has been developed which is applicable to the quantitative description of the rheological properties of high polymeric materials. Particular classes of deformations have been investigated. Special emphasis has been placed upon nonlinear effects in viscoelastic fluids such as normal stresses and variable viscosity. Two new classes of flows are defined: sufficiently smooth flow and isoelastic flow.

## 1. INTRODUCTION

Due to the tremendous growth of the polymer industries in the last quarter century, many new problems have been brought to the attention of the engineer and the applied scientist. Among the most important of these are the deformation and flow behavior of high polymeric systems in the processes which fabricate plastics, fibers, and elastomers. These developments have led Bernhardt and McKelvey[4] to define *polymer processing* as a new distinct area of engineering endeavor.

Prior to World War II, most materials of significance to engineering design were nearly rigid solids (e.g., metals) and linear purely viscous fluids (e.g., air, water, light hydrocarbons) for which stress analysis and calculation of velocity profiles and frictional drag are well known and exist in standard texts. The new polymeric materials (both thermoplastic and crosslinked) did not fall into these categories. Below their glass temperature,[6,91] in general, high molecular weight polymers tend to be hard, brittle, glassy solids which exhibit significant stress relaxation and creep when deformed. Above the glass temperature, polymers become soft, flexible, and rubbery, with thermoplastic materials eventually going through a melting range to become transparent, highly viscous liquids which still maintain significant "elastic" properties, the most noticeable of which is recoil upon stoppage of flow. Solutions of thermoplastics exhibit similar elastic properties but usually to a lesser degree. This property of high polymeric fluids was first fully recognized by Weissenberg.[38,99]

High polymers below their glass temperature may usually be considered to be subjected to infinitesimal deformations, and stress analysis prob-

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lems may be attacked by using the linear theory of viscoelasticity, which, though dating back to the nineteenth century, did not begin to receive adequate attention until the last two decades.[1,45,46,91] Methods of solution of stress analysis have been considered in detail by Lee and his co-workers,[46] some of these procedures having recently been extended to include nonisothermal effects.[60,61]

The treatment of the deformation of polymers above their glass temperatures is more difficult due to the essential nonlinearity of the problem. Stress analysis methods for crosslinked amorphous materials such as rubber, which are subjected to large deformations, have received increased attention since 1940. Investigations based upon the approximation of purely elastic deformations are carried out by the British Rubber Producers' Research Association, particularly by Rivlin and co-workers. The theoretical and experimental results of these investigators are largely summarized in the texts by Green and Zerna,[36] Green and Adkins,[31] Eringen,[23] and the review of Truesdell.[95]

Much of the processing of fibers and thermoplastics takes place in states in which the assumption of purely elastic deformations is hardly valid, relaxation, creep, and flow being quite significant. The analysis of the dynamics of this processing requires the study of nonlinear viscoelastic media. Of concern are problems such as the design of screw extruders and dies, fiber spinning, calendering, molding, etc. The present state of the art in most of these areas is either empirical or makes use of largely oversimplified one-dimensional rheological models (A number of reviews have been published.[6,18,53–55]). Now many authors have called attention to observed nonlinear viscoelastic effects in processing operations,[2,52–56] and preliminary analytical investigations of some of these effects were made in an earlier paper.[101]

In order to treat general deformations of high polymeric materials both in the solid and fluid states it is necessary to develop a constitutive equation for the stress which is applicable to the nonlinear as well as the linear range of rheological behavior. Though as has been pointed out on several occasions,[23] some of the mechanics of constructing such a constitutive equation were known to Cauchy in the time of Louis Philippe and had been studied by Zaremba and Jaumann during the early years of the present century, it was not until the publications of Oldroyd[65] and Noll[62] in the 1950's that a firm foundation existed to this phase of continuum mechanics. Significant contributions to the foundations of nonlinear continuum theories were also made in the early fifties by Truesdell[95,96] and Rivlin and Ericksen.[84] In 1957, Green and Rivlin[33] culminated many of these studies by publishing what is the only *a priori* satisfactory theory of nonlinear hereditary materials. The Green-Rivlin theory is based upon the assumption that the stress is an hereditary function of the deformation history, the medium being assumed isotropic in the ground state. The concepts of Green and Rivlin have been extended and clarified by Rivlin and co-workers[34,35,75,88] and put in an elegant Hilbert Space formulation by Noll and Coleman.[13,14,63] Recently Ericksen[21,22] has suggested an alternate approach to nonlinear viscoelastic fluids based upon assuming the stress to be dependent upon the deformation rate and a vector. This approach is suggested by the concept of molecular orientation in flow. It would appear, however, that this theory of anisotropic fluids is inadequate in comparison with the Green-Rivlin theory of isotropic hereditary media, though it is an area of continuing study.

The author believes that further study of the mechanics and thermodynamics of nonlinear viscoelastic media is necessary to improve the current status of polymer process engineering. It is believed that the approach of Green and Rivlin is the most satisfactory for such studies, constitutive equations investigated by others[66,67,101] being inadequate due to their weak *a priori* basis. In this paper, the Green-Rivlin approach is reformulated and in so doing a new series of kinematic tensors is derived. Important kinematic situations will be critically discussed and applications to polymer processing evaluated. This paper continues the investigations of earlier work,[101] where a much simpler theory of viscoelasticity was derived and applied to polymer process operations.

## 2. KINEMATIC PRELIMINARIES AND FORMULATION OF CONSTITUTIVE EQUATIONS

In this section we outline some fundamental concepts of kinematics and continuum physics and apply them to the derivation of a constitutive equation applicable to high polymeric media. We shall use in this study two coordinate frames: a cartesian system $x$ fixed in space which is used to denote spatial points and coordinate frame $\xi$ embedded in the medium with which we denote material points. At a past time $\phi$, the distance between two differentially separated material points at $\xi$ and $\xi + d\xi$ is

$$d\xi(\phi) = \sum_\alpha \gamma_\alpha\,(\phi)d\xi^\alpha = \sum_a \mathbf{e}_a d\bar{x}_a(\phi) \tag{1}$$

where $\gamma_\alpha$ are the covariant base vectors of the embedded frame and $\mathbf{e}_a$ are the orthogonal unit vectors of the cartesian frame. At time $t$, the differential line segment has moved from a spatial location $\mathbf{x}$ to a location $\mathbf{x}$

$$d\xi(t) = \sum_a \gamma_\alpha\,(t)d\xi^\alpha = \sum_j \mathbf{e}_j dx_j(t) \tag{2}$$

An embedded differential area element in the medium may be similarly specified

$$\begin{aligned} d\bar{\alpha} &= \mathbf{n}d\bar{\alpha} = d\xi' \times d\xi_2 \\ &= \sum_\delta \gamma^\delta\Big(\sum_\alpha\sum_\beta \epsilon_{\delta\alpha\beta} d\xi_1{}^\alpha e\xi_2{}^\beta\Big) = \sum_a \mathbf{e}_a\Big(\sum_b\sum_c \epsilon_{abc} d\bar{x}_{1b} d\bar{x}_{2c}\Big) \\ &= \sum_\delta \gamma^\delta(\phi) d\bar{\alpha}_\delta(\phi) = \sum_a \mathbf{e}_a d\bar{a}_a(\phi) \end{aligned} \tag{3}$$

where the $\gamma^\delta$ are the contravariant base vectors of the embedded frame.

Deformation at a material point in a continuous medium may be specified in terms of either the variation of a line segment or area element located at that point, or other arbitrarily constructed nongeometric measures. The classical studies of Cauchy and Stokes[89] as well as the more recent work of Rivlin,[80] Rivlin and Ericksen,[84] and Green and Rivlin[33] essentially make use of the properties of a differential line segment. Here a deformation measure based upon a differential area element is used, such a measure being first noted by Truesdell[97] (see also Eringen[23] and Grossman[37]). The strain in the medium at $\xi$ incurred from time $\phi$ to time $t$ may be specified as follows:

$$[d\bar{\alpha}(\phi)]^2 - [d\alpha(t)]^2 = 2[\mathbf{E}\cdot d\boldsymbol{\alpha}].d\boldsymbol{\alpha} \tag{4a}$$

$$= \sum_\alpha\sum_\beta [\gamma^{\alpha\beta}(\phi) - \gamma^{\alpha\beta}(t)]d\alpha_\alpha d\alpha_\beta$$

$$= 2\sum_\alpha\sum_\beta \varepsilon^{\alpha\beta} d\alpha_\alpha d\alpha_\beta \tag{4b}$$

$$= 2\sum_i\sum_j E_{ij}\, d\alpha_i\, da_j \tag{4c}$$

The element $d\boldsymbol{\alpha}$ is located in the spatial frame at $\mathbf{x}$ and the element $d\bar{\alpha}$ at $\bar{x}$. Thus

$$\mathbf{x} = \bar{\mathbf{x}} + \mathbf{u} + \mathbf{c}$$

$$\sum \mathbf{e}_j x_j = \sum \mathbf{e}_a(\bar{x}_a + u_a + c_a)$$

where $\mathbf{u}$ represents the actual deformation of the body and $\mathbf{c}$ the contribution of rigid displacement. It may be shown that (see Appendix)

$$E_{ij} = \left(\frac{1}{2}\right)\left[J^2 \sum_a \left(\frac{\partial x_i}{\partial \bar{x}_a}\right)\left(\frac{\partial x_j}{\partial \bar{x}_a}\right) - \delta_{ij}\right] \tag{6a}$$

$$= \left(\frac{J^2}{2}\right)\left[\left(\frac{\partial u_i}{\partial \bar{x}_j}\right) + \left(\frac{\partial u_j}{\partial \bar{x}_i}\right) + \sum_m \left(\frac{\partial u_i}{\partial \bar{x}_m}\right)\left(\frac{\partial u_j}{\partial \bar{x}_m}\right)\right] + \left[\frac{(J^2-1)}{2}\right]\delta_{ij} \tag{6b}$$

For incompressible materials ($J = 1$), this is identical to the Piola-Finger strain tensor (e.g., Eringen[23]).

Also of importance are the rate and accelerations of deformation

$$(-1)\left(\frac{d^n}{dt^n}\right)(d\alpha^2) = (\mathbf{B}_n\cdot d\boldsymbol{\alpha})\cdot d\boldsymbol{\alpha} \tag{7a}$$

$$= \sum_\alpha\sum_\beta \overset{(n)}{\overline{(J^2\gamma\alpha\beta)}} \left(\frac{1}{J_?}\right) d\alpha_\alpha\, d\alpha_\beta \tag{7b}$$

$$= \sum_i\sum_j \overset{(n)}{B_{ij}}\, da_i\, da_j \tag{7c}$$

It may be shown that in Cartesian spatial coordinates the components of $B_n$ are (see Appendix)

$$\overset{(1)}{B}_{ij} = \left(\frac{\partial v_i}{\partial x_j}\right) + \left(\frac{\partial v_j}{\partial x_i}\right) - \delta_{ij}\left[2\sum_m\left(\frac{\partial v_m}{\partial x_m}\right)\right] \tag{8a}$$

$$\overset{(n+1)}{B}_{ij} = \left(\frac{D}{Dt}\right)\overset{(n)}{B}_{ij} + \overset{(n)}{B}_{ij}\left[2\sum_m\left(\frac{\partial v_m}{\partial x_m}\right)\right] - \sum_m\left(\frac{\partial v_i}{\partial x_m}\right)\overset{(n)}{B}_{mj} - \sum_m\left(\frac{\partial v_j}{\partial x_m}\right)\overset{(n)}{B}_{im} \tag{8b}$$

For incompressible materials, the $B_n$ become equivalent to kinematic tensors used earlier by Giesekus[29,30] and White and Metzner.[101]

For a curvilinear coordinate frame having a metric tensor $g_{ij}$ and conjugate metric tensor $g^{ij}$ we have (in summation notation)

$$\overset{(1)}{B}{}^{ij} = v_{,m}{}^{i}\, g^{mj} + v_{,m}{}^{j}\, g^{im} - 2g^{ij}v_{,m}{}^{m} \tag{9a}$$

$$\overset{(n+1)}{B}{}^{ij} = \left(\frac{D}{Dt}\right)\overset{(n)}{B}{}^{ij} + 2\overset{(n)}{B}{}^{ij}\, v_{,m}{}^{m} - v_{,m}{}^{i}\overset{(n)}{B}{}^{mj} - v_{,m}{}^{j}\overset{(n)}{B}{}^{im} \tag{9b}$$

We are now in a position to formulate a constitutive relation for the stress-deformation behavior of a high polymeric medium. In so doing the following fundamental principles are recognized: (*A1*) The stress at a material point $\boldsymbol{\xi}$ located at time $t$ at a spatial point $\mathbf{x}$ is determined by the entire past history of the deformation of an arbitrary small neighborhood of $\boldsymbol{\xi}$. (*A2*) The constitutive equation is form-invariant under a rigid motion in the spatial frame.

The known physical properties of high polymeric media may be used to place additional restrictions on the constitutive equation. With little loss in the applicability of our result the following may be assumed: (*B1*) The stress in the medium is determined by the entire history of the deformation such that strains in the distant past have less effect on the present value of the stress than deformations in the recent past. The duration of the memory may be taken, say, as $T$. (*B2*) The medium is isotropic in the ground state. (*B3*) The medium is incompressible.

Making use of principles (*A1–A2*) and (*B1–B3*) the stress may be written

$$\boldsymbol{\tau}\,(\xi,t) = -p\mathbf{I} + \mathcal{G}\underset{\phi=t-T}{\overset{\phi=t}{[\mathbf{E}(t-\phi)]}} \tag{10}$$

Equation (10) may be written in the form of an expansion. To see how this is done, two related problems will be considered. First, following Volterra[98] we note that a similar scalar functional may be written in a form analogous to a Taylor series.

$$f\underset{t-T}{\overset{\phi=t}{[x(t-\phi)]}} = \sum_n \int_{t-T}^{t}\cdots\int_{t-T}^{t} k_n(t-\phi_1,\ldots t-\phi_n)x(\phi_1)\ldots x(\phi_n)\, d\phi_1\ldots d\phi_n \tag{11a}$$

Secondly we consider a constitutive equation of the form

$$\tau = -p\mathbf{I} + \mathcal{G}^{(n)}\,[\mathbf{E}(t-\phi_i)\ldots\ldots\mathbf{E}(t-\phi_n)] \tag{11b}$$

which becomes equivalent to eq. (10) when $N \to \infty$. Following procedures originally introduced by Reiner[77,78,95] and developed by Rivlin and Spencer[80,81,84,88] we may expand Eq. (11b) as a symmetric matrix polynomial in the $E(\phi_j)$ with the coefficients being functions of the invariants of $E$.

$$\tau = -pI + \sum_n \int_{t-T}^{t} \cdots\cdots \int_{t-T}^{t} \mathbf{\Phi}^{(n)}\,[t-\phi_i,\cdots t-\phi_n,\ \mathbf{E}(\phi_1)\cdot\cdot\mathbf{E}(\phi_n)]\,d\phi_1\cdot\cdot\cdot d\phi_n \tag{12}$$

where $\mathbf{\Phi}^{(n)}$ is a symmetric isotropic matrix polynomial of degree $n$ in the elements of the $\mathbf{E}(\phi_j)$ and linear in each of them. The coefficients of the matrix products are polynomials in the invariants of the matrices $\mathbf{E}(\phi_j)$ and scalar functions of $(t-\phi_j)$. A more detailed account leading to equations of this type is given by Green, Rivlin, and Spencer.[33,35,88]

Expanding eq. (11) yields

$$\tau = -p\mathbf{I} + \int_{t-T}^{t} \Phi(t-\phi)\mathbf{E}(\phi)d\phi + \int_{t-T}^{t}\int_{t-T}^{t} \Psi\,(t-\phi_1)(t-\phi_2)\,\mathbf{E}(\phi_1)\mathbf{E}(\phi_2)d\phi_1 d\phi_2 + \int_{t-T}^{t}\int_{t-T}^{t} \Sigma\,(t-\phi_1)t-\phi_2)\,[\mathrm{tr}\ \mathbf{E}\ (\phi_1)]\mathbf{E}(\phi_2)\ d\phi_1 d\phi_2 + \cdots \tag{13}$$

Equations of this form containing one term were considered by Lodge[47,48] and by Fredrickson.[25] More recently Coleman and Noll[14] and Bernstein, Kearsley, and Zapas[5] have investigated the properties of expansions containing three terms of the types given above.

## 3. STRESS RELAXATION

There exist different classes of deformation in which considerable simplification may be made in eq. (12). In this section a class of deformation of significance of "near-solid" polymers will be investigated and in following sections the flow behavior of viscoelastic fluids will be studied.

Consider a medium to remain in the unstressed ground state until time $\phi = 0$ and then to remain in this strained state until the present. On examining eq. (4) it is seen that

$$\mathbf{E} = \mathbf{C} - \mathbf{I} = \text{constant} \qquad \phi < 0$$

$$\mathbf{E} = \mathbf{O} \qquad \phi > 0$$

Equation (13) becomes

$$\tau = -p\mathbf{I} + \left[\int_{t-T}^{0} \Phi(t-\phi)d\phi\right]\mathbf{E} + \left[\int_{t-T}^{0}\int_{t-T}^{0} \Psi\ (t-\phi_1,\ t-\phi_2)d\phi_1 d\phi_2\right]\mathbf{E}_2 + \left[\int_{t-T}^{0}\int_{t-T}^{0} \Sigma\ (t-\phi_1,\ t-\phi_2)\ d\phi_1 d\phi_2\right](\mathrm{tr}\ \mathbf{E})\mathbf{E} + \cdots \tag{14}$$

Using the Cayley-Hamilton theorem one obtains

$$\tau = -p\mathbf{I} + \alpha_1 (t - T, t)\mathbf{C} + \alpha_2 (t-T, t)\mathbf{C}^2 \tag{15}$$

If it is assumed that the deforming process is elastic, $\alpha_1$ and $\alpha_2$ have the following values at time $t = 0$.

$$\alpha_1 = 2\left(\frac{\partial W}{\partial I_1} + I, \frac{\partial W}{\partial I_1}\right) \tag{16a}$$

$$\alpha_2 = -2\frac{\partial W}{\partial I_2} \tag{16b}$$

where $W$ is the strain energy function and $I_1$ and $I_2$ are invariants given by

$$I_1 = \mathrm{tr}\,\mathbf{C}$$

$$I_2 = \left(\frac{1}{2}\right)[(\mathrm{tr}\,\mathbf{C})^2 - \mathrm{tr}\,\mathbf{C}^2]$$

It may further be noted that when $t > T$, where $T$ is the duration of the memory

$$\alpha_1 = \alpha_2 = 0$$

From eqs. (16), it may be seen that the many solutions derived in the theory of large elastic deformations of isotropic materials[23,31,36] may be used to solve stress relaxation problems by means of the substitution of

$$\frac{\partial W}{\partial I_1} = \left(\frac{1}{2}\right)[\alpha_1 + I_1\alpha_2]$$

$$\frac{\partial W}{\partial I_2} = -\left(\frac{1}{2}\right)\alpha_2$$

where $\alpha_1$ and $\alpha_2$ are time-dependent quantities. This result was noted by Rivlin[83] from different reasoning.

The British Rubber Producers' Research Association has performed an extensive series of experiments to obtain the form of the strain energy function for elastic deformations.[27,31,85,92,93] The results of one series of experiments were in addition used successfully to predict the forces and deformations of experiments in different geometries. Rivlin and Saunders[85] found that the strain energy function for the several vulcanizates of rubber they investigated was

$$W = c_1(I_1 - 3) + F[I_2] \tag{18a}$$

where $F$ is a decreasing function of $I_2$ which is generally somewhat smaller than the first term. Gent and Thomas[28] have noted that the Rivlin-Saunders data may be fitted by the empirical expression

$$W = c_1 (I_1 - 3) + c_2\ln (I_2/3) \tag{18b}$$

Expanding the logarithm in a Taylor series we find the first-order approximation to eq. (18b) is

$$W = c_1 (I_1 - 3) + c_2 (I_2 - 3) \tag{18c}$$

which was first proposed by Mooney[58] in 1940. (Note the discussion of eq. (18c) by Treloar[93]).

It is of interest to note that the expression

$$W = c_1 (I_1 - 3) \tag{18d}$$

is readily derivable from statistical mechanics.[9,24,93] Recently Ciferri and Flory[10] have performed a series of experiments using uniaxial extension deformations and claim that eq. (18d) is the true expression for the strain energy function and the observed dependence of $W$ upon $I_2$ is due to hysteresis and other nonequilibrium effects. However their use and interpretation of uniaxial extension data appears to be subject to question.[93,94]

There has been considerable interest in stress relaxation measurements, notably by Tobolsky and his students.[90,91] However these authors have limited themselves to uniaxial extension measurements and have interpreted their data on the basis of $\alpha_2$ being zero. Though this work appears to contribute to some areas of physical characterization it does not give more than qualitative aid to the interests of this paper. Although the Leaderman-Tobolsky time–temperature superposition principle is now well known, the generality of its applicability in stress analysis problems remains open to question.

Of more interest are the experiments of Bernstein, Kearsley, and Zapas[5] on stress relaxation in more general types of deformation. These researchers are using equations similar to eqs. (12) and (13) to interpret their results.

## 4. VISCOELASTIC FLUIDS AND SUFFICIENTLY SMOOTH FLOWS

In the previous section, deformations were studied which take place in solidlike rubbery polymers, whereas here we shall be concerned with materials that are basically fluids. The concept of fluidity is based upon two considerations. The first of these is that fluids can sustain a steady shearing motion indefinitely under nonzero shearing tractions. The second notion is that a fluid has neither preferred intrinsic directions nor preferred states of strain. (It is to be noted that the theory of anisotropic fluids developed by Ericksen[21,22] does not satisfy the second notion of fluidity.) In this section, we consider a general class of deformations for fluid materials and derive a simpler form of eq. (12).

Our concept of smooth flows is based upon an idea due originally to Green and Rivlin[33] of expanding the strain developed in the fluid between time $\phi$ and time t, i.e. $\mathbf{E}(\phi)$, as an infinite Taylor series of matrices of (convected) strain rates and accelerations. If we consider the convected components of the strain tensor

$$
\begin{aligned}
\varepsilon^{\alpha\beta}(\phi) &= (1/2)\,[\gamma^{\alpha\beta}(\phi) - \gamma^{\alpha\beta}(t)] \\
&= \varepsilon^{\alpha\beta}(t - s) \\
&= \varepsilon^{\alpha\beta}(t) + \sum_n \left[\frac{(-1)^n s^n}{n!}\right]\left(\frac{d^n \varepsilon^{\alpha\beta}(t-s)}{ds^n}\right)_{s=0} \\
&= \sum_n \left[\frac{(-1)^n s^n}{n!}\right]\left(\frac{d^n \varepsilon^{\alpha\beta}}{ds^n}\right)_{s=0}
\end{aligned}
\tag{19a}
$$

From eqs. (4) and (7)

$$E_{ij}(\phi) = \sum_{n=1} \left[\frac{(-1)^{n+1}(t-\phi)^n}{2n!}\right] \overset{(n)}{B}_{ij} \tag{19b}$$

or

$$\mathbf{E}(\phi) = \sum_{n=1} \left[\frac{(-1)^{n+1}\,(t - \phi)^n}{2n!}\right] \mathbf{B}_n \tag{19c}$$

Flows for which we may express the strain in the medium by eq. (19) are said to be sufficiently smooth.

Substitution of eq. (19c) into eq. (12) and integration of the variables allows us to write the stress tensor as a symmetric matrix polynomial in the $B_n$.

$$\boldsymbol{\tau} = -p\,\mathbf{I} + \mathfrak{F}\,[\mathbf{B}_1, \mathbf{B}_2, \ldots \mathbf{B}_n \cdots] \tag{20}$$

If the kinematics of flow are specified *a priori*, it is possible to specify the $B_n$ matrices and use matrix representation theorems[77,81,84,88] to write $\mathfrak{F}$ in a closed form. However in general this is not possible, and the kinematics must be calculated from Cauchy's law of motion. Thus approximate forms of eq. (20) must be obtained to attack the general flow problem. This has been considered by Langlois and Rivlin[44] and by Coleman and Noll[13] using different formulations of the hydrodynamic theory of viscoelastic fluids. By substituting $\varepsilon v'$ for $v$ in eq. (20) and using a matrix representation theorem due to Spencer and Rivlin[88] it may be shown that

$$\boldsymbol{\tau} = -p\mathbf{I} + \varepsilon \mathcal{S}_1 + \varepsilon^2 \mathcal{S}_2 + \varepsilon^3 \mathcal{S}_3 + 0\,(\varepsilon^4) \tag{21}$$

where

$$\varepsilon \mathcal{S}_1 = \omega_1 \mathbf{B}_1 \tag{22a}$$

$$\varepsilon^2 \mathcal{S}_2 = \omega_2 \mathbf{B}_1{}^2 + \omega_3\,\mathbf{B}_2 \tag{22b}$$

$$\varepsilon^3 \mathcal{S}_3 = (\omega_4\,\mathrm{tr}\,\mathbf{B}_1{}^2)\mathbf{B}_1 + \omega_5 \mathbf{B}_3 + \omega_6(\mathbf{B}_1\mathbf{B}_2 + \mathbf{B}_2\mathbf{B}_1) \tag{22c}$$

the $\omega_j$ being constant coefficients. It may be seen that for very slow flows the behavior approximates the Newtonian fluid as developed by Stokes.[89] The next higher approximation includes the Reiner-Rivlin[77,80] cross-viscous term and an additional acceleration tensor. The third term includes three new nonlinear elements.

Equations (21) and (22) may be interpreted in two fashions. Most obviously the development indicates a perturbation about the state of rest. However, an alternate interpretation is a perturbation about Newtonian flow and solutions of eqs. (21) and (22) together with Cauchy's law of motion may be considered as perturbing about the Navier-Stokes equations.

In the remainder of this paper, we shall consider special simple flow situations where exact solutions are possible. In particular we study the kinematic significance of these flows and their application to calculation of the $\omega_j$ coefficients.

## 5. ISOELASTIC FLOW

Weissenberg[38,99,100] first pointed out the significance of the recoverable elastic strain which flowing viscoelastic fluids possess. Later authors, notably Mooney,[59] Jobling,[39] and Philippoff[70,73,74] studied and re-emphasized the importance of Weissenberg's concepts. In this section, we shall treat flows in which material points travel along paths having everywhere the same value of the recoverable strain tensor. Such flows are said to be *locally isoelastic* with respect to this streamline and if every material point in the fluid traverses such a path the flow will be called *globally isoelastic.* Clearly, the recoverable strain will only remain constant if a point traverses a path along which the kinematics of deformation does not vary. Thus along isoelastic streamlines the $B_n$ tensors should be everywhere the same value. It would appear that the concept of isoelastic flow is related to Coleman's substantially stagnant motions[11] and Noll's motions having a constant stretching history.[64]

As the $B_n$ tensors must be everywhere the same on isoelastic streamlines, the kinematics of motion in many of such cases may be specified *a priori.* When this is the case, the stress may be calculated from the use of matrix theorems. Three special cases of isoelastic motion are worthy of discussion.

### a. Quasi-Potential Flow

This type of fluid motion may be specified by

$$\mathbf{v} = U\mathbf{e}_1 + 0\mathbf{e}_2 + 0\mathbf{e}_3 \tag{23}$$

where $U$ is a constant or in sufficiently rapid flows it may depend on $x$, if the fluid is only slightly viscoelastic. This kinematic example would exist in the problem or the flow of an infinite fluid around a submerged object at large distances from its surface. It might be expected that potential flow theory is applicable to this type of motion, but there exist difficulties in such a presumption as shown by Slattery[87] and in general quasi-potential flow is rotational. For these motions

$$\mathbf{B}_n = 0 \qquad \text{(for all } n) \tag{24a}$$

$$\mathbf{E}(\phi) = 0 \tag{24b}$$

and

$$\begin{vmatrix} \tau_{11} & \tau_{12} & \tau_{13} \\ \tau_{21} & \tau_{22} & \tau_{23} \\ \tau_{31} & \tau_{32} & \tau_{33} \end{vmatrix} = - \begin{vmatrix} p & 0 & 0 \\ 0 & p & 0 \\ 0 & 0 & p \end{vmatrix} \tag{24c}$$

### b. Laminar Shearing Motion

This type of motion is specified by

$$\mathbf{v} = v^{(1)}\,(x^2)\mathbf{e}_1 + 0\mathbf{e}_2 + 0\mathbf{e}_3 \tag{25}$$

where the $\mathbf{e}_j$ are orthonormal vectors. (Note that orthogonal curvilinear coordinates are included as well as cartesian.) These flows include Couette flow between parallel planes and coaxial cylinders and Poiseuille flow between parallel planes and in a tube. (Flow between coaxial cones and torsional flow approximate laminar shearing flow.) The earliest analysis of this type of motion for viscoelastic fluids was by Rivlin[82] (for Rivlin-Ericksen fluids). More recent analyses have been given by Ericksen,[16,20] Giesekus,[30] Coleman and Noll,[12] and White and Metzner.[101] For these motions

$$\mathbf{B}_1 = \begin{vmatrix} 0 & \Gamma & 0 \\ \Gamma & 0 & 0 \\ 0 & 0 & 0 \end{vmatrix}$$

$$\mathbf{B}_2 = -2\begin{vmatrix} \Gamma^2 & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & 0 \end{vmatrix}$$

$$\mathbf{B}_n = 0 \qquad n > 2 \tag{26a}$$

$$\mathbf{E}(\phi) = \left(\frac{(t-\phi)}{2}\right)\mathbf{B}_2 - \left(\frac{(t-\phi)^2}{4}\right)\mathbf{B}^2 \tag{26b}$$

The stress tensor is given by

$$\boldsymbol{\tau} = -p\mathbf{I} + \mathfrak{F}\,[\mathbf{B}_1, \mathbf{B}_2] \tag{27}$$

Using a matrix representation theorem derived by Rivlin,[81] it follows that

$$\begin{aligned} \boldsymbol{\tau} = {} & -p\mathbf{I} + \lambda_1\mathbf{B} + \lambda_2\mathbf{B}_1^2 + \lambda_3\mathbf{B}_2 + \lambda_4\mathbf{B}_2^2 \\ & +\lambda_5(\mathbf{B}_1\mathbf{B}_2 + \mathbf{B}_2\mathbf{B}_1) + \lambda_6\,(\mathbf{B}_1^2\,\mathbf{B}_2 + \mathbf{B}_2\mathbf{B}_1^2) \\ & +\lambda_4\,(\mathbf{B}_1\mathbf{B}_2^2 + \mathbf{B}_2^2\mathbf{B}_1) + \lambda_8\,(\mathbf{B}_1^2\mathbf{B}_2^2 + \mathbf{B}_2^2\,\mathbf{B}_1^2) \end{aligned} \tag{28}$$

where the $\lambda_j$ are functions of $\Gamma^2$. On substituting eq. (26a) into eq. (28), it is found that this matrix polynomial is equivalent to

$$\boldsymbol{\tau} = -p\mathbf{I} + \mu\mathbf{B}_1 - \left(\frac{1}{2}\right)\beta_1\mathbf{B}_2 + \beta_2\left[\mathbf{B}_1^2 + \left(\frac{1}{2}\right)\mathbf{B}_2\right] \tag{29}$$

$$\begin{vmatrix} \tau_{11} & \tau_{12} & \tau_{13} \\ \tau_{21} & \tau_{22} & \tau_{23} \\ \tau_{31} & \tau_{32} & \tau_{33} \end{vmatrix} = - \begin{vmatrix} p & 0 & 0 \\ 0 & p & 0 \\ 0 & 0 & p \end{vmatrix} + \begin{vmatrix} \beta_1\Gamma^2 & \mu\Gamma & 0 \\ \mu\Gamma & \beta_2\Gamma^2 & 0 \\ 0 & 0 & 0 \end{vmatrix} \tag{30}$$

where $\mu$, $\beta_1$, and $\beta_2$ are dependent upon $\Gamma$.[2]

Laminar shearing flow is the most significant type of isoelastic motion. It is not only important due to its many applications in industrial processes, these being discussed in an earlier paper,[101] but it affords us a method of determining the $\omega_j$ coefficients in eq. (22). On comparing eqs. (29) and (30) with eq. (22) it is seen that

$$\omega_1 = \lim_{\Gamma\to 0} (\mu) \tag{31a}$$

$$\omega_2 = \lim_{\Gamma\to 0} (\beta_2) \tag{31b}$$

$$\omega_3 = \lim_{\Gamma\to 0} \left[\frac{(\beta_2 - \beta_1)}{2}\right] \tag{31c}$$

$$\omega_4 - \omega_6 = \lim_{\Gamma\to 0} \left[\frac{(\mu - \omega_1)}{2\Gamma^2}\right] \tag{31d}$$

The coefficient $\mu$ is well known as the apparent viscosity and has been investigated for many years. Detailed discussions of the apparent viscosity of polymer solutions is found in the two decade-old book by Philippoff[68] and in the now classic text by Reiner.[79] Apparent viscosities of polymer solutions are readily measured, and data appear frequently in the literature.[7,8,40,41] Measurements of the viscosities of polymer melts over a range of shear rates are given by Bernhardt[3] and Philippoff and Gaskins.[72]

Measurements of $\beta_1$ and $\beta_2$ have been made during the last decade. The experimental techniques are summarized in the literature.[26,49,102] Considerable controversy exists over the results of these measurements, especially in conjunction with the hypothesis of Weissenberg[100] that $\beta_2$ is zero. The experimental researches of Roberts,[86] Philippoff,[8,71] and Kotaka et al.[40] support this conclusion. Notably Markovitz[49,50] and Zapas and Kearsley[103] have disagreed with this result and present data to support their conclusion. Most researchers agree, though, that $\beta_2$ is much smaller than $\beta_1$.

$\beta_1$ has been determined for some polymer–solvent systems at low and moderate shear rates (less than 500 reciprocal seconds)[7,8,40,41,51,69,74,102] by using mainly rotational and birefringence instruments and at high shear rates (greater than 5000 reciprocal seconds) by using a jet extrusion instrument.[57] In obtaining these data, $\beta_2$ has often been assumed to be zero. Limited (and also questionable) data exist for polymer melts[2,17,56,73] over narrow ranges of shear rates. The coefficients $\omega_1$, $\omega_2$, and $\omega_3$ for two polymer–solvent systems calculated from such data are given in Table I.

TABLE I

| System | $\omega_1$, dyne-sec.$^2$/cm.$^2$ | $\omega_2$, dyne-sec.$^2$/cm.$^2$ | $\omega_3$, dyne-sec.$^2$/cm.$^2$ | Reference |
|---|---|---|---|---|
| Polyisobutylene (15%) in decalin | 9,320 | Negligible | −22,500 | Philippoff[69] |
| Polyethylene at 150°C. | 410,000 | Negligible | −3,075,000 | Dexter et al.[17] |
| Ethylcellulose (11%) in cyclohexane | 610 | Negligible | −140 | Brodnyan et al.[8] |

Before concluding this section, it is both interesting and important to note that there are hydrodynamic flows which though at first appearing to be isoelastic are actually not. The most interesting example is the inability of laminar shearing flow to exist in noncircular ducts unless $\beta_2 = K\mu$. This restriction was first noted by Ericksen,[16,19] and secondary flow patterns have been calculated by Green and Rivlin[32] and Langlois and Rivlin.[44] If $\beta_2$ is zero as Weissenberg suggests, then laminar shearing flow may exist. A second type of motion is laminar shearing flow between coaxial cones which cannot exist unless $\beta_1 + \beta_2 = (K/\Gamma^2)$.[20,66,102] Langlois[43] has calculated secondary flow patterns. A further example occurs in laminar shearing flow between concentric spheres.[42]

### c. Steady Extension

This type of motion is specified by

$$\mathbf{v} = a_1 x^1 \mathbf{e}_1 + u_2 x^2 \mathbf{e}_2 + a_3 x^3 \mathbf{e}_3 \tag{32a}$$

where

$$a_1 + a_2 + a_3 = 0 \tag{32b}$$

(by incompressibility).

Steady extension of viscoelastic fluids was first analyzed by Coleman and Noll.[15] For these flows

$$\mathbf{B}_1 = 2\begin{vmatrix} a_1 & 0 & 0 \\ 0 & a_2 & 0 \\ 0 & 0 & a_3 \end{vmatrix}$$

$$\mathbf{B}_2 = (-4)\begin{vmatrix} a_1^2 & 0 & 0 \\ 0 & a_2^2 & 0 \\ 0 & 0 & a_3^2 \end{vmatrix}$$

$$\mathbf{B}_n = (-1)^{n+1}(\mathbf{B}_1)^n \tag{33a}$$

$$\mathbf{E}(\phi) = \sum_n \left[\frac{(t-\phi)^n}{2n!}\right](\mathbf{B}_1)^n = \frac{1}{2}\exp\left\{\mathbf{B}_1(t-\phi)\right\} \tag{33b}$$

The stress tensor is

$$\tau = -p\mathbf{I} + \mathfrak{F}\,[\mathbf{B}_1] \tag{34}$$

and by the Cayley-Hamilton theorem

$$\begin{vmatrix} \tau_{11} & \tau_{12} & \tau_{13} \\ \tau_{21} & \tau_{22} & \tau_{23} \\ \tau_{31} & \tau_{32} & \tau_{33} \end{vmatrix} = - \begin{vmatrix} p & 0 & 0 \\ 0 & p & 0 \\ 0 & 0 & p \end{vmatrix} + \nu_1 \begin{vmatrix} a_1 & 0 & 0 \\ 0 & a_2 & 0 \\ 0 & 0 & a_3 \end{vmatrix} + \nu_2 \begin{vmatrix} a_1^2 & 0 & 0 \\ 0 & a_2^2 & 0 \\ 0 & 0 & a_3^2 \end{vmatrix} \tag{35}$$

where $\nu_1$ and $\nu_2$ are functions of the invariants of $B_1$.

Steady extension affords an approximation to many processing operations involving stretching of high polymeric materials. Unfortunately no quantitative data exist in the literature for directly calculating $\nu_1$ and $\nu_2$. We can, however, obtain the values of these parameters at very low deformation rates from the values of $\omega_1$, $\omega_2$, and $\omega_3$, derived from laminar shearing flow experiments. Comparing eqs. (33a) and (35) with eqs. (21) and (22a), it is seen that in slow flows

$$\tau = -p\,\mathbf{I} + \omega_1\,\mathbf{B}_1 + (\omega_2 - \omega_3)\mathbf{B}_1^2$$

From Table I, we obtain for polyethylene at 150°C.:

$$\nu_1 \sim +\ 820{,}000 \text{ dyne-sec./cm.}^2$$

$$\nu_2 \sim +\ 12{,}300{,}000 \text{ dyne-sec./cm.}^2$$

## 6. CONCLUDING REMARKS

In this paper, the Green-Rivlin theory of nonlinear viscoelasticity has been reformulated and applied to important classes of problems. Especial attention has been given to the kinematics of deformation of viscoelastic fluids. Two types of fluid motion, sufficiently smooth flows and isoelastic flows, have been discussed in some detail. It has been shown that for the latter type of fluid motion where the kinematics may be specifed *a priori*, exact closed forms of the constitutive equation are obtainable. For the more general class of sufficiently smooth flows this is not possible and contracted matrix polynomial forms are given for slow motions.

The results of this paper provide us with tools to attack hydrodynamic and stress analysis problems arising in processing operations, and studies in this direction are now in progress.

## APPENDIX

### Derivation of Kinematic Tensors

Beginning with eq. (3), it may be noted that a differential material volume element is

$$\begin{aligned} d\bar{v}(\phi) = d\bar{\alpha}\cdot d\xi_3 &= \Big(\sum_a \mathbf{e}_a \sum_b \sum_c \epsilon_{abc}\, d\bar{x}_{1b}\, dx_{2c}\Big)\cdot\Big(\sum_m \mathbf{e}_m d\bar{x}_m\Big) \\ &= \sum_a \sum_b \sum_c \epsilon_{abc}\, d\bar{x}_{1a}\, d\bar{x}_{2b}\, d\bar{x}_{3c} \end{aligned} \tag{A-1}$$

The mass of the volume element $d\nu$ is an invariant of the motion

$$\rho(\phi)\; d\bar{\nu}(\phi) = \rho(t)\; d\nu\; (t) = \text{constant}$$

$$d\bar{\nu}(\phi) = J\; d\nu(t) \tag{A-2}$$

$$\sum_o\sum_b\sum_c \epsilon_{abc}\, d\bar{x}_a d\bar{x}_b d\bar{x}_c = J \sum_i\sum_j\sum_k \epsilon_{ijk}\, dx_i\, dx_j\, dx_k$$

and thus

$$d\bar{\alpha}_a = J \sum_i \left(\frac{\partial x_i}{\partial \bar{x}_a}\right) da_i \tag{A-3a}$$

$$da_i = \left(\frac{1}{J}\right) \sum_a \left(\frac{\partial x_a}{\partial \bar{x}_i}\right) d\bar{a}_a \tag{A-3b}$$

The strain in the medium is defined by eq. (14)

$$[d\bar{\alpha}(\phi)]^2 - [d\alpha(t)]^2 = \sum_a d\bar{a}_a d\bar{a}_a - \sum_i da_i\, da_i \tag{A-4}$$

Substitution of eq. (A-3a) into eq. (A-4) yields

$$[d\bar{\alpha}(\phi)]^2 - [d\alpha(t)]^2 = \sum_i\sum_j \left[J^2 \sum_a \left(\frac{\partial x_i}{\partial \bar{x}_a}\right)\left(\frac{\partial x_j}{\partial \bar{x}_a}\right) - \delta_{ij}\right] da_i\, da_j \tag{A-5}$$

which is equivalent to eq. (6a). Equation (6b) follows immediately from substituting eq. (5) into eq. (A-5).

The $\mathbf{B}_n$ tensors are defined by eq. (7). It may be seen that

$$(-1)\frac{d^{n+1}}{dt^{n+1}}\,[d\alpha^2] = \frac{d}{dt}\left[\sum_i\sum_j \overset{(n)}{B}_{ij}\, da_i\, da_j\right]$$

Thus

$$\sum_i\sum_j \overset{n+1}{B}_{ij}\, da_i\, da_j = \sum_i\sum_j \left[\left(\frac{D}{Dt}\overset{(n)}{B}_{ij}\right) da_i\, da_j + \overset{(n)}{B}_{ij}\, \dot{da}_i\, da_j + \overset{(n)}{B}_{ij}\, da_i\, \dot{da}_j\right] \tag{A-6}$$

From eq. (A-3b)

$$\dot{da}_i = \left[\sum_a \left(\frac{\partial \bar{x}_a}{\partial x_i}\right) d\bar{a}_a\right]\left(\frac{D}{Dt}\right)\left(\frac{1}{J}\right) + \left(\frac{1}{J}\right)\sum_a \left(\frac{D}{Dt}\right)\left(\frac{\partial \bar{x}_a}{\partial x_i}\right) d\bar{a}_a$$

$$= \left(\frac{-1}{J^2}\right)\frac{DJ}{Dt}\left[\sum_a \left(\frac{\partial \bar{x}_a}{\partial x_i}\right) d\bar{a}_a\right] + \left(\frac{1}{J}\right)\sum_a \left[\frac{\partial}{\partial t}\left(\frac{\partial \bar{x}_a}{\partial x_i}\right)\right.$$

$$\left. + \sum_{ma} v_m \frac{\partial}{\partial x_m}\left(\frac{\partial \bar{x}_a}{\partial x_i}\right)\right] d\bar{a}_a$$

$$= \left(\frac{-1}{\rho}\right)\frac{D\rho}{Dt}\left[\sum_a \left(\frac{\partial \bar{x}_a}{\partial x_i}\right) d\bar{a}_a\right] + \left(\frac{1}{J}\right)\left[(-1)\sum_{ma}\left(\frac{\partial v_m}{\partial x_i}\right)\left(\frac{\partial \bar{x}_a}{\partial x_m}\right)\right] d\bar{a}_a$$

Using eq. (A-3b), we have

$$\dot{da}_i = \sum_j \left[\sum_m \left(\frac{\partial v_m}{\partial x^u}\right)\delta_{ij} - \frac{\partial v_j}{\partial x_i}\right] da_j \tag{A-7}$$

Substituting eq. (A-7) into eq. (A-6) yields

$$\sum_i\sum_j \overset{(n+1)}{B}_{ij}\, da_i\, da_j = \sum_i\sum_j \left[\left(\frac{D}{Dt}\right)\overset{(n)}{B}_{ij} + 2\sum_m \left(\frac{\partial v_m}{\partial x_m}\right)\overset{(n)}{B}_{ij} - \sum_m \left(\frac{\partial v_i}{\partial x_m}\right) B_{mj} - \sum_m \frac{\partial v_i}{\partial x_m}\overset{(n)}{B}_{im}\right] da_i\, da_j$$

which is equivalent to eq. (8).

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## Résumé

Une théorie continue du comportement viscoélastique non-linéaire a été dévelopée et est applicable à la description quantitative des propriétés rhéologiques des hauts polymères. Des classes particulières de déformations ont été étudiées. On s'est spécialement intéressé aux effets non-linéaires dans licas des fluides viscoelastiques tels que les tensions normales et les viscosités variables. Deux nouvelles classes d'écoulement sont définies: écoulement suffisamment égal et écoulement isoélastique.

## Zusammenfassung

Es wurde eine zur quantitativen Beschreibung der rheologischen Eigenschaften hochpolymerer Stoffe brauchbare Kontinuumstheorie des nichtlinearen Viskositätsverhaltens entwickelt und eine Untersuchung einiger spezieller Deformationsklassen durchgeführt. Dabei wurde den in viskoelastischen Flüssigkeiten auftretenden nichtlinearen Effekten wie Normalspannungen und veränderlicher Viskosität besonderes Augenmerk zugewandt. Es werden zwei neue Klassen von Fliessvorgängen definiert, nämlich das hinreichend glatte und das isoelastische Fliessen.

Received May 13, 1963