Prediction of the Mechanical Properties of FRP's by Means of the Concept of Hybrid Interphase

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ABSTRACT

The concept of hybrid interphase in composite materials is a recently introduced by the authors concept according which, the thickness of the interphase area depends not only on the fiber and the matrix material combination but on the property under consideration at the time as well. Up to now by the term 'extent/thickness of fiber-matrix interphase' was meant the geometrical concept of this area having a specific radius irrespectively of the property considered. Based on the old boundary interphase concept, according which the interphase thickness was independent on the property considered at the time, a great number of theoretical models have been developed by numerous authors. However, as recently stated by the authors, the extent of the boundary interphase is not a simple geometrical concept. According to the new definition of the so-called *'hybrid interphase'* as extent of the boundary interphase is considered the extent from the fiber-matrix interface in which a specific property of the matrix is affected by the presence of the fiber or the inclusion in general. Thus, for a specific material combination, the interphase extent strongly depends on the property considered at the time, as well as on the fiber-matrix degree of adhesion and the fiber volume fraction. In the present investigation, the hybrid interphase model is presented and based on this model a prediction of the macromechanical properties of FRP's is attempted.

1. INTRODUCTION

The rapid growth in the use of composite materials in engineering applications dictates the need to study these materials thoroughly and understand their behavior completely. The main reason for their increasing use is that these materials perform equally well in structures, with the traditional ones, without disadvantages such as heaviness, corrosion, weathering etc. These materials often consist of stiff fibers embedded in a soft matrix, with the fibers oriented in the direction of the applied load. The existence of two different phases in the material leads to the creation of a complex region between them, the interphase. This region has properties different, although not independent, from those of the constituents. Also, the properties of this area vary on the direction normal to the surface and can be affected from chemical reactions or sorption between the main constituents.

As stated by Papanicolaou et al. in a series of previous publications [1-5] the definition of the interphasial area can be the following: 'Around an inclusion embedded in a matrix, a rather complex situation develops consisting of areas of imperfect bonding, where mechanical stresses are abundantly developed due to shrinkage and high stress gradients or even stress singularities due to the geometry of the inclusion are apparent and finally voids, microcracks, and other similar discontinuities may be created. In this case the composite may be considered as consisting of three phases, that is the two actual phases and a third one, which may also arise during thermal treatment of the material, because of component interaction. This extra phase is what we call 'interphase' and it is obviously inhomogeneous.'

It has already been experimentally proven that the interphase area really exists. Jajaraman et al.[6] have discussed several recent techniques for physical characterization of the interphase. Chouchaoui et al.[7] studied the effect of the interphase in the micro and macro mechanical properties of a glass/epoxy composite.

This interphase has a specific thickness and properties different from those of the fiber and the matrix.

Pompe et al.[8] assume that the interphase is a part of the matrix surrounding the fiber pocessing local properties different from those of the bulk matrix. The type and the extent of the area vary strongly, and they both depend on the nature of the fiber, its surface and the polymer matrix. The structure and the size of the interphase are both system and condition specific. Chemical reaction and preferential adsorption of matrix components onto the fiber surface are mechanisms that contribute to the interphase formation. Yang et al.[9] suggested a multi-layer adsorption-desorption-reaction model for a binary fluid mixture in contact with a solid surface in order to study the kinetics of interphase formation near bare fiber surfaces in thermosetting composite systems. Using this model they predicted composition and thickness evolution of the interphase as a function of time.

The most important assumption concerning the modeling of the FRP's behavior has to do with the inhomogeneity of the interphase area. The thickness of the area depends on the volumetric composition of the system, but also on the efficiency of bonding between the two constituents. Elastic properties may be further influenced by the processing conditions. This effect is introduced with the term of the adhesion parameter, which represents the percentage of the property value in the fiber surface relatively to the value in the bulk fiber. The perfect bonding between the main phases implies continuity of tractions and displacements at the interphase boundary surfaces. This phase transmits all the interactions between primary components, thus it affects the overall behavior of FRP's. Many empirical models, based on experimental evidence, have been developed to visualize the interphase performance. It is essential to employ the appropriate method, in order to understand the macromechanical behavior of the system.

Because of large differences in thermal expansion coefficients between primary material constituents, thermal stresses develop in the system. These stresses can become large enough and cause material damage. The transmission of these stresses occurs through the interphase, and it depends strongly on the bonding efficiency. Local singularities into the interphase area deplete the bonding efficiency, resulting a decreased capability for transmitting and sustain loading. The continuity conditions on displacements and stresses are still fulfilled, but the properties of this phase are considered much softer than those of the fiber.

A great number of researchers have been investigating thermal response of FRP's [2,5,10,11]. The classical research work assumes a homogeneous area surrounding the inclusion, in order to avoid analytical difficulties that may rise when formulating such a problem. Many recent works use analytical methods to investigate the thermal behavior of a non-homogeneous interphase. The most common model is a concentric cylinder model, consisting of three concentric cylinders, representing the fiber, the interphase and the bulk matrix respectively. Up to now the extent of the interphase was considered constant, and it was affected only by the volumetric composition of the system. In a previous publication by Kim et al.[11] the thickness of the interphase in a glass epoxy composite was measured. The authors used three different experimental techniques (nanoindentation, nanoscratch and DSC tests) and their results show three different values of the interphase thickness, for the same material. They imputed the variations to the different sensitivity of each method used. In the current work a new concept of the interphase is suggested: its thickness depends on the property considered. Thus, when different experimental techniques are used, every result is based in the evaluation of a different property, and of course it returns

different values for the extent of the interphase. The newly presented model is called the *hybrid interphase model* and the new definition of the area based on this concept, can be expressed as following: The interphase volume fraction represents the percentage of the bulk matrix surrounding the inclusions in which a specific matrix property is strongly affected by the existence of the reinforcement, while the interphase thickness represents the maximum radial distance from the inclusion boundary at which this property varies. This means that the interphase is not a simply geometrical concept but it is also property-depended.

In the present work the concept of the hybrid interphase is explicitly presented, and modeled, and a technique, based on this model is suggested, in order to predict macromechanical response of the system.

2. THE HYBRID INTERPHASE MODEL

The representative volume element selected for a unidirectional FRP consists of three concentric cylinders, which represent a single fiber, the interphase and the bulk matrix respectively. The boundary surface between fiber-interphase is well defined at the radius of the inner cylinder, while the respective surface between the interphase and the matrix depends on various parameters referred to below. The fiber and the matrix are homogeneous and isotropic and their properties are defined with the index f and m respectively. The properties of the third phase, denoted by the index i, depend on a number of parameters, such as the overall anisotropy of the composite, the adhesion efficiency, the property considered and the fiber volume fraction. It is well known that the material properties below T_g are nearly constants, thus, we assume that all thermal changes take place in a temperature range well below T_g so that all properties are temperature independent.

The fiber volume fraction, $V_f = (r_f / r_m)^2$ is also a parameter that plays important role in the overall composite behavior. The anisotropy of the composite is defined by the ratio of the transverse value of the property P_t and the longitudinal one P_l, namely, P_t / P_l, where P refers to the property considered, that is, modulus of elasticity E, Poisson's ratio v, or thermal expansion coefficient, α.

The bonding efficiency is defined as the abrupt jump of each property value, from the one in r_f^- to the one in r_f^+. It is denoted as k and its value ranges from 0, for a complete lack of adhesion, to 1 for the perfect bonding. Thus for each property considered the conditions are: $P(r_f^-) = P_f$, and $P(r_f^+) = k P_f$. If the adhesion is perfect, then there is no change in the property value, and in the case of no adhesion the property value just outside the fiber surface is zero.

The interphase thickness is assumed to depend on the bonding efficiency and the property under consideration. Based on these conditions, the expression for the interphase thickness takes the following simple form

$$r_i - r_f = r_f \frac{P_t}{P_l} \frac{1-k}{k} \tag{1}$$

This relationship gives a zero thickness when the adhesion is perfect ($k = 1$) and an infinite one (namely, the whole matrix is modified) when there is no adhesion ($k = 0$). We also assume that the rate of variation of each material property into the interphase region is proportional to the property and converse to its thickness. So the differential equation describing the property variation in the area is

$$\frac{dP_i(r)}{dr} = \frac{\Delta P_i}{r_i - r_f} \tag{2}$$

The solution of this equation that satisfies the conditions

$$P_i(r_f^+) = kP_f \tag{3}$$

$$P_i(r_m) = P_m \tag{4}$$

is the following

$$P(r) = P_m + (kP_f - P_m)\exp(-\frac{k}{1-k}\frac{P_l}{P_t}\frac{\Delta r}{r_f}) \tag{5}$$

Eq. (5) expresses the variational law for the elastic properties into the interphase area. Each property, $E_i(r)$ for the elastic modulus, $\alpha_i(r)$ for the thermal expansion coefficient and $v_i(r)$ for the Poisson's ratio, is described by adhesion efficiency, material inhomogeneity and fiber volume fraction terms. Many different interphases can be modeled using this exponential law, as long as the above parameters are known.

3. PREDICTION OF THE MACROMECHANICAL BEHAVIOR OF THE COMPOSITE

It is well known that for perfect adhesion conditions the longitudinal and transverse values of each property are given by:

$$P_l = P_f \cdot V_f + P_m \cdot (1 - V_f) \tag{6}$$

$$P_t = \frac{P_f \cdot P_m}{P_f \cdot (1 - V_f) + P_m \cdot V_f} \tag{7}$$

These forms though, cannot be used when the adhesion efficiency is assumed to affect the overall behavior of the system. When the adhesion parameter's value is below unity then it is essential to consider that only a relative amount of the fibers are bonded to the matrix and affect the system. This amount equals to kV_f and based on that assumption the above expressions become

$$P_L = P_f \cdot kV_f + P_m \cdot (1 - kV_f) \tag{8}$$

$$P_T = \frac{P_f \cdot P_m}{P_f \cdot (1 - kV_f) + P_m \cdot kV_f} \tag{9}$$

Where P_L and P_T are the experimentally derived longitudinal and transverse values of the property considered. From the above equations we obtain for the adhesion parameter k the following relation

$$k = \frac{P_L - P_m}{P_f - P_m}\frac{1}{V_f} = \frac{P_f}{P_T}\frac{P_T - P_m}{P_f - P_m}\frac{1}{V_f} \qquad (10)$$

Thus, we obtain an equation that provides us the value of the adhesion parameter k, reliant on the experimental values of P_L or P_T respectively. It is obvious that with only one experiment calculating one of the above values, the degree of adhesion can be estimated with accuracy. Since our model for the interphase property variation includes the degree of adhesion, it is essential that this degree is not hypothetically introduced, but accurately calculated. Also, the above relationship associates the longitudinal with the transverse value of each property. This means that by calculating one of them, automatically the other one is derived.

4. APPLICATION IN A CARBON EPOXY SYSTEM

In order to check the model we applied the suggested model to a widely used carbon epoxy composite. The constituents' properties are shown in the table below

Table I

| material	Elastic modulus E GPa	Thermal expansion coefficient α grad^{-1}	Poisson's ratio v
Carbon fiber	231	9.10^{-6}	0.25
Epoxy matrix	3	64.10^{-6}	0.3

For this material the results from the suggested model are shown in the diagrams below. The interphase radius, based on E (r_{iE}), v (r_{iv}), and α ($r_{i\alpha}$), respectively, is shown in fig. 1a, 1b, 1c. It is plot versus both adhesion degree and volume fraction in a 3D diagram. The calculation is based on eq.(1).


(a)   (b)

(c)
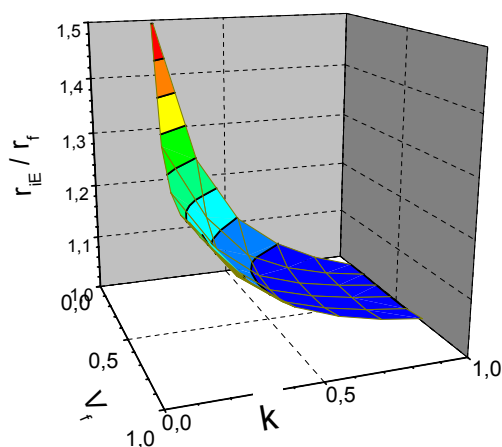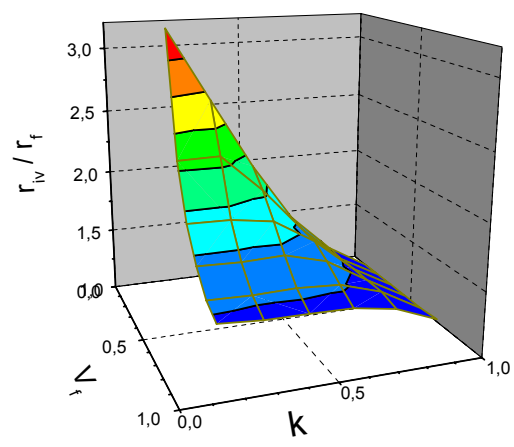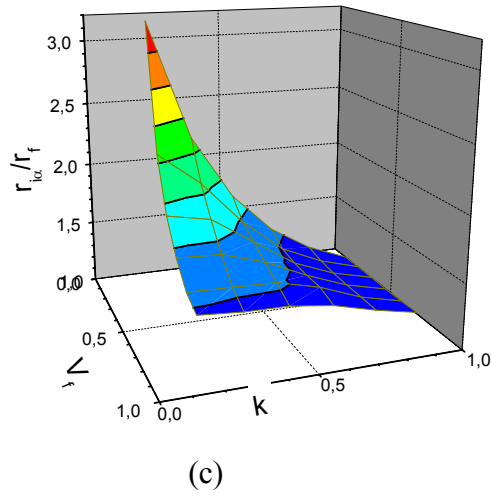
Figure 1. 3D plot of the maximum interphase radius based on a) the Elasticity modulus, b) the Poisson's ratio, and c) the thermal expansion coefficient

From eq.(5), which shows the variational law for the interphase properties into the interphase area, and for the system given in table I, we obtain the following diagrams for the modulus of elasticity, Poisson's ratio and thermal expansion coefficient respectively, in Fig. 2, 3, and 4. All results are given for 65% fiber volume fraction.
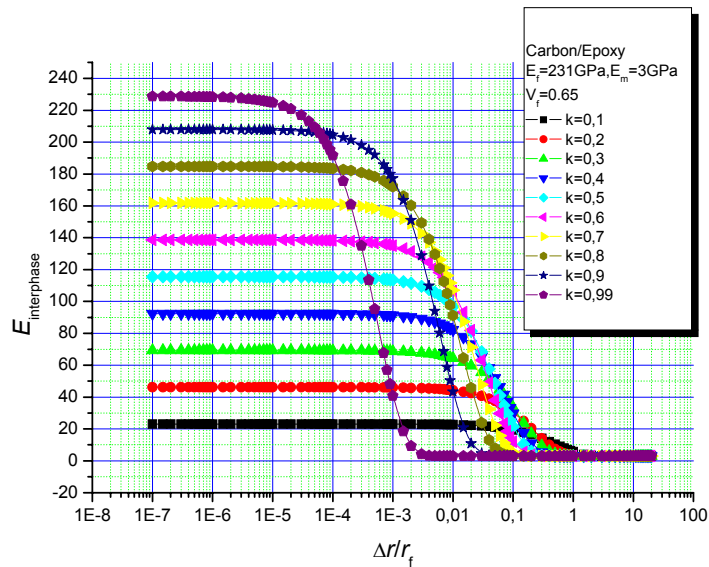
Figure 2. Plot of the Elasticity modulus versus the normalized interphase thickness, for various degrees of adhesion and V_f:65%
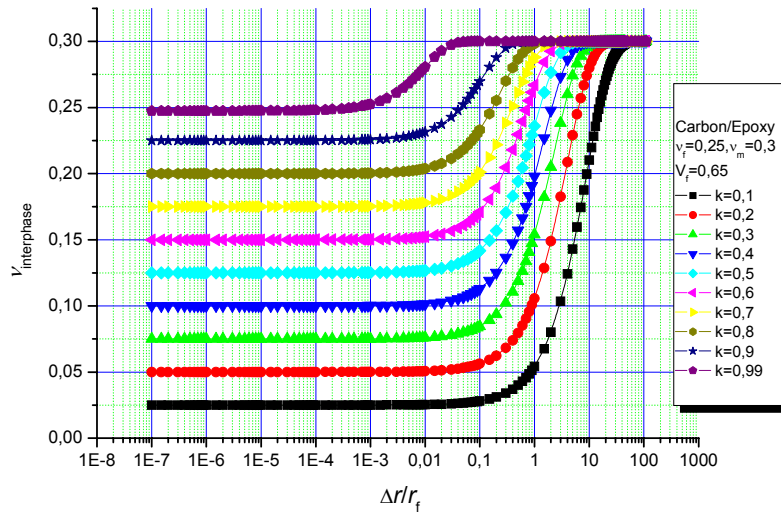
Figure 3. Plot of the Poisson's ratio versus the normalized interphase thickness, for various degrees of adhesion and V_f:65%
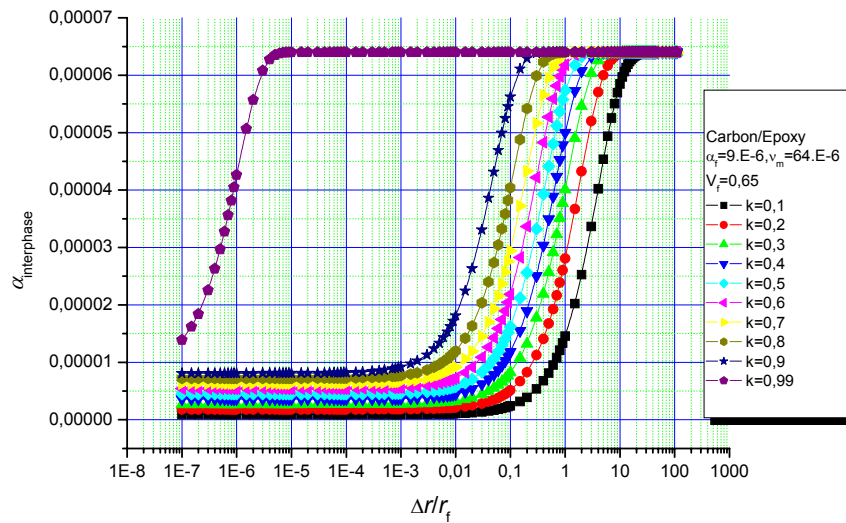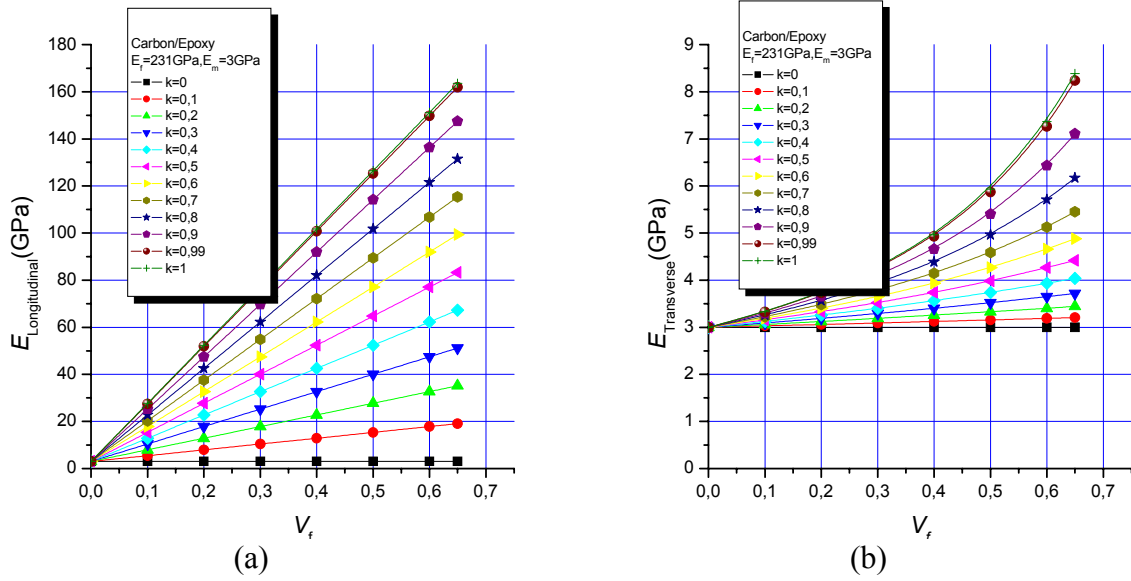

Figure 4. Plot of the thermal expansion coefficient versus the normalized interphase thickness, for various degrees of adhesion and V_f:65%

From eq. (6),(7), the longitudinal and transverse values are plotted for the elasticity modulus, versus the volume fraction and for different adhesion degrees.

Figure 5 Plot of the a) longitudinal and b) transverse elastic modulus, versus V_f and for different adhesion degrees

For a given system consisting of carbon fibres in an epoxy matrix, the following values were experimentally measured as

Table II

V_f	E_f (GPa)	E_m (GPa)	E_L (GPa)	E_T (GPa)
0.635	259	4.3	161	9.6

For these values and from the eq. (10) the degree of adhesion $k = 0.96$.

5. CONCLUSIONS

The dependence of the interphase radius on the property considered is shown in figures 1a, b, c. The plots show the r_i normalized with r_f and it is obvious that the r_i calculated via the Elastic modulus is almost half of the one calculated via Poisson's ratio. Also, the dependency on the adhesion efficiency and the V_f is very strong, as shown in fig.1a,b,c the largest interphase thickness emerges in poor adhesion conditions and small fiber volume fraction values. As the adhesion becomes stronger, the interphase reduces, when perfect adhesion is considered ($k = 1$) then the model becomes a two phase one without interphasial layer.

In Figs 2-4 the graphs of the different properties for the interphase area, show the exponential variation of each property within the interphase. When the bonding efficiency is strong (larger k values), then interphase thickness minimizes and the property reaches the matrix value almost immediately. In poor adhesion conditions, the property reaches the matrix value in a greater distance from the fiber surface.

Finally, the presented theory offers the opportunity to derive accurately a value for the degree of adhesion coefficient by simply using one of the longitudinal or transverse values of a property of the composite under investigation. The bonding efficiency is a

parameter that was always assumed to have a specific value, but there was never before any suggestion for its numerical calculation.

References

1. **G.C. Papanicolaou, S.A. Paipetis, P.S. Theocaris**, 'The concept of the boundary interphase in composite mechanics', Colloid and Polymer Science, 7, (1978), 625-630
2. **G.C.Papanicolaou, P.S.Theocaris**, Thermal properties and volume fraction of the boundary interphase in metal filled epoxies', Colloid and Polymer Science, 3, (1979), 239-246
3. **A.V. Pournaras, G.C. Papanicolaou**, 'Elastic interphase with variable properties in fibrous composites', Journal of reinforced Plastics and composites, 11, 1, (1992), 82-97
4. **P.A. Kakavas, N.K.Anifantis, K. Baxevanakis, D.E. Katsareas, G.C.Papanicolaou**, 'The effect of interfacial imperfections on the micromechanical stress and strain distribution in fiber-reinforced composites', Journal of Materials Science, 30, (1995), 4541-4548
5. **G.C. Papanicolaou, M.V.Michalopoulou, N.K.Anifantis**, 'Thermal stresses in fibrous composites incorporating hybrid interphase regions', Composites Science and Technology, 62, (2002) 1881-1894
6. **K. Jayaraman, K.L. Reifsnider, R.E. Swain**, 'Elastic and thermal effects in the interphase: Part II. Comments on modeling studies', Journal of Composites Technology and Research, 15, (1993), 14-22
7. **C.S. Chouchaoui, M.L. Benzeggah**, 'The effect of interphase on the elastic behavior of a glass/epoxy bundle', Composites Science and Technology, 57, (1997), 617-622
8. **G. Pompe, E. Mäder**, 'Experimental detection of a transcrystalline interphase in glass-fibre/polypropylene composites', Composites Science and Technology, 60, (2000), 2159-2167
9. **F. Yang , R. Pitchumani**, 'Modelling of interphase formation on unsized fibers in thermosetting composites', Proceedings of the ASME Heat Transfer Division, HTD-Vol 366, (2000), pp329-337
10. **F.T. Fisher, L.C.Brinson**, 'Viscoelastic interphases in polymer matrix composites: theoretical models and finite element analysis', Composites Science and Technology, 61, (2001), 731-748
11. **J.K. Kim, M.L. Sham, J. Wu**. 'Nanoscale characterization of interphase in silane treated glass fiber composites', Composites: Part A, 32, (2001), 607-618