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An Upper Bound of Longitudinal Elastic Modulus for Unidirectional Fibrous Composites as Obtained from Strength of Materials Approach

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Abstract: In this paper, the authors introduce an upper bound of the longitudinal elastic modulus of unidirectional fibrous composites to strength of materials approach, provided that the fibre is much stiffer than the matrix. In the mathematical derivations resulting in this bound, the concept of boundary interphase between filler and matrix was also taken into consideration. The novel element of this work is that the authors have not taken into account any particular variation law to approach the stiffness of this intermediate phase. The theoretical predictions were compared with those obtained from some accurate analytical models as well as with experimental data found in the literature, and a satisfactory accordance was observed.

Keywords: fibrous composites; longitudinal modulus; upper bound; strength of materials; interphase

1. Introduction

The variational energy principles of classical elasticity theory have been widely used to designate upper and lower bounds on the stiffness of unidirectional fibre-reinforced composites in the longitudinal and transverse direction of fibres respectively. For instance, Paul [1] applied the principles of minimum energy and minimum complementary energy to determine the bounds on the elastic modulus of a macroscopically isotropic, two-phase composite with arbitrary phase geometry. Yet, Hill [2] achieved to derive the same bounds via an alternative formalistic approach. Besides, Hashin and Rosen [3] restricted Paul's bounds in order to obtain a more useful estimation of moduli for isotropic heterogeneous composites. However, approaches on the basis of energy principles generally result in bounds which may not be adequate in engineering practice. A thorough and effective critique on theories predicting thermal and elastic properties of fibrous composite materials was performed by Chamis and Sendeckyj [4]. Concurrently, a detailed survey, the aim of which was to review the analysis of composites from the applied mechanics and engineering viewpoint, was performed previously [5].

On the other hand, a large amount of models towards the prediction of elastic properties of composites have the following common characteristic: The fibre–matrix boundary interface is assumed to be a perfect mathematical surface. Nonetheless, in reality the situation is much different mainly due to the roughness of the filler. Thus, around an inclusion embedded in a matrix a rather complicated condition takes place, which is characterized by regions of imperfect bonding, permanent stresses resulting from shrinkage, and high-stress gradients or even stress singularities, due to inclusion shape, voids, microcracks, etc. In addition, the interaction between filler and matrix is generally an extremely complex situation and evidently not just a simple mechanical effect. Indeed, the presence of filler constraints the segmental and molecular mobility of the polymeric matrix, as absorption interaction in polymer surface layers into inclusions appears. It is then obvious that, under such circumstances, the quality of adhesion is difficult to be quantified and thus a more detailed study by supposing the existence of an intermediate phase between matrix and filler is necessary.

Indeed, the existence of a boundary interphase was experimentally verified by Lipatov [6] who measured its thickness both for fibrous and particulate composites by means of Differential Scanning Calorimetry (DSC) experiments. In this considerable work, it was also proved that the size of these heat capacity jumps for unfilled and filled polymers is related to interphase thickness via empirical relationships.

Amongst several analytical models appeared in the literature, some of them take into consideration the existence of this natural intermediate phase, developed during the preparation of the composite material which plays the central role on its overall mechanical behaviour, as it characterises the effectiveness of the bonding between phases and thus defines an adhesion factor of the composite material.

In a simplified approach which was adopted in previous papers [7,8], this natural intermediate phase was assumed to be a homogeneous and isotropic material, whereas in another groups of studies [9–11] more advanced and prominent models were introduced, the main feature of which was the fibre to be occupied by a series of successive coaxial cylinders, each of which has a different stiffness in a step-function variation in terms of polar radius. Further, a valuable experimental study towards the estimation of mechanical and thermal properties of unidirectional fibrous composite materials was carried out by Clements and Moore [12] whereas a theoretical and experimental investigation of mechanical properties of polymeric particulate and unidirectional fibrous composites by the interphase concept was performed in a previous paper [13]. In the meanwhile, an alternative standpoint on the boundary interphase stiffness concerning both particulate and fibrous composites is the two and three-term unfolding models introduced by Theocaris [14] which are based on the fact that the intermediate "phase" (termed mesophase annulus) constitutes a transition zone between fibres usually with high stiffness and matrix usually with rather low stiffness. In this framework, the variable mesophase modulus is expressed with in terms of the polar radius of an amended form of Hashin–Rosen cylinder assemblage model by relations of negative powers of the radius, which are compatible with their limits i.e., the moduli of fibre and matrix respectively. In addition, Sideridis et al. [15] introduced strength of materials and elasticity approaches to estimate the elastic constants of unidirectional fibrous composites, by taking into consideration the concept of boundary interphase. In this work, referring to longitudinal modulus the strength materials approach resulted in a modified form of standard mixtures law, whilst classical elasticity approach yielded an upper bound of this property. Also, the mode of variation of the variable interphase elastic properties was an n-th degree polynomial function in terms of interphase radius was initially considered, and for $n = 2$ it yielded a parabolic law. Nevertheless, given that the interphase layer is actually a natural phase (in particular a somewhat deteriorated polymeric matrix), and not an artificial one, in trying to cover the overall spectrum of the variation of its thermal and/or mechanical properties several laws have been adopted, e.g., linear, parabolic, hyperbolic, logarithmic, and exponential law [16]. In the past years, many valuable research works have been carried out for the evaluation of elastic constants of unidirectional fibrous composites and for the investigation of the effect of several influential factors such as filler–matrix interaction, vicinity, adhesion efficiency, and fibre arrangement etc. In a previous study [17] a prediction of the mechanical properties and a micro-scale simulation of fibrous composite materials via the bridging micromechanics model was carried out, whilst for a detailed study on the effective properties of fibrous composite media of periodic structure, one may refer to a previous paper [18]. Also, the effect of size and stacking of glass fibres on the mechanical properties of the fibre-reinforced-mortars was investigated previously [19]. Besides, in a past paper [20] the influence of the statistical nature of fibre strength on the predictability of tensile properties of polymer composites reinforced with natural filler was studied by means of comparison between the well-known linear and power-law Weibull models.

In addition, for a detailed investigation on the effective elastic properties of continuous fibre reinforced composites, with the concurrent consideration of the boundary interphase concept, one may refer to a previous paper [21]. Finally, in a past paper [22], by the use of a novel homogenization technique on the basis of Finite Element Analysis, a thorough study on the influence of interphase zone on unidirectional fibrous composites was carried out.

In the current work, the authors derived an upper bound of the longitudinal elastic modulus of unidirectional fibrous composites reinforced with continuous fibres according to strength of materials approach, provided that the fibre is much stiffer than the matrix a fact that generally concerns polymeric composites. To estimate this bound the concept of an inhomogeneous interphase layer developed between fibre and matrix having variable properties was also taken into consideration. The novelty of the present investigation is that the authors have not considered any particular variation law to approach the interphase stiffness.

2. Towards the Determination of an Upper Bound for Longitudinal Modulus of the Composite

It is known that the use of the standard and inverse rule of mixtures to calculate the longitudinal and transverse modulus respectively for a two-phase composite reinforced with unidirectional continuous fibres is based on the strength of materials approach and requires the following conditions to be fulfilled:

1. The fibre arrangement inside the matrix is uniform.
2. The adhesion efficiency is perfect.
3. Matrix is free of voids.
4. The applied loads are either parallel or perpendicular to the fibre direction.
5. The entire material is initially in a stress free condition, a fact that implies that no residual stresses occur.
6. Fibre and matrix behave as linearly elastic isotropic materials.

In a previous paper [15] the concept of boundary interphase was applied in the framework of a coaxial three-layer cylinder model that constitutes a modified form of Hashin–Rosen cylinder assemblage model. Its cross-sectional area is exhibited in Figure 1.

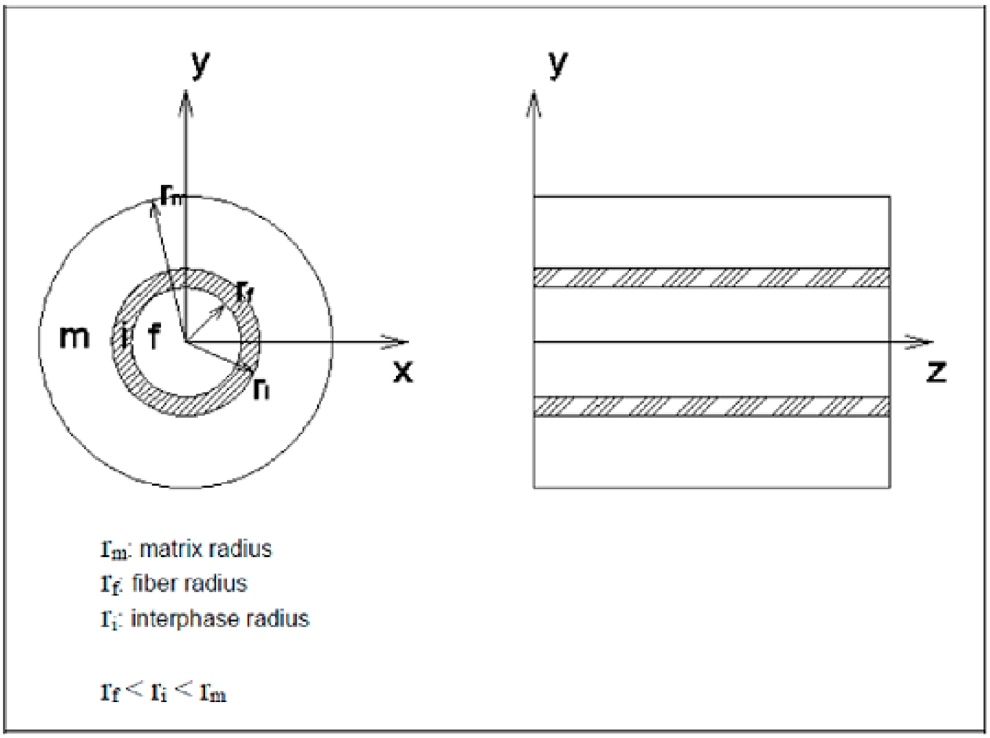

Figure 1. Cross-sectional area and the three phase cylinder model.

If we denote by $r_{\mathrm{f}}; r_i; r_m$ the outer radii of the fibre, the interphase and the matrix circular sections respectively, then the volume fractions $U_{\mathrm{f}}; U_i; U_m$ are given as

$$U_f = \frac{r_f^2}{r_m^2} \tag{1a}$$

$$U_i = \frac{r_i^2 - r_f^2}{r_m^2} \tag{1b}$$

$$U_m = \frac{r_m^2 - r_i^2}{r_m^2} \tag{1c}$$

Apparently, as the filler volume fraction is increased the proportion of macromolecules characterized by a reduced mobility is also increased. This fact is synonymous with an augmentation in interphase concentration by volume. Lipatov [6] has shown that, if calorimetric measurements are performed in the neighbourhood of the glass transition zone of the composite, energy jumps will be observed. These jumps are too sensitive to the amount of filler added to the matrix and can be used to evaluate the boundary layers developed around the inclusions. This fact supports the empirical conclusion presented in a past paper [6], according to which the extent of the interphase expressed by its thickness Δr motivates the variation of the amplitudes of heat capacity jumps appearing at the glass transition zones of the matrix material and the composite with various filler-volume fractions. Moreover, the size of heat capacity jumps for unfilled and filled materials is directly related to Δr by an empirical relationship given in Ref. [6].

This expression defines the thickness Δr corresponding to the interphase and is written out below

$$\left(\frac{r_f + \Delta r}{r_f}\right)^2 - 1 = \frac{\lambda}{1 - U_f} \tag{2a}$$

where the coefficient λ is given by

$$\lambda = 1 - \frac{\Delta C_p^f}{\Delta C_p^0} \tag{2b}$$

Here, the numerator and the denominator of the fraction appearing in the right member of Equation (2b) are the sudden changes of the heat capacity for the filled and unfilled polymer respectively. It has been proved [23,24] that for unidirectional fibrous composites filled either with continuous or with short fibres the fibre and interphase concentrations by volume are related to each other through a two-degree parabolic function in the general form $y = a \cdot x^2$, where the independent variable is the fibre content. We shall write out this relationship later on. Now, on the basis of the experimental data of a previous study, Figure 2 illustrates the variation of dimensionless parameter λ and interphase volume fraction versus fibre content.

Here, one may observe that the parameter λ decreases in a linear manner with respect to U_f.

Next, to evaluate the volume fraction of the interphase layer, let us formulate Equation (1b) as follows:

$$U_i = \frac{(r_f + \Delta r)^2 - r_f^2}{r_m^2} \Leftrightarrow U_i = \frac{2r_f \Delta r + (\Delta r)^2}{r_m^2} \tag{3a}$$

Since $(\Delta r)^2 << r_m^2$ it implies that

$$\frac{(\Delta r)^2}{r_{\mathrm{m}}^2} \cong 0 \tag{3b}$$

and therefore

$$U_i = \frac{2r_f \Delta r}{r_m^2} \tag{3c}$$

Equation (3c) can be combined with (1a) to yield

$$U_i = \frac{2U_f \Delta r}{r_f} \tag{4}$$

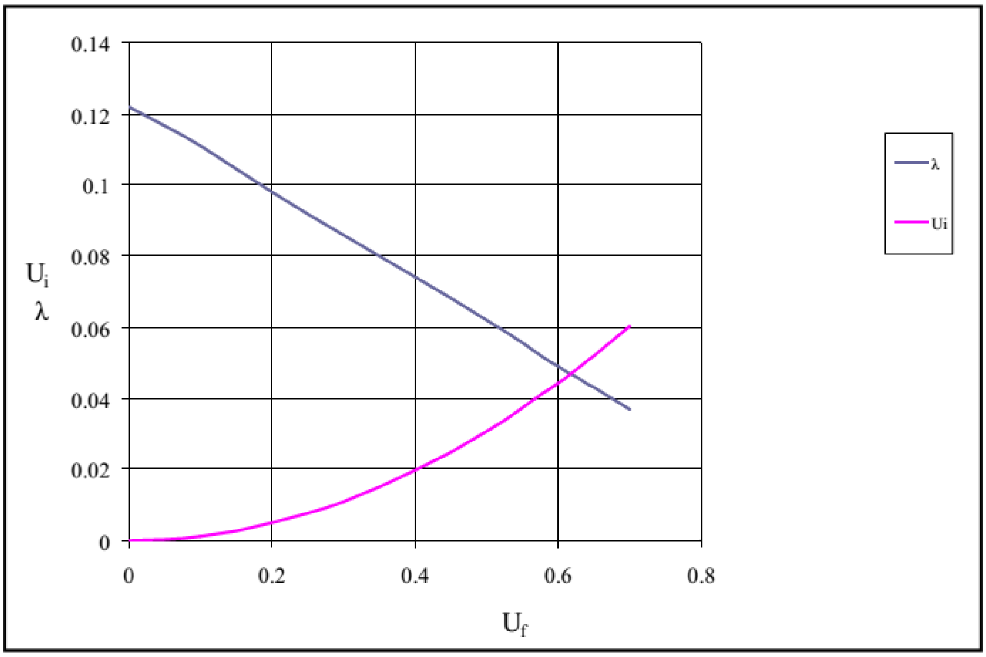

Figure 2. Variation of interphase content and parameter λ versus filler content.

In addition, according to Strength of Materials approach, the longitudinal elastic modulus E_L for a fibrous composite material reinforced with unidirectional continuous fibres can be obtained from the following modified form of standard mixtures law, initially introduced previously.

$$E_L = E_f U_f + E_m U_m + E_i U_i \tag{5}$$

Actually, the above relationship constitutes a "refined" expression of standard mixtures law for the apparent Young's modulus in the direction of fibres.

Here, we emphasize that fibre, matrix and interphase which is somewhat an altered matrix, are isotropic.

Now, as we have stated beforehand, in the current investigation we shall not take into consideration any specific variation law to predict the interphase stiffness. On the contrary, the mathematical derivations resulting in an upper bound of the composite longitudinal modulus are based only on the assumption that the following inequality holds

$$E_m + E_i < E_f \tag{6}$$

Since the matrix is polymeric, this consideration does not generally violate the generality.

Moreover, the following inequality is evident

$$E_m \leq E_i < E_f \tag{7}$$

Thus we can write out

$$\begin{cases} E_m \leq E_i \\ \wedge \\ E_i < E_f \end{cases} \Leftrightarrow \tag{8a}$$

$$\begin{cases} 4\left(\frac{E_m}{2}\right)^2 \leq E_i^2 \\ \wedge \\ 4E_i^2 < 4E_iE_f \end{cases} \tag{8b}$$

and therefore

$$4\left(\frac{E_m}{2}\right)^2 + 4E_i^2 < E_i^2 + 4E_iE_f \Rightarrow E_i^2 < \frac{4}{3}\left[E_iE_f - \left(\frac{E_m}{2}\right)^2\right] \Leftrightarrow E_i^2 < \frac{4}{3}E_iE_f - \frac{E_m^2}{3} \tag{9}$$

In addition, on the basis of inequalities (6) and (7) one may deduce that the following inequalities also hold

$$\left(E_f - E_i\right) \leq E_f + \left(E_f - E_m\right) \tag{10a}$$

$$\left(E_f - E_m\right) \leq \left(E_f - E_i\right) + E_f \tag{10b}$$

$$E_f \leq \left(E_f - E_m\right) + \left(E_f - E_i\right) \tag{10c}$$

Besides, according to Figure 1 the following inequality is plausible

$$r_f < r_i < r_m$$

and therefore

$$r_f^2 < r_i^2 < r_m^2 \tag{11a}$$

or equivalently

$$\frac{r_f^2}{r_m^2} < \frac{r_i^2}{r_m^2} < 1 \tag{11b}$$

Inequality (11b) by the aid of Equations (1a)–(1c) yields

$$U_f < U_i + U_f < 1 \tag{11c}$$

Now, for facility reasons let us set

$$1 = x \tag{12a}$$

$$U_i + U_f = y \tag{12b}$$

$$U_f = z \tag{12c}$$

where the auxiliary variables $x; y; z$ such that $x > y > z$ lie in the interval $[0, 1]$.

In continuing, let us introduce the following continuous single-valued function in terms of the argument z: $f : R \to R_+$, defined by the formula $f(z) = \left[(E_f - E_i)(x - y) - E_f(y - z)\right]^2$.

Here, on the basis of Equations (12a)–(12c), one may observe that this formula contains all involved terms of the fibrous composite system (moduli and volume fractions of three phases) given that $U_f + U_i + U_m = 1$. In addition, we elucidate that the variable z (i.e., U_f) is the only independent one, since as we have already reported it has been shown [23,24] that for unidirectional fibrous composites reinforced either with long or with short fibres the fibre and interphase contents are linked with each other by a two-degree parabolic function.

Evidently, according to the definition of function f, the following inequality holds identically

$$\Big[(E_f - E_i)(x - y) - E_f(y - z)\Big]^2 \geq 0 \tag{13a}$$

To give a more realistic interpretation in the above relationship, one may combine it with (12a)–(12c) to obtain

$$\Big[(E_f - E_i)U_m - E_f U_i\Big]^2 \geq 0 \Leftrightarrow \Big[(E_f(U_m - U_i) - E_i U_m\Big]^2 \geq 0 \tag{13b}$$

Here, it was taken into account that $U_f + U_i + U_m = 1$.

This inequality shows somehow the balance between matrix and interphase, given that the latter is somewhat an altered matrix. Indeed, if no interphase occurs there will be no deterioration of the matrix material.

Now, on the basis on Equation (13a) it implies that

$$\begin{gathered}
(E_f - E_i)^2(x - y)^2 + E_f^2(y - z)^2 - 2(E_f - E_i)E_f(x - y)(y - z) > 0 \Leftrightarrow \\
(E_f - E_i)^2(x - y)[(x - z) - (y - z)] + E_f^2(y - z)[-(x - y) - (z - x)] - 2(E_f - E_i)E_f(x - y)(y - z) > 0 \Leftrightarrow \\
(E_f - E_i)^2(x - y)(x - z) - E_f^2(x - y)(y - z) - (E_f - E_i)^2(x - y)(y - z) - 2(E_f - E_i)E_f(x - y)(y - z) + E_f^2(z - x)(z - y) > 0 \Leftrightarrow \\
(E_f - E_i)^2(x - y)(x - z) - \Big[E_f^2 + (E_f - E_i)^2 + 2(E_f - E_i)E_f\Big](x - y)(y - z) + E_f^2(z - x)(z - y) > 0 \Leftrightarrow \\
(E_f - E_i)^2(x - y)(x - z) - \Big[E_f + (E_f - E_i)\Big]^2(x - y)(y - z) + E_f^2(z - x)(z - y) > 0
\end{gathered} \tag{14}$$

Concurrently, according to inequality (10b) we infer

$$(E_f - E_m)^2 \leq \Big[E_f + (E_f - E_i)\Big]^2 \Leftrightarrow -(E_f - E_m)^2 \geq -\Big[E_f + (E_f - E_i)\Big]^2 \tag{15}$$

Then given that the terms $(x - y); (y - z)$ agree in sign, inequality (14) can be combined with (15) to yield

$$\begin{gathered}
(E_f - E_i)^2(x - y)(x - z) - (E_f - E_m)^2(x - y)(y - z) + E_f^2(z - x)(z - y) > 0 \Leftrightarrow \\
\Big(E_f - E_i\Big)^2(x - y)(x - z) + \Big(E_f - E_m\Big)^2(y - x)(y - z) + E_f^2(z - x)(z - y) > 0 \Leftrightarrow \\
E_f^2(x - y)(x - z) + E_i^2(x - y)(x - z) + \Big(E_f - E_m\Big)^2(y - x)(y - z) + E_f^2(z - x)(z - y) > 2E_f E_i(x - y)(x - z)
\end{gathered} \tag{16}$$

Finally, since the terms $(x - y); (x - z)$ agree in sign, inequality (16) can be combined with (9) to yield

$$\begin{gathered}
E_f^2(x - y)(x - z) + \left(\tfrac{4E_iE_f}{3} - \tfrac{E_m^2}{3}\right)(x - y)(x - z) + \Big(E_f - E_m\Big)^2(y - x)(y - z) + E_f^2(z - x)(z - y) > 2E_f E_i(x - y)(x - z) \Leftrightarrow \\
E_f^2(x - y)(x - z) - \tfrac{E_m^2}{3}(x - y)(x - z) + \Big(E_f - E_m\Big)^2(y - x)(y - z) + E_f^2(z - x)(z - y) > \left(2 - \tfrac{4}{3}\right)(x - y)(x - z)E_f E_i \Leftrightarrow \\
E_i < \frac{E_f^2(x-y)(x-z) - \frac{E_m^2}{3}(x-y)(x-z) + \big(E_f - E_m\big)^2(y-x)(y-z) + E_f^2(z-x)(z-y)}{\frac{2}{3}E_f(x-y)(x-z)}
\end{gathered} \tag{17}$$

Since we have set $1 = x; U_i + U_\mathrm{f} = y; U_\mathrm{f} = z$ it follows that

$$E_i < \frac{E_f^2(1 - U_i - U_\mathrm{f})(1 - U_\mathrm{f}) - \frac{E_m^2}{3}(1 - U_i - U_f)(1 - U_f) + \big(E_f - E_m\big)^2(U_i + U_f - 1)U_i + E_f^2(1 - U_f)U_i}{\frac{2}{3}E_f(1 - U_i - U_\mathrm{f})(1 - U_\mathrm{f})} \tag{18}$$

Also, given that $U_f + U_m + U_i = 1$ inequality (18) yields

$$E_i < \frac{\left(E_f^2 - \frac{E_m^2}{3}\right)U_m(1 - U_f) + E_f^2(1 - U_f)U_i - \Big(E_f - E_m\Big)^2 U_m U_i}{\frac{2}{3}E_f U_m(1 - U_f)} \tag{19}$$

Here one may pinpoint that the above relationship is independent of any variation law that could be adopted to predict how the interphase modulus varies with respect to the radius of the coaxial cylinder model. We emphasize that the interphase zone is a natural phase which is developed in reality between filler and polymer matrix and is neither an artificial one, e.g., created by the immersion of the fibres in an agent, nor a pseudophase being contrived to simulate the microstructure of the composite.

Now, one may observe that according to the proposed technique the following three intermediate steps concerning the process of determining the stiffness of the overall composite material are bypassed:

i. Approximation of the stiffness of interphase layer by a polynomial function or any other arbitrary continuous function with respect to the radius of the coaxial cylindrical three layer model.
ii. Estimation of the averaging values of stiffness for the interphase zone. This procedure takes place to accommodate the calculations, as can be observed in a past paper [15].
iii. Measurement of the thickness of interphase zone by means of Differential Scanning Calorimetry (DSC) experiments.

Also, as we have previously pointed out, it was proved [23,24] that for unidirectional fibrous composites reinforced either with long or with short fibres, the ordered pairs (U_i, U_f) fit in an excellent manner a two degree parabola.

This parabola is expressed by

$$U_i = 0.123 \cdot U_f^2 \tag{20}$$

It can therefore be noticed that the process of calculating the longitudinal modulus of the final material has shortened considerably, when compared with the corresponding procedures presented in past studies [11,14–16]. In this context, one may observe that by means of the introduced analytical technique, the interphase elastic modulus has been represented directly in terms of fibre content without having previously been expressed as a single-valued function of the polar radius of the coaxial three phase cylinder model.

Then Equation (5) can be combined with (19) to yield an upper bound for the longitudinal modulus of the overall material in the following explicit form

$$E_{L,UB} = E_f U_f + E_m U_m + \frac{\left[\left(E_f^2 - \frac{E_m^2}{3}\right) U_m (1 - U_f) + E_f^2 (1 - U_f) U_i - \left(E_f - E_m\right)^2 U_m U_i\right] \cdot U_i}{\frac{2}{3} E_f U_m (1 - U_f)} \tag{21}$$

Thus, Equation (21) in association with the Equation (20) results in the direct calculation of an upper bound for the longitudinal composite modulus in terms of fibre volume fraction. Besides, one may observe that the radius r of the coaxial cylinder model (in particular the inner and outer radius of the interphase annulus) does not appear in the previous mathematical procedure resulting in Equation (21).

3. Results and Discussion

In Table 1 the theoretical predictions concerning the upper bound of the composite longitudinal modulus, as obtained from Equation (21) in combination with Equation (20) appear with respect to fibre concentration by volume which is up to 0.65. Roughly speaking, one may state that this value generally constitutes the optimum fibre volume fraction above which the reinforcing action of the fibres is upset [22]. For facility reasons, and to be in accordance with the experimental work of Clements and Moore [12], we considered an epoxy composite reinforced with E-glass fibers, i.e., $E_f = 72$ GN/m^2, and $E_m = 3.5$ GN/m^2 whereas the Poisson's ratios of fibre and matrix are $\nu_f = 0.2$ and $\nu_m = 0.35$, respectively. In the same table, the theoretical values obtained from Theocaris et al. [11], according to linear, hyperbolic, and parabolic variation laws also occur. Besides, the theoretical values yielded by two and three term unfolding models derived from Theocaris [14] are presented. Finally, the theoretical values achieved by the expression for apparent Young's modulus in the direction of fibres obtained from Sideridis et al. [15], according to three variation laws are exhibited.

Table 1. Theoretical and experimental values of longitudinal modulus with respect to fibre concentration.

E_L GN/m^2 / υ_f	**Authors**	**Theocaris et al. [11] Linear Law**	**Theocaris et al. [11] Hyperbolic Law**	**Theocaris et al. [11] Parabolic Law**	**Sideridis et al. [15] Linear Law**	**Sideridis et al. [15] Hyperbolic Law**	**Sideridis et al. [15] Parabolic Law**	**Two Term Unfolding Model [14]**	**Three Term Unfolding Model [14]**	**Clements and Moore [12]**	**Sideridis Exp. [13]**
0	3.5	3.5	3.5	3.5	3.5	3.5	3.15	3.5	3.5		3.45
0.1	10.47845	10.39	10.385	10.372	10.1126	10.1089	10.0821	10.28992	10.7423438		10.3
0.2	17.71406	17.37	17.37	17.31	17.4122	17.2385	17.1024	17.42867	17.9270779		17.26
0.3	25.207991	24.43	24.43	24.3	24.8958	24.3515	24.107	23.28899	24.2137138		
0.4	32.963901	31.57	31.57	31.35	32.4742	32.1485	32.104	28.26454	30.2908271		
0.5	40.993581	38.8	38.79	38.45	40.171	40.1509	39.988	34.09573	36.2452983		38.14
0.6	49.339712	46.11	46.09	45.6	48.7423	48.3837	47.124	40.14736	43.3375487	38.28	45.1
0.65	53.67567	49.75	49.73	49.13	52.798	52.2038	51.0952	45.1047	48.0763212	45.24	48.5

For a brief description of these rigorous theoretical formulae used for comparison, let us refer to Appendix A Section. On the other hand, the experimental values obtained from Clements and Moore [12] and Sideridis [13] are performed as well. Here, one may observe that amongst the variation laws that were adopted by Theocaris et al. and Sideridis et al. to approach the interphase stiffness in the formulae presented in past papers [11,15], the linear ones yield the highest predictions.

Next, Figure 3 designates the theoretical values for the upper bound of the composite longitudinal modulus, yielded by Equation (21) associated with Equation (20) versus fibre volume fraction, together with those obtained from Theocaris et al. (linear, parabolic and hyperbolic variation law) [11] and Sideridis et al. (linear, parabolic and hyperbolic variation law) [15]. Moreover, the theoretical predictions arising from Theocaris' two and three term unfolding model [14] are performed. For a brief description of these theoretical formulae, let us refer to Appendix A Section. Finally, the experimental data obtained from Clements and Moore [12] and Sideridis [13] appear.

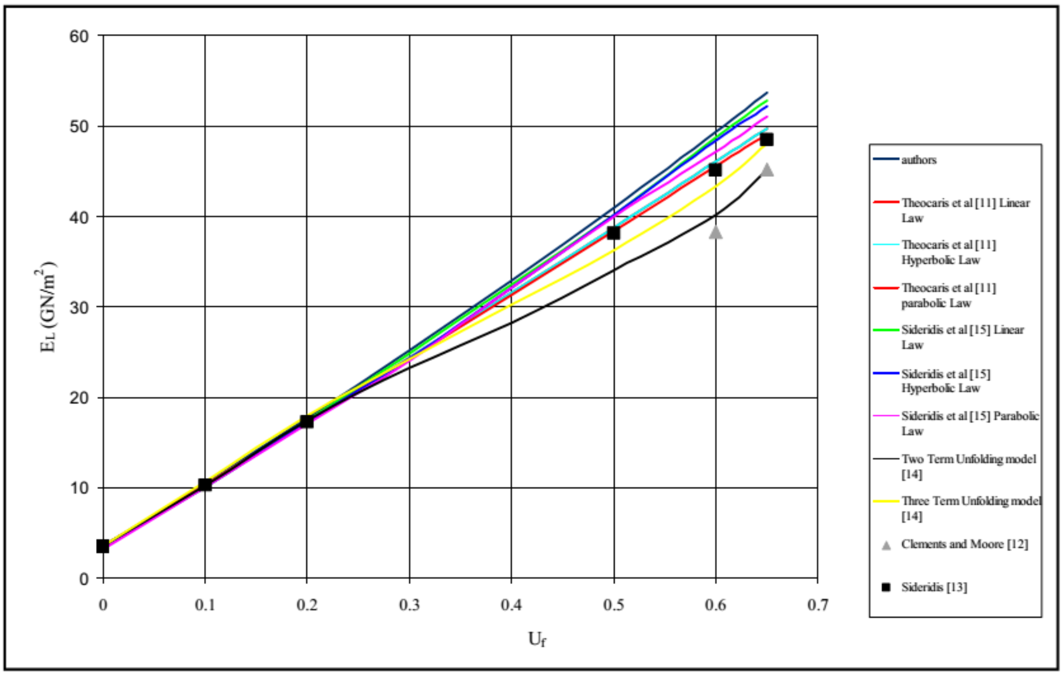

Figure 3. Variation of Longitudinal modulus against fibre volume fraction.

By focusing in Figure 2, one may observe that for low fibre contents the theoretical values of E_L arising from Equation (21) by the aid of (20) are very close to those yielded by all the other theoretical formulae used for comparison. In addition, they are in good agreement with the experimental values obtained from Sideridis [13]. Next, for medium fibre concentrations by volume one may point out a deviation, especially between the values obtained from Equation (21), as well as from Sideridis' upper bound [15] with the predictions given by Theocaris' two and three term unfolding model. Yet, a comparison between the values obtained from Equation (21) and those arising from Theocaris et al. [11] yields a smaller deviation.

However, an increment of this discrepancy is noticed at high fibre contents up to 0.65. Besides, the theoretical predictions of Equation (21) are above the experimental data obtained from Sideridis [13] and well above those of Clements and Moore [12]. Of course one may elucidate that such discrepancies could be generally expected given that the aim of Equation (21) and Sideridis formula [15], is to signify an upper bound of the longitudinal modulus. Moreover, some discrepancies are also attributed to the fact that some theoretical assumptions and conceptions cannot be fulfilled in praxis.

In the meanwhile, one may also observe that for high fibre concentrations by volume the theoretical values yielded by Theocaris' two and three term unfolding model [14] are in consensus with the experimental results obtained from Clements and Moore [12]. Finally, it can be said that Equation (21) constitutes a slight but concrete improvement when compared with Sideridis' upper bound performed previously [15].

Nevertheless, a shortcoming of Equation (21), which illustrates the upper bound of longitudinal composite moludus derived from strength of materials approach, is that the mathematical derivations were based on the hypothesis that the fibre is much stiffer that the matrix i.e., $E_m + E_i < E_f$ and hence an analogous expression for Poisson ratio of the composite cannot be obtained according to this reasoning. Thus the overall methodology leading to an upper bound of composite modulus without the consideration of any variation law, cannot be used to improve a theoretical formula arising from elasticity approach, such as the other formulae used from comparison without the adoption of several variation laws to approach interphase Poisson's ratio. Thus, one could not know beforehand which variation law of interphase Poisson ratio would yield the highest predictions of E_L in the final expression of longitudinal modulus, although it was observed [25] that the parabolic variation law generally yields the lowest values for the interphase stiffness of unidirectional fibrous composites when compared with other laws that are commonly used. On the other hand, one may also pinpoint that since according to strength of materials approach fibres, matrix and interphase are supposed somewhat as solid blocks the volumes of which are proportional to their relative abundance in the overall material instead of the modified form of Hashin–Rosen cylinder assemblage model presented in Figure 1 one may adopt the following simplified model (see Figure 4) to simulate the microstructure of the unidirectional fibrous composite.

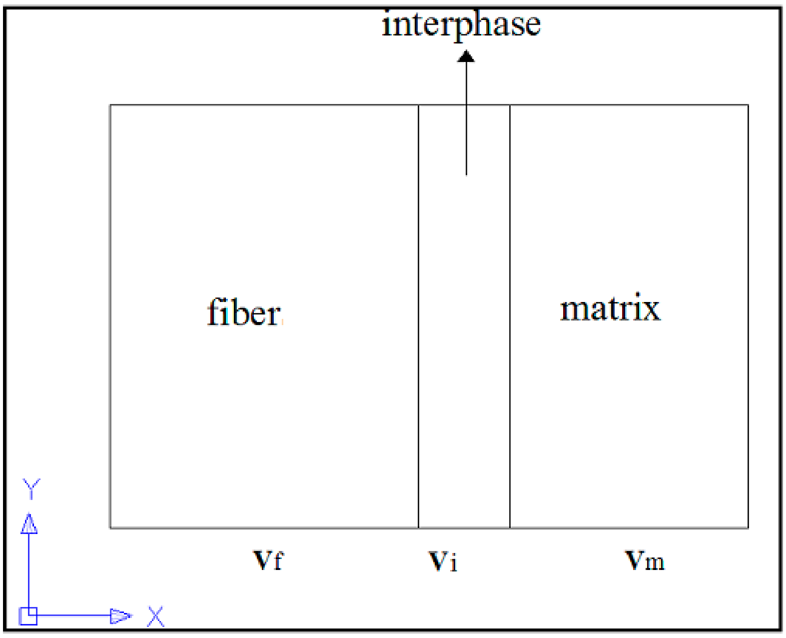

Figure 4. Simplified model of the composite structure.

Evidently the following expressions hold

$$U_m = \frac{V_m}{V}; U_f = \frac{V_f}{V}; U_i = \frac{V_i}{V} \tag{22}$$

with $V = V_m + V_f + V_i$.

Obviously, since the inequality $U_f < U_i + U_f < 1$ holds, the overall mathematical procedure resulting in Equation (19) and in Equation (21) remains as is.

In this context, the three-phase modified version of Hashin–Rosen model exhibited in Figure 1 could be omitted, given that the radius of this coaxial cylinder model does not take place in the mathematical derivations carried out by the author's to arrive at the upper bound of composite modulus. Hence, the overall mathematical derivation leading to this bound may alternatively result from the consideration of a simplified rectangular model and possibly seems closer to the basis of a three-phase "solid blocks" unit cell than a coaxial cylinder model. However, it is the authors' opinion that the adoption of the model presented in Figure 1 is very useful, since the radii of the three embedded cylinders signify in a more elegant and comprehensive manner the way that the interphase region surrounds the unidirectional fibre in the form of numerous successive annuli [24].

4. Conclusions

In this theoretical work, constituting a continuation of the author's on-going investigation into elastic properties of fibrous materials, an upper bound of longitudinal modulus of three phase fibrous-reinforced composites was a determined according to strength of materials approach, with respect to the constituent material properties, provided that the fibre is much stiffer than the matrix. This hypothesis generally concerns polymeric fibrous composites. The fibres that reinforce the polymer, which is supposed to be macroscopically homogeneous are unidirectional, continuous and isotropic. Concurrently, the concept of interphase in the context of a cluster of three coaxial cylinders was taken into account. In this framework, a rephrased form of Hashin–Rosen cylinder assemblage model was adopted. The novel element here is that the authors did not suppose any particular variation law to approach the interphase stiffness.

In this context, one may deduce that the following three basic intermediate steps referring to the process of estimating the stiffness of the overall material were bypassed:

i. Theoretical approximation of interphase stiffness,
ii. Estimation of its averaging values,
iii. Measurement of interphase thickness via DSC experiments.

In closing, it can be said that the proposed formula contributes in a considerable manner to the encapsulation of several analytical techniques for evaluating the stiffness of three-phase unidirectional fibrous composites.

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Appendix A

In this section, let us make the following brief theoretical remarks referring to some reliable theoretical formulae resulting in the direct estimation of longitudinal modulus for a general class of unidirectional fibrous composites reinforced with continuous fibres.

(1) Theocaris, Sideridis, and Papanicolaou formula [11]

Here, the adopted microstructural model to simulate the periodic fibrous composite is a coaxial three layer cylindrical model similar to that presented in Figure 1. The longitudinal modulus E_L, was calculated in the framework of energy balance for the overall material. In this context, the following relationship holds

$$\begin{aligned}\int_0^{r_m} E_L \varepsilon^2 r dr = \int_0^{r_f} \left[8C^2(1 - v_f - 2v_f^2) + E_f^2 \varepsilon^2\right] r dr + \int_{r_f}^{r_i} \frac{1}{E_i}\left[\frac{2K^2}{r^4}(1 + \nu_i) + 8M^2(1 - v_i - 2v_i^2) + E_f^2 \varepsilon^2\right] r dr + \\ + \frac{1}{E_m}\int_{r_i}^{r_m}\left[\frac{2F^2}{r^4}(1 + \nu_m) + 8H^2(1 - v_m - 2v_m^2) + E_m^2 \varepsilon^2\right] r dr\end{aligned} \tag{A1}$$

In the above representation, both interphase modulus and Poison's ratio are functions of the polar distance from the fibre according to a three phase coaxial cylinder model. To integrate the second term, four different laws of variation were taken into account.

Hence the following expressions hold:

(a) Linear Law for Interphase Stiffness and Poisson's Ratio

$$E_L = E_f \frac{r_f^2}{r_m^2} + \frac{\left(E_f r_i - E_m r_f\right)}{r_m^2}\left(r_i + r_f\right) - \frac{2}{3}\frac{\left(r_i^2 + r_i r_f + r_f^2\right)\left(E_f - E_m\right)}{r_m^2} + \\ + \left[\frac{1-\nu_m - 2\nu_m^2}{E_m} + E_m\right]\frac{\left(r_m^2 - r_i^2\right)}{r_m^2} \tag{A2}$$

Also according to Lipatov's experimental method [6] the following equality holds

$$\frac{r_f^2}{r_i^2} = \frac{U_f}{U_f + U_i} = \frac{1 - U_f}{1 - U_f(1-\lambda)} \tag{A3}$$

thus it follows

$$E_L = E_f U_f + \frac{1}{3}\left[\left(E_f + 2E_m\right)(1 - U_m) - \left(2E_f + E_m\right)U_f + \left(E_f - E_m\right)\sqrt{U_f(1-U_m)}\right] + \\ + \left[\frac{1-\nu_m-2\nu_m^2}{E_m} + E_m\right]U_m \tag{A4}$$

(b) Hyperbolic law for interphase stiffness and Poisson's ratio

$$E_L = E_f \frac{r_f^2}{r_m^2} + E_m\left(\frac{r_m^2 - r_i^2}{r_m^2}\right) + \frac{E_m r_i - E_f r_f}{r_m^2}\left(r_f + r_i\right) + 2\left(E_f - E_m\right)\frac{r_f r_i}{r_m^2} + \left[\frac{1-\nu_m-2\nu_m^2}{E_m} + E_m\right]\left(\frac{r_m^2 - r_i^2}{r_m^2}\right) \tag{A5}$$

Then, by the aid of Equation (A3) it implies that

$$E_L = E_f U_f + \left(E_m\sqrt{1-U_m} - E_f\sqrt{U_f}\right)\left(\sqrt{1-U_m} + \sqrt{U_f}\right) + 2\left(E_f - E_m\right)\left(\sqrt{U_f(1-U_m)}\right) + \left[\frac{1-\nu_m-2\nu_m^2}{E_m} + E_m\right]U_m \tag{A6}$$

(c) Two degree parabolic law for interphase stiffness and Poisson's ratio

$$E_L = E_f \frac{r_f^2}{r_m^2} + \frac{\left(E_f - E_m\right)\left(r_i^3 + r_i^2 r_f + r_i r_f^2 + r_f^3\right)}{2r_m^2\left(r_i - r_f\right)} - \frac{4}{r_m^2}\frac{\left(E_f - E_m\right)r_i\left(r_i^2 + r_f r_i + r_f^2\right)}{r_i - r_f} + \\ + \frac{\left(E_f r_i^2 + E_m r_f^2 - 2E_m r_f r_m\right)\left(r_f + r_i\right)}{r_m^2\left(r_i - r_f\right)} + \left[\frac{1-\nu_m-2\nu_m^2}{E_m} + E_m\right]\left(\frac{r_m^2 - r_i^2}{r_m^2}\right) \tag{A7}$$

and by the aid of Equation (A3) it implies that

$$E_L = E_f U_f + E_m U_m + \frac{3\left(E_f - E_m\right)\left(\sqrt{(1-U_m)^3} + \sqrt{U_f}(1-U_m) + \upsilon_f\sqrt{1-U_m} + \sqrt{U_f^3}\right)}{6\left(\sqrt{1-U_m} - \sqrt{U_f}\right)} - \\ - \frac{8\left(E_f - E_m\right)\left(\sqrt{1-U_m}\right)\left(1 - U_m + U_f + \sqrt{U_f(1-U_m)}\right)}{6\left(\sqrt{1-U_m} - \sqrt{U_f}\right)} + \left[\frac{1-\nu_m-2\nu_m^2}{E_m} + E_m\right]U_m \tag{A8}$$

(2) Theocaris' Two-Term Unfolding Model for Fibrous Composites [14]

$$E_{LC} = E_m + E_f U_f - \frac{E_m U_f}{3} + \frac{E_f U_f}{\eta - 1}\left(1 -^{\eta - 1}\right) + \frac{E_f U_f^{\eta}}{3}\left(1 + \frac{1}{\sqrt{}} - \frac{2}{}\right) - \frac{E_m U_f}{3}\left(\frac{1}{\sqrt{}} + \frac{1}{}\right) \tag{A9}$$

where the coefficient η, was experimentally determined previously [14], additionally, the real quantity B depends on the fibre volume fraction and the coefficient λ and signifies the implicit role of the mesophase annulus in this formula.

(3) Theocaris' Three-Term Unfolding Model for Fibrous Composites [14]

$$E_{LC} = E_m + E_f U_f - E_m U_f + U_f \left[\frac{E_f}{\frac{\eta}{2} - 1} \left(1 - {}^{\frac{\eta}{2} - 1} \right) - \frac{E_m}{\eta - 1} \left(1 - {}^{\eta - 1} \right) \right] \tag{A10}$$

Again, the quantities η and B are determined in the same way as in Two-Term Unfolding Model.

(4) Sideridis-Papadopoulos-Kyriazi formula [15]

According to a classical elasticity approach, an upper bound for longitudinal modulus of unidirectional fibrous composites reinforced with long fibres is given in a rigorous manner by the following explicit expression

$$E_L = \frac{(1 - v_f - 4vv_f + 2v_L^2)}{(1 - v_f - 2v_f^2)} E_f U_f + \frac{(1 - v_i - 4vv_i + 2v_L^2)}{(1 - v_i - 2v_i^2)} E_i U_i + \frac{(1 - v_m - 4vv_m + 2v_L^2)}{(1 - v_m - 2v_m^2)} E_m U_m \tag{A11}$$

with

$$v_L = \frac{(1 - v_f - 2v_f^2) E_f U_f v_f + (1 - v_i - 2v_i^2) E_i U_i v_i + (1 - v_m - 2v_m^2) E_m U_m v_m}{(1 - v_f - 2v_f^2) E_f U_f + (1 - v_i - 2v_i^2) E_i U_i + (1 - v_m - 2v_m^2) E_m U_m} \tag{A12}$$

Again, the Poisson's ratio of interphase zone named v_i can be evaluated for linear, hyperbolic and parabolic variation respectively.

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