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# Model Rheological Equations of State in the Linear Viscoelasticity of Polymeric Composites

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## Summary

The utility of model rheological equations of state is now a well established question in case of polymeric materials. Using the viscoelastic operators method, we indicate the possibility to derive such equations on the basis of mechanical models to be used for polymeric composite materials.

## Introduction

The evaluation of elastic and viscoelastic properties of multiphase polymeric media is a problem of the greatest interest and there are now some authoritative monographs (NIELSEN 1974, MANSON and SPERLING 1976) and a lot of valuable critical reviews (KARDOS, HALPIN and NICOLAIS 1975, LIPATOV 1977, KAUSCH 1977, DICKIE 1978, SHEN and KAWAI 1978) in the field, where significant information and many references can be found.

In the theory of elastic composites are well konwn the so—called extreme bounds, corresponding to uniform stress (Reuss approximation) and to uniform strain (Voigt approximation), which establish the necessary conditions to be satisfied in models calculation.

Takayanagi and co—workers (TAKAYANAGI, HARIMA and IWATA 1963) proposed models for heterogeneous polymeric materials, and they and also a number of other authors reported significant succes in representing the viscoelastic properties of a variety of such materials in terms of these models. It is relevant that in these works, as a first step, by a correspondence principle, the results obtained for elastic components are extended to viscoelastic ones, for simple parallel and series models. Then, in order to correlate in a reasonable way the theory and the experimental data, the so—called Takayanagi models are proposed.

The method to be presented below provides rather the composite rheological equation of state (RES) and consequently the explicit form of the composite rheological parameters, than the composite complex modulus, as is given in the literature. Naturally, the mechanical response of the composite, expressed by different quantities, results in a simpe way, too.

## Theory

The linear viscoelastic behavoir of polymeric materials can be described by the operator form of the RES (ALFREY 1948, FULGGE 1976, PAVEN 1978)

$$P\sigma = Q\varepsilon \quad , \qquad P=\sum_{r=0}^{m} p_r D^r \quad , \qquad Q=\sum_{r=0}^{n} q_r D^r , \qquad (1)$$

where P and Q are the characteristic linear viscoelastic operators, $p_r$ and $q_r$ the rheological parameters of the behavior model, $D^r = d^r/dt^r$ the r—th order time derivative, and $\sigma$ and $\varepsilon$ the stress and the strain in the uni—dimensional case.

In order to derive the explicit form of the composite RES, the rheological parametres of which are expressed as functions of the rheological parameters of

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the components and of their volume fractions, we will consider first the two basic—parallel and series models.

The "a" and "b" linear viscoelastic behavior models are characterized by the $P_a$, $Q_a$ and $P_b$, $Q_b$ operators, respectively. Further, the corresponding volume fractions are $v_a$ and $v_b$ ($v_a + v_b = 1$, $v_b = v$, $v_a = 1 - v$), see Fig.1.

Fig. 1 Parallel (1) and series (2) models

<u>The parallel coupling.</u> The "a" and "b" components, representing linear viscoelastic behavior models, obey to individual RES of the form (1). On the other hand, the definition relationship for the composite stress, $\sigma$, and strain, $\varepsilon$, are

$$\sigma = v_a \sigma_a + v_b \sigma_b \quad , \qquad \varepsilon = \varepsilon_a = \varepsilon_b \quad , \tag{2}$$

where $\sigma_a$, $\sigma_b$ and $\varepsilon_a$, $\varepsilon_b$ are the individual component stresses and strains. Taking into account the relations (1) and (2), one obtains the composite RES

$$[P_a P_b]\,\sigma = [(1-v)P_b Q_a + v P_a Q_b]\,\varepsilon \;, \tag{3}$$

which is similar to eq (1), i.e. also a linear viscoelastic law.

<u>The series coupling.</u> The "a" and "b" components are described by individual RES of the form (1). However, the definition relationships for the composite stress and strain changes now as follows

$$\varepsilon = v_a \varepsilon_a + v_b \varepsilon_b \quad , \qquad \sigma = \sigma_a = \sigma_b \quad , \tag{4}$$

where $\sigma$, $\sigma_a$, $\sigma_b$ and $\varepsilon$, $\varepsilon_a$, $\varepsilon_b$ have the same significance as above. The corresponding composite RES is given by

$$[(1-v)P_a Q_b + v P_b Q_a]\,\sigma = [Q_a Q_b]\,\varepsilon \;, \tag{5}$$

which means that the rheological behavior of the composite is again of linear viscoelastic type.

It results that, in general, the composite RES differs from those of the components, not only quantitatively but also qualitatively; in the case of some simple forms of the component RES it is possible to get to qualitatively analogous forms of the composite RES. Of course, the resulting composite RES (3) and (5) are at least quantitatively different. An another significant consequence of this approach concerns the possibility to obtain, as a second step, the form of the composite operator modulus, and the correspondents of the famous "rule of mixtures", irrespective the "inverse rule of mixtures" (PAVEN and DOBRESCU 1980).

As pointed above, the Takayanagi approach appeared as an attempt to express the average mechanical response between bounds, by simple paralleland series rules of mixing. It is straightforward to obtain now the rheological correspondent of the Takayanagi models, as it results by the operator description of the composite RES. In the case of model I (parameters $\lambda_I, \varphi_I$) one obtains,on the basis of the relationships (3) and (5) and after some mathematical manipulations, the resulting RES as

$$\{P_a\,[P_b Q_a + (1-\varphi_1)\lambda_1\,(P_a Q_b - P_b Q_a)]\}\,\sigma = \\ = \{Q_a[P_b Q_a + \lambda_1(P_a Q_b - P_b Q_a)]\}\,\varepsilon \quad , \qquad (6)$$

and analogously

$$\{P_a\,[P_a Q_b + \varphi_2\,(P_b Q_a - P_a Q_b)]\}\,\sigma = \\ = \{Q_a[P_a Q_b + (1-\lambda_2)(P_b Q_a - P_a Q_b)]\}\,\varepsilon \ , \qquad (7)$$

in the case of model II (parameters $\lambda_2, \varphi_2$), see Fig. 2. The well known equivalence condition of the two models results now immediately to be $\lambda_2 = v(1+v-\lambda_1)^{-1}$, if $P_a Q_b \neq P_b Q_a$, v being the volume fraction of the "b" component in the "a" matrix component.

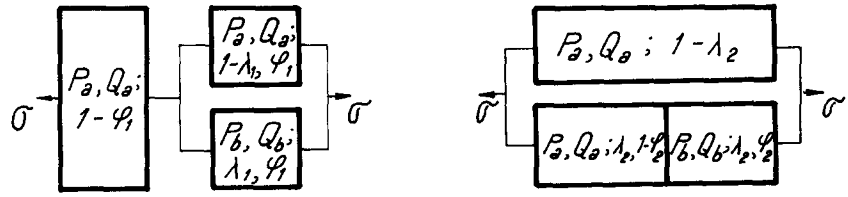

Fig. 2 The Takayanagi models I(1) and II (2).

It appearsworthwhile to write now explicitly , on the basis of equations (3), (5)—(7) the form of the rheological parameters in the case of a typical composite material of elastic (Hooke)/ viscoelastic standard linear (Zener) type. The individual components RES are given by

$$\sigma = q_{H,0}\,\varepsilon \ , \qquad (p_{Z,0} + p_{Z,1} D)\,\sigma = (q_{Z,0} + q_{Z,1} D)\,\varepsilon \ , \qquad (8)$$

where $q_{H,0}$ and $p_{Z,0}$, $p_{Z,1}$ , $q_{Z,0}$, $q_{Z,1}$ are the "H" (Hooke) and "Z" (Zener) rheological parameters of the component models, respectively. In the case of the basic—parallel and series models results

$$(p_{Z,0} + p_{Z,1} D)\,\sigma = \{[(1-v)p_{Z,0}\,q_{H,0} + v q_{Z,0}] + [(1-v)p_{Z,1}\,q_{H,0} + v q_{Z,1}]\,D\}\,\varepsilon, \quad (9)$$

and

$$\{[(1-v)q_{Z,0} + v p_{Z,0}\,q_{H,0}] + [(1-v)q_{Z,1} + v p_{Z,1}\,q_{H,0}]\,D\}\,\sigma = \\ = (q_{H,0}\,q_{Z,0} + q_{H,0}\,q_{Z,1}\,D)\,\varepsilon \quad , \qquad (10)$$

respectively. The rheological parameters of the composite RES, appearing as factors of the D operators are clearly functions of the rheological parametersof "H" and "Z" models. In the case just considered the two RES exprime quantitatively different, but qualitatively analogous rheological behaviors.

The rheological correspondent of the Takayanagi approach results as follows: in the case of a Hooke/Zener composite we have

$$\{\{[1-(1-\varphi)\lambda]\,p_{Z,0}\,q_{H,0} + (1-\varphi)\lambda\,q_{Z,0}\} + \{[1-(1-\varphi)\lambda]\,p_{Z,1}\,q_{H,0} + (1-\varphi)\lambda\,q_{Z,1}\}\,D\}\,\sigma = \\ = \{[(1-\lambda)\,p_{Z,0}\,q_{H,0}^2 + \lambda\,q_{H,0}\,q_{Z,0}] + [(1-\lambda)\,p_{Z,1}\,q_{H,0}^2 + \lambda\,q_{H,0}\,q_{Z,1}]\,D\}\,\varepsilon \quad , \qquad (11)$$

and for a Zener/Hooke composite the composite RES becomes

$$\{\{[1-(1-\varphi)\lambda]\,p_{Z,0}\,q_{H,0} + (1-\varphi)\lambda\,p_{Z,0}^2\,q_{H,0}\} + \{[1-(1-\varphi)\lambda]\,p_{Z,0}\,q_{Z,1} + \\ + p_{Z,1}\,q_{Z,0}) + 2(1-\varphi)\lambda\,p_{Z,0}\,p_{Z,1}\,q_{H,0}\}\,D + \{[1-(1-\varphi)\lambda]\,p_{Z,1}\,q_{Z,1} + \\ + (1-\varphi)\lambda\,p_{Z,1}^2\,q_{H,0}\}\,D^2\}\,\sigma = \{[(1-\lambda)\,q_{Z,0}^2 + \lambda\,p_{Z,0}\,q_{H,0}\,q_{Z,0}] \ +$$

$$+\left[2(1-\lambda)\,q_{Z,0}\,q_{Z,1}+\lambda\left(p_{Z,0}\,q_{H,0}\,q_{Z,1}+p_{Z,1}\,q_{H,0}\,q_{Z,0}\right)\right]D+$$
$$+\left[(1-\lambda)\,q_{Z,1}^{2}+\lambda\,p_{Z,1}\,q_{H,0}\,q_{Z,1}\right]D^{2}\Big\}\,\varepsilon\;, \qquad (12)$$

respectively. It is obvious that the more elaborated form of this approach results in a more complicated dependence of the composite rheological parameters on the rheological parameters and the volume fractions of the components. It is interesting to note the significant rheological difference between the two physically distinct cases represented by the considered possibilities of mixing two given components, one being elastic and the other viscoelastic.

The opportunity of using the above presented approach is apparent in the case of polymeric composites when the morphology is not clearly defined, especially when this morphology varies with composition. Moreover, the method is suitable to provide directly the mechanical response of the composite, corresponding to different types of stress (or strain) histories. Of course, it is necessary to develop further the capabilities of this approach both towards the rheological translation of the existing data in the literature on the mixture rules and also towards the obtaining the rheological information in the case of more complicated situations represented by hybrid polymeric composites.

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