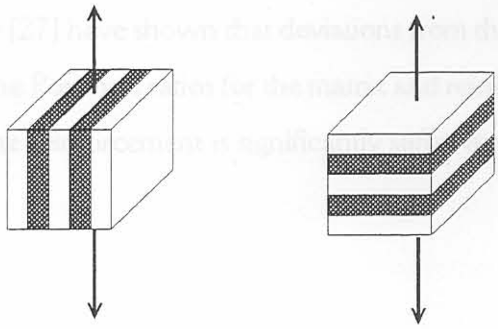
4. YOUNG'S MODULUS

In practice both the strength and stiffness of particulate composites are important. Ahmed and Jones presented an extensive review of the available theories for predicting these properties. [24] The theory for the strength of particulate composites is less developed than that for moduli. This is because it involves many more factors that need to be considered, i.e. the complex interplay between the properties of the reinforcement, the polymer and the interfacial layer.[24] Variables that are important include the shape, size and distribution of filler particles and the strength of the interfacial bond between filler and matrix. The fact that the reinforcements are discontinuous complicates the analysis. The reinforcing agents may have a non-uniform size and may even be non-uniformly distributed in the matrix. [27]

Fibrous reinforcements allow properties to be maximized in the direction parallel to the fibre orientation. [27] Planar reinforcements allow mechanical properties to be developed in the plane of the reinforcement. Such planar reinforcements include: flakes, ribbons and continuous films. [27] Mica, the filler of interest in this study, approaches a flake structure. The focus of this chapter is on methods to predict the modulus of planar flake reinforced composites. A more detailed review is given by Ahmed and Jones. [27]

4.1 The Young's modulus for lamellar composites

The available models for predicting the Young's modulus vary from empirical to highly theoretical. One of the simplest models idealise the composite as alternating layers of high modulus reinforcement and a more compliant matrix. The elastic properties of these laminated composites depend on their orientation relative to the applied stress as shown in Figure 1. The assumption is made that the layers are strongly bonded and this implies that the volume fraction, rather than the thickness of the individual layers determines the mechanical properties. The effective moduli when the layers are in parallel or in series yield the Voigt and Reuss average moduli respectively. [28] Maximum stiffness is obtained when the stress is applied parallel with the layers. The assumption is that the strain will be the same in all the composite layers, i.e. the isostrain condition applies. The effective Young's modulus is given by Equation 1A.



A: Isostrain B: Isostress

Figure 1: Mixing rule conditions for layered composites

When the layers are orientated transverse to the applied stress, the effective modulus is much lower. (Figure 1B) In this case each layer is subjected to the same force. As it is assumed that the area remains constant through the stack, the stress is also the same in each layer, i.e. the isostress condition applies. The effective modulus for this case is given by Equation 1B.

$$E_C = E_m V_m + E_p (1 - V_m) \ldots\ldots\ldots\ldots A$$

$$\frac{1}{E_C} = \frac{V_m}{E_m} + \frac{(1 - V_m)}{E_p} \ldots\ldots\ldots\ldots\ldots\ldots B$$

Equation 1: The classical rule of mixtures

By analogy for these theoretically correct models, these equations are also used in the form of mixing rules for more general applications. In summary, the classical mixing rules are then:

- isostrain, where the force acting on the composite is equal to the sum of the forces acting on each of the elements.
- isostress, where the total strain is equal to the sum of the strains in each element. [24,29]

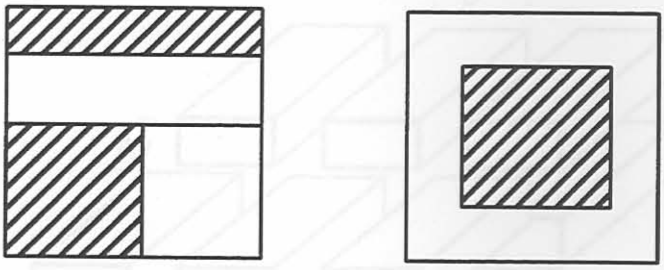
Padawer and Beecher [27] have shown that deviations from the isostress model do occur due to differences in the Poisson's ratios for the matrix and reinforcement. However, this effect is small when the reinforcement is significantly stiffer than the matrix. [27]

4.2 Empirical modifications to the classical mixing rules

Both forms of the mixing rule are applicable to unidirectional long fibre reinforced composites. [24] For composites in general, the isostrain and isostress mixing rules provide upper and lower bounds of the actual behaviour. It is therefore of interest to consider modelling the modulus in terms of appropriate combinations of the mixing rules as in the Hirsch and Counto models. They are based on the geometric models for the composites shown in Figure 2. The Hirsch model (Equation 2A) constitutes a linear combination of the two mixing rules whereas the Counto model (Equation 2B) is more complicated. Both are based on the assumption of perfect adhesion between the two phases.

$$E_c = y(E_p v_p + E_m v_m) + (1-y)\frac{E_p E_m}{E_p v_m + E_m v_p} \qquad (2A)$$

$$\frac{1}{E_C} = \frac{1 - v_p^{1/2}}{E_m} + \frac{1}{(1 - v_p^{1/2}) / v_p^{1/2} E_m + E_p} \qquad (2B)$$



A: Hirsch B: Counto

Figure 2: Schematic representation of the Hirsch and Counto models. [24]

Jacquet et al. have further modified the rule of mixture to account for isolated particulate inclusions, e.g. micro spheres. [29] In essence their model is based on a three-dimensional array of Counto repeat units. Figure 3 shows how the composite is divided into columns to which the classical rules of mixture are applied to calculate the overall modulus. The result is a parameter free model.

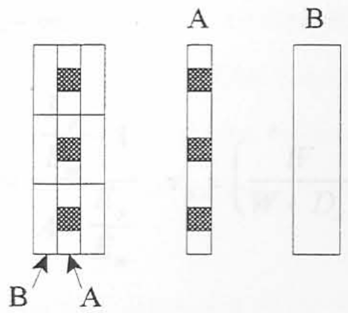


Figure 3: The Jacquet et al. model [29]

$$E = \frac{\alpha^2 E_m E_p}{\alpha E_p + (1-\alpha)E_m} + (1-\alpha^2)E_m$$

$$\alpha = \sqrt[3]{V_m} \qquad (3)$$

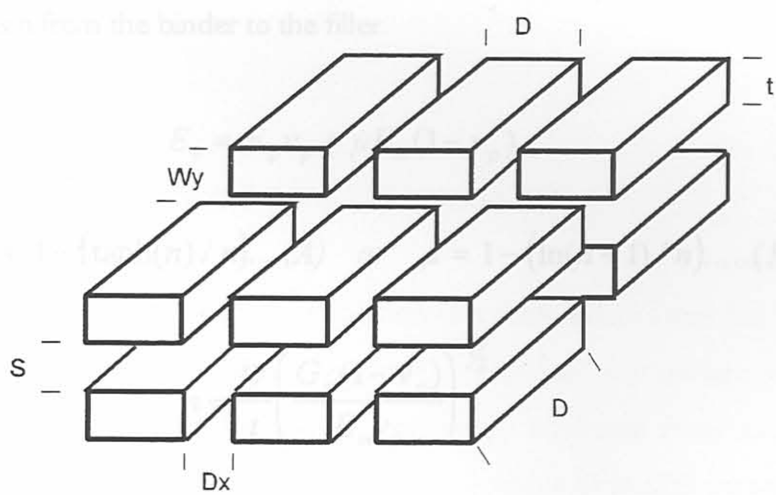


Figure 4: The Halpin and Tsai model [30] for regular platelet or ribbon reinforcement

Halpin and Tsai [30] derived a model for the case of unidirectional plane-parallel ribbon or platelet reinforced composites (Equation 4). E_c is the composite modulus in the plane of orientation (See Figure 4 for definition of symbols). [30] This model reduces to the isostrain mixing rule when L→ ∞.

$$E_c = E_m \frac{1 + ABv_p}{1 - Bv_p} \quad B = \frac{\frac{E_p}{E_m} - 1}{A + \frac{E_p}{E_m}} \quad v_p = \left(\frac{W}{W + D_x}\right)\left(\frac{D}{D + D_x}\right)\left(\frac{t}{t + S}\right) \tag{4}$$

$$A = 2\left(\frac{W}{t}\right)$$

To calculate the transverse in-plane-of-orientation modulus , L/t can be replaced by W/t. To calculate the transverse out-of-plane modulus, the inverse mixing rule can be used.

The models developed by Padawer and Beecher [27] (Equation5A) and Lusis et al. [24] (Equation 5B) assume a stress transfer mechanism between the polymer and the filler. However, only the model by Lusis et al. [27] accounts for platelet interactions at high platelet concentrations. [18,30] It is also assumed that stress is transferred via a shearing mechanism from the binder to the filler.

$$E_c = E_p v_p + \mu E_m (1 - v_p)$$

$$\mu = 1 - \left(\tanh(n)/n\right) \ldots.(A) \quad or \quad \mu = 1 - \left(\ln(n+1)/n\right) \ldots..(B) \tag{5}$$

$$n = \frac{W}{t}\left(\frac{G_p(1 - v_p)}{E_m v_p}\right)^{1/2}$$

The Kerner and Lewis [23] model (Equation 6) takes into account that the mechanical behaviour of composites depends on the degree of interfacial adhesion between the phases, the maximum packing fraction of the filler (ϕ_m) and the Poisson's ratio of the polymer (ν_{ps}). The model assumes the following:

- initially all filler particles are well bonded to the matrix. (ϕ_d=0)
- as the material is strained the filler becomes progressively debonded from the matrix (ϕ_d = debonded filler volume fraction)
- the completely debonded composite behaves similar to a foamed matrix ($\phi_d = v_p$)

The incorporation of a void faction due to the debonding process, lowers the effective modulus of the composite.

$$E_c = E_p E_1 E_2$$

$$E_1 = \frac{1 + A_1 B_1 (v_p - \phi_d)}{1 - B_1 \psi (v_p - \phi_d)} \quad E_2 = \frac{1 - \phi_d}{1 - B_2 \psi \phi_d} \quad A_1 = \frac{(7 - 5\nu_{ps})}{(8 - 10\nu_{ps})} \tag{6}$$

$$B_2 = -\frac{1}{A_1} \quad \psi = 1 + \frac{v_p (1 - \phi_m)}{\phi_m^2}$$

4.3 Limitations of existing theoretical models

Most models described in literature assume that the polymer forms the continuous phase with the filler suspended in it. Practically composites may deviate from the idealized models if the filler particles are not completely separated from each other and the reinforcement element will therefore be an aggregate of smaller particles. The applied stress will therefore not be distributed evenly between the particles and the aggregates and the assumption of either isotress or isostrain will not be valid.

Furthermore, the most general assumptions are:

- the reinforcement and polymer are linear elastic materials, with uniform moduli
- the flakes have uniform width and thickness
- the flakes are uniformly spaced and aligned in a plane-parallel fashion
- the polymer adheres perfectly to the reinforcement.

In Chapter 3 it was shown that the mechanical properties of a composite depend on many factors including:

- the volume fraction filler
- the adhesion between the phases
- particle size and distribution (and therefore aspect ratio)
- shape and orientation of the filler
- the voidage in the composite.

Any model that predicts the mechanical properties of a composite should therefore account for these variables. However, most theoretical models predict that the mechanical properties of the composite only depends on the volume fraction of the filler. This represents a serious limitation for all these models.

The effect of particle shape, orientation and size distribution will show up in the maximum possible packing of a filler. Polydispersed particle mixtures can pack more densely since smaller particles can fill the voids between larger particles. [27] Odd shaped particles will also pack more loosely than highly regular particles such as spheres. One model that does recognise this phenomenon is the Kerner and Lewis equation. [23] Despite other limitations of this model [27] this is one of the few models that does consider the influence of other factors on the mechanical properties of the composite.

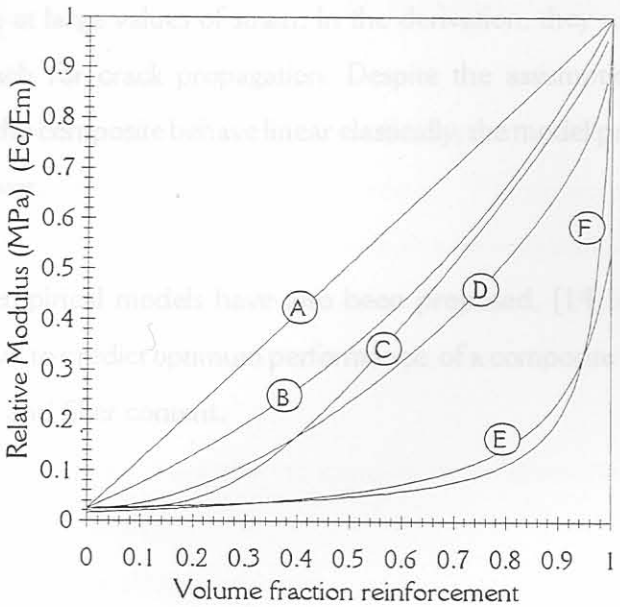


Figure 5: The predicted variations of the tensile modulus of a composites: A: Isostrain (1A), B: Jacquet el al. (4) , C: Padawer and Beecher (5A), D: Lusis et al. (5B), E: Kerner and Lewis (6), F: Isostress (1B). Quantities in brackets indicate the equation numbers in the main text.

A good model will provide accurate prediction over the whole concentration spectrum. Most of the models discussed in the previous section are based on various modifications to the mixing rule. Figure 5 shows the predicted effect of volume fraction on the relative modulus. All these models suffer the same drawback. They all predict that the composite modulus will approach the filler modulus when its volume fraction approaches one. Considering that the filler is present in the form of discrete particles, this is clearly incorrect. A bed of loose filler particles is expected to have no tensile properties unless the filler particles are bound together. This obviously implies the presence of a binder.

Any model used to describe the mechanical behaviour of particulate composites should therefore be able to predict a decrease in mechanical properties, approaching zero, as the amount of binder present approaches zero volume fraction. Additional effects such as voidage should also be considered. The presence of voids will lower the modulus of the composite because they cannot carry any load.

Anderson [13] derived a model that takes into account the debonding process between filler and matrix at large values of strain. In the derivation, they used the Griffith energy balance approach for crack propagation. Despite the assumption that the individual components of the composite behave linear elastically, the model predicts highly nonlinear stress-strain curves.

Various other empirical models have also been proposed. [14,16,24] Some even use experimental data to predict optimum performance of a composite with respect to particle size distribution and filler content.