



## A note on empirical use of time-dependent rules of mixtures



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### ARTICLE INFO

#### Article history:

Received 24 March 2014  
Received in revised form 12 February 2015  
Accepted 16 February 2015  
Available online 21 February 2015

#### Keywords:

A. Laminate  
B. Mechanical properties  
C. Elastic properties  
D. Stress relaxation

### ABSTRACT

Under a wide range of conditions, an empirical addition of two time-dependent moduli of the phases in a binary mixture gives similar results to an empirical addition of time-dependent terms corresponding to the regular and inverse rules of mixtures. We give some examples of conditions necessary for the difference to be non-negligible.

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### 1. Introduction

Composite rheological properties can be divided into three groups: time-independent elastic moduli, large deformation and fracture properties, and time/frequency dependence. Of these groups, attempts to model time-independent elastic moduli of composites, henceforth  $E_c$ , have received the greatest attention, and several models have been suggested. In the following we present the pertinent models for binary composites, but they are easily generalized to any number of phases. The most popular model to calculate  $E_c$  is probably the linear, or regular, rule of mixtures, also known as the upper bound:

$$E_{C,Upper} = E_1\varnothing_1 + E_2\varnothing_2 \quad (1)$$

where  $E_1$  and  $E_2$  are the elastic moduli of two phases in a binary composite with respective volume fractions  $\varnothing_1$  and  $\varnothing_2$ . It is easily generalized by summing over any arbitrary number of phases. The rule of mixtures is an isostrain model that follows directly from parallel connection of the elements (mechanically, two or more springs). Conversely, the inverse rule of mixtures, also known as the lower bound, corresponds to a series connection of springs, resulting in an equal stress, but different strains, on the elements. It is given with:

$$E_{C,Low} = (\varnothing_1/E_1 + \varnothing_2/E_2)^{-1} \quad (2)$$

which again can be generalized in a straight-forward manner to any number of phases. The regular and inverse rules of mixtures have

been used to predict other properties than  $E$ . For instance, the regular rule of mixtures, as we will refer to Eq. (1), successfully predicted the thermal and electrical conductivity of fiber-polymer composites [1], while it underestimated the change in thermal conductivity and expansion of polymer composites on addition of metal filler particles [2]. In application to mechanical properties, Eqs. (1) and (2) are sometimes called the Takayanagi models, after the pioneering application by Takayanagi et al. [3] in mechanical characterization of polymer blends.

It is important to recognize that conceptually, the rules of mixtures refer to blends of continuous phases. More specifically, the rules of mixtures are accurate for layered structures (laminates), where Eqs. (1) and (2) should hold for Young's moduli measured in the directions of the layers and perpendicularly to them, respectively. These rules have been used, however, to describe elastic moduli of filled systems, where finite size (often spherical) particles of a discontinuous phase act as a filler of a continuous phase. One attempt to rationalize the use of Eqs. (1) and (2) for filled composites is that in the case of rigid filler, the filler particles are deformed less than the matrix, and both phases experience the same stress, while when the matrix has a higher modulus than the filler, the matrix experiences a higher stress than the filler and both phases experience the same strain. Experimental evidence, however, has shown that Eqs. (1) and (2) fail to predict the elastic moduli of filled composites [4–7], or that the “wrong” limit describes the data, e.g., reports on aluminum [8] and silica-filled [9] polymers where Eq. (2) should hold, but Eq. (1) was close to the experimental values. One notable exception in the reported literature was a cork granulate-filled mortar, where the theoretically appropriate Eq. (1) could reasonably describe the data [10]. For other

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composites, apart from sporadic reports on polymer blends [11–13], experimental evidence has shown that Eqs. (1) and (2) usually fail to predict  $E_C$ , as in the case of many biphasic biopolymer gels [14–17], where  $E_C$  is intermediate between the two limits, and of composite polymer–fiber [18,19] and polymer–clay composites [20], where  $E_C$  generally exceeds the upper bound (Eq. (1)). As already noted, one notable exception where Eqs. (1) and (2) are expected to hold are highly ordered macroscopically laminated composites. The ability of Eqs. (1) and (2) to correctly predict the rheological moduli of an aluminum-reinforced resin laminate has been demonstrated experimentally [21]. It has been pointed out, however, that even for laminates, the rules of mixtures cannot be extended to the material strength at fracture (i.e., outside the linear regime) [22].

For completeness sake, we note that mixture models based directly on inclusion of one phase in another include the isotropic van der Poel model [6], based on homogeneous inclusion of filler spheres, and tensoral homogenization schemes that take into account anisotropy of the inclusions, such as the Eshelby inclusion models [23].

As explained by Ross-Murphy [17], when the elastic modulus of a composite falls between the upper and lower bounds of the rules of mixtures, an engineering approach that may be applied is to calculate the effective contribution of each limit to the composite. A simple way to combine the series and parallel components to recover the experimentally measured  $E_C$  is to connect them in parallel:

$$E_C = A_{\text{Upp}}(E_1 \varnothing_1 + E_2 \varnothing_2) + A_{\text{Low}}(\varnothing_1/E_1 + \varnothing_2/E_2)^{-1} \quad (3)$$

where  $A_{\text{Upp}}$  and  $A_{\text{Low}}$  represent the contributions of the upper and lower bounds ( $A_{\text{Upp}} + A_{\text{Low}} = 1$ ).

## 2. Theory – empirical calculations of composite time-dependent moduli

The simplest approximation of the time-dependent elastic modulus of a composite  $E_C(t)$  is probably addition of the individual time-dependent moduli with appropriate coefficients:

$$E_C(t) = A_1 E_1(t) + A_2 E_2(t) \quad (4)$$

where  $A_1$  and  $A_2$  are adjusted so that  $E_C(0)$  is correctly predicted ( $A_1 + A_2 = 1$ ). Another empirical approach to approximate the time dependence of the elastic time-dependent elastic modulus of a composite,  $E_C(t)$ , can be trivially proposed as an extension of Eq. (3):

$$E_C(t) = A_{\text{Upp}} E_{C,\text{Upp}}(t) + A_{\text{Low}} E_{C,\text{Low}}(t) \quad (5)$$

where  $A_{\text{Low}}$  and  $A_{\text{Upp}}$  are again adjusted so that  $E_C(0)$  is correctly predicted. To find the appropriate terms to use in Eq. (5), we should derive  $E_{C,\text{Upp}}(t)$  and  $E_{C,\text{Low}}(t)$ . The former term can be obtained from the time dependence of two viscoelastic elements connected in parallel:

$$E_{C,\text{Upp}}(t) = \varnothing_1 E_1(t) + \varnothing_2 E_2 \quad (6)$$

Eq. (6) is the time dependent regular rule of mixture.

For the time-dependent inverse rule of mixture, we can refer to the general approach to calculate composite properties, which we quote verbatim from Hashin [24] – “If the effective elastic moduli... of a multiphase specimen are known as functions of phase moduli and phase geometry, the effective transform-domain moduli of the corresponding viscoelastic specimen are found by replacement of the elastic-phase moduli by the transform-domain moduli of the phases”, where the transform-domain modulus refers to the Laplace transform of the time-dependent viscoelastic modulus. Accordingly, time-dependent properties of composites can be calculated by calculating the Laplace transform of the elastic limit solution of the composite, and obtaining the time-dependent property from the inverse Laplace transform. This approach gives

immediately the time-dependent version of the inverse rule of mixtures:

$$E_{C,\text{Low}}(t) = L^{-1} \left( \frac{\widehat{E}_1(s) \widehat{E}_2(s)}{\varnothing_2 \widehat{E}_1(s) + \varnothing_1 \widehat{E}_2(s)} \right) \quad (7)$$

where  $L^{-1}$  denotes the inverse Laplace transform, and  $\widehat{E}(s)$  is the Laplace transform of  $E(t)$ :

$$\widehat{f}(s) = L(f(t)) = \int_0^\infty \exp(-st) f(t) dt \quad (8)$$

We note that Eq. (7) can also be obtained by calculating the composite creep modulus,  $J_C(t)$ , and then using the known relation between  $J(t)$  and  $E(t)$  (see, for instance, [25]):

$$E(t) = L^{-1} \left( \frac{1}{s^2 \widehat{J}(s)} \right) \quad (9)$$

The composite creep modulus  $J_C(t)$  of the series connected elements is given with:

$$J_{C,\text{Low}}(t) = \varnothing_1 J_1(t) + \varnothing_2 J_2(t) \quad (10)$$

which, by successive applications of Eq. (9) allows derivation of Eq. (7).

Because calculation of the appropriate  $E_{C,\text{Upp}}(t)$  and  $E_{C,\text{Low}}(t)$  terms to use in Eq. (5) requires application of the Laplace transform and its inverse, Eq. (4) is easier to implement. In this short note we demonstrate that under a wide range of conditions, Eq. (4) yields similar results to Eq. (5), so that calculation of the latter offers no advantage.

## 3. Results

We will now analyze a simple composite made of two phases, each characterized by a single relaxation time:

$$E_1(t) = e^{-t}; E_2(t) = Ke^{-\alpha t} \quad (11)$$

For the composite in question, the volume fraction of phase 1 will be given with  $\phi$ . We can now investigate the difference between Eqs. (4) and (5) for different values of  $\phi$ ,  $K$ ,  $\alpha$  and  $t$ . One more parameter is needed in this investigation that relates the composite modulus  $E_C$  to the upper and lower bounds,

$$Z = \frac{E_C(0) - E_{C,\text{Low}}(0)}{E_{C,\text{Upp}}(0) - E_{C,\text{Low}}(0)} \quad (12)$$

Understandably, comparing Eqs. (4) and (5) is only meaningful for  $0 < Z < 1$ , i.e., for values of the composite modulus  $E_C$  between the lower and upper bounds.

Fig. 1 shows  $t'$ , defined as the time at which the difference between Eqs. (4) and (5) exceeds 10%, as a function of  $Z$  and  $K$

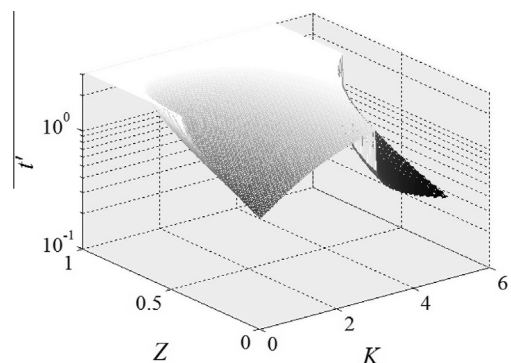


Fig. 1. Time where Eqs. (4) and (5) differ by 10%,  $t'$ , as a function of  $K$  and  $Z$  for  $\alpha = 2$  and  $\phi = 0.5$ . All  $t'$  values  $> 3$  were set to 3.

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