



EFFECTIVE MODULI FOR LAMINATED RECYCLED POLYMERIC MATRIX COMPOSITES: A MICROMECHANICAL APPROACH

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***Abstract.** The purpose of this paper is drawing the potential use of fully recycled melt-blended matrices in polymeric matrix composites, and its application for construction of low cost houses in emergent countries. To achieve such goal a two-step homogenization procedure is proposed. The melt-blended matrix is homogenized by applying the concentric spheres model under weak interface condition and the linear functional of transformation. The overall composite effective properties are estimated from the composite cylinder assemblage model under weak interface condition for each lamina. An HDPE/PET-E glass composite is studied. Different types of interface conditions are simulated and its influence on the overall effective moduli are studied. The results are compared against the perfect bonding condition and some conclusions are set down.*

Keywords: Computer modeling, Recycling, Polymeric matrix composites, Weak interface condition.

1. INTRODUCTION

Polymeric matrix composites (PMC) are used in engineering applications as they present low density and high strength. However, they are not used in large-scale applications due to their high cost. The large variety of thermoplastic matrices allows us to experiment different types of resin combinations creating the so-called melt-blended matrices. The objective is not only cost reduction but also increase specific properties such as strength. One low cost source of such type of resins is recycled thermoplastics. Post-consumer polyethylene terephthalate (PET), for example, has a cost of five cents/pound while the polystyrene (PS), high and low density polyethylene (HDPE, LDPE), and polypropylene (PP) have an even lower cost. Their cost range from three to one and half cents/pound. Such low cost is due to the large amount of post-consumer plastic waste generated daily in large cities worldwide. A city in an emergent country with a population of three million inhabitants, for example, produces each day around 400 ton of plastic waste. Countries like the U.S. have already begun to search for solutions by funding research on the recycling field (Burgiel *et al.*, 1994). The purpose here is to develop new technologies into the polymeric waste recycling field so that these new technologies can

be applied into the construction of low cost houses in emerging world countries privileging a social-environmental approach.

2. TWO STEP HOMOGENIZATION PROCEDURE

The major problems on the melt-blended PMC are the chemical reactions between the combined matrices, and between the resulting matrix and the fibers. To be able to model such phenomena, a two-step homogenization procedure is proposed. This homogenization procedure is based on phenomenological observations and it is applied only for a group of melt-blended matrices - binary blends made of recycled materials. Such resulting melt-blended matrix is then applied to unidirectional fibers to get laminated PMCs.

Binary blends have been studied by Acierno and Di Maio (1995) with regard to the possible recycling uses. They are more interested in the manufacturing/re-manufacturing process, in special how the extrusion process is affected by the polymer granulometry and the viscosity phases. Their approach is essentially experimentalist, and they do not consider the existence of a third phase, e.g. a copolymer or a compatibilizer. Effects of different types of compatibilizers for recycling blends as in Park *et al.*(1996) will not be considered into this paper. The reason is the virtual impossibility of modeling such type of chemical reactions by the micromechanical approach.

Many researchers as Vaccaro *et al.* (1997), Teh *et al.* (1994), study blend microstructures and their influence on the mechanical properties. They show that for most of immisible thermoplastics the resulting array can be assumed as spheroid inclusions in a suspension (see Figure 1). The idea of a spherical domain is also applied by Lyngaae-Jørgensen & Utracki (1991) for calculation of dual phase continuity in polymer blends. However, their attention is focused on the percolation phenomena and its influence on phase continuity.

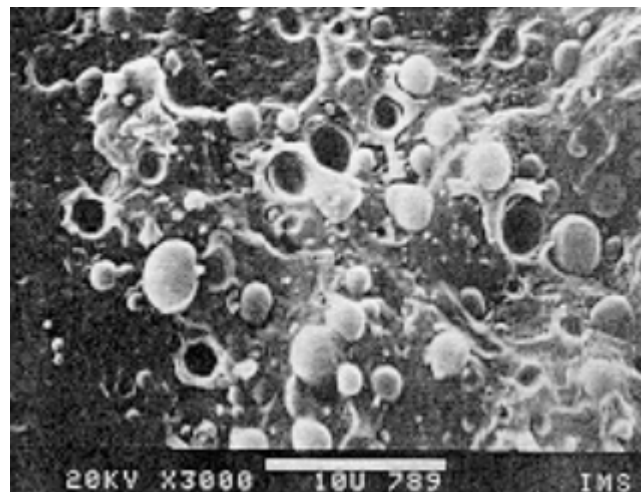


Figure1: Microstructure of PP/PET blend (Vaccaro *et al.*, 1997)

Considering such type of microstructure configuration it is feasible to assume the concentric spheres model (Christensen & Lo, 1979; Ávila, 1999) for computing the effective properties. Kolarik (1996) proposes a scheme to predict the Young's modulus and the yield (or tensile) strength of binary blends. However, he considers a perfect interface adhesion. Such assumption can not be applied when recycled materials are involved. According to Nicolais *et al.* (1997), there is an interface formation between the matrices and the effective material properties are highly affected by the interface conditions. To be able to model such interfacial phenomena, it is assumed the weak interface condition proposed by Hashin (1992).

Besides the weak interface condition a functional of transformation is also applied due to the material properties changes during the recycling process. According to Mancini *et al.* (1998), the mechanical properties of recycled thermoplastics are highly dependent on the number of recycles suffered by the material. Therefore, for the first step of the homogenization procedure, the linear functional of transformation must be incorporated into the concentric spheres model. This procedure is called pre-homogenization. Once this step is completed the overall composite effective properties are obtained on variation of the Composite Cylinder Assemblage model (CCA) under weak interface condition proposed by Ávila (1998). This procedure is so-called post-homogenization procedure.

2.1 Pre-homogenization procedure

The pre-homogenization procedure proposed is based on phenomenological observations. The objective here is to obtain the melt-blended matrix effective properties of a binary system. As we are dealing with fully recycled thermoplastics, it is needed to estimate how the material properties change after each recycling process. To achieve such goal, it is proposed a transformation functional that can artificially change the mechanical properties of a virgin material. This functional is highly dependent on the material properties and on the manufacturing/re-manufacturing process. Such linear functional will be called mutation ratio due to the material changes during the recycling process. Figure 2 shows an example of the mutation ratio for a specific thermoplastic, PET. A 5th order polynomial approximation is used to represent this linear functional.

$$\psi = -0.009\gamma^5 + 0.1146\gamma^4 - 0.5494\gamma^3 + 1.2211\gamma^2 - 1.1672\gamma + 1 \quad (1)$$

where ψ is the mutation ratio, γ the number of recycling, and the R^2 parameter for this curve fitting is equal to unity.

The mutation ratio is a linear functional and follows the same properties as cited in Szabó and Babuska (1991). The physical interpretation of the mutation ratio is the rate of changing of the mechanical properties, e.g. strength, during the recycling process. The number of recycling processes are material dependent, and it is a usual practice among manufactures/re-manufactures to consider that the material is not able of recycling anymore when a significant decrease on strength from one recycling process to another is observed (see Pearson, 1993). In the present case, it will be postulated that any material with mutation ratio below 0.4 will be considered useless for engineering applications.

It is considered that each phase of the melt-blended matrix is isotropic, and the inclusions have the spherical shape. The overall composite behavior is assumed to be isotropic. By assuming such hypotheses, the melt-blended matrix effective bulk modulus – lower and upper bounds - can be described by:

$$K_{m(+)}^* = \psi_1 K_1 v_1 + \frac{\psi_2 K_2 v_2}{1 + 3\psi_2/aD_n} \quad (2)$$

$$K_{m(-)}^* = \left(\frac{v_1}{\psi_1 K_1} + \frac{v_2}{\psi_2 K_2} + \frac{3v_2}{aD_n} \right)^{-1} \quad (3)$$

where K is the phase bulk modulus, G represents the each phase shear modulus and v_1 and v_2 define the suspension and the inclusion volume fractions, respectively. The lower bound is denoted by the minus signal between parenthesis, and upper bounds by plus signal also between parenthesis. The effective properties are identified by the superscript *.

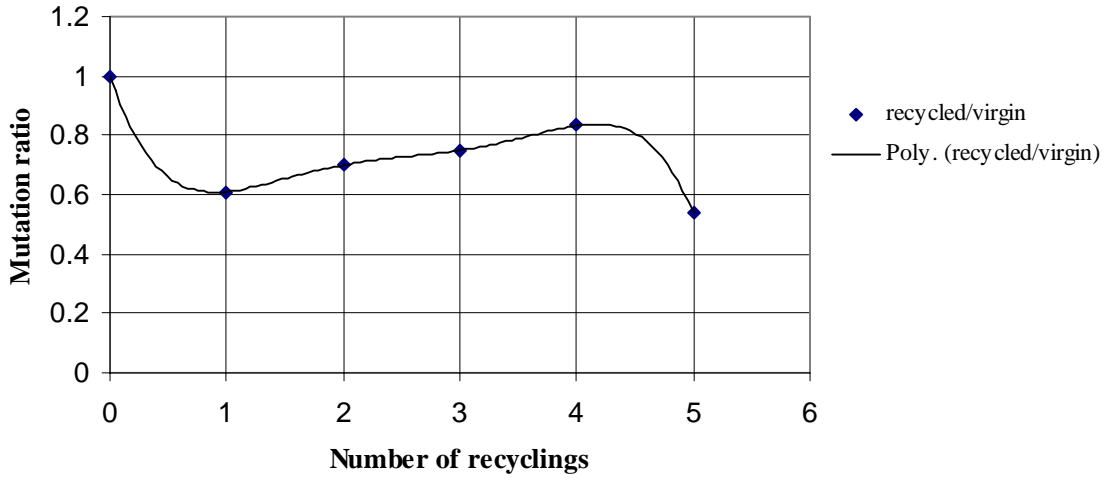


Figure 2 – PETmutation ratio

According to Hashin (1992), the variables D_t , D_n , and D_s are the interface parameters on the n , s , t system of coordinates. Such parameters are spring-type constants acting at the interface region. For the case of isotropic interface, the spring-type constants are defined by:

$$D_n = \frac{\psi_3 (K_3 + 1.33G_3)}{t} \quad (4)$$

and

$$D_s = D_t = \frac{\psi_3 G_3}{t} \quad (5)$$

where 3 indicates interfacial properties and t the interface thickness. It is assumed that the interface properties follow the modified rule of mixtures (Jones, 1999). However, the mutation ratio is presumed to be described by the properties of a linear functional

The effective melt-blended matrix shear modulus upper and lower bounds are described by the following expressions:

$$G_{m(+)}^* = \psi_1 G_1 v_1 + \frac{\psi_2 G_2 v_2}{1 + 5\psi_2 G_2 / (2D_n + 3D_s + 3D_t)a} \quad (6)$$

and

$$G_{m(-)}^* = \left[\frac{v_1}{\psi_1 G_1} + \frac{v_2}{\psi_2 G_2} + \frac{v_2}{a} \left(\frac{0.8(D_s D_t) + 1.2D_n(D_t + D_s)}{D_n D_s D_t} \right) \right]^{-1} \quad (7)$$

where a is the inclusion radius. An important relation between the interface parameters D_n and D_s is proposed by Hashin (1992), and it can be helpful for this case.

$$\frac{D_n}{D_s} = \frac{2(1 - \nu_3)}{1 - 2\nu_3} \quad (8)$$

where ν_3 is the interface Poisson's ratio. It should be noticed that Eqn.(8) is valid for isotropic interfaces only.

By using the theory of elasticity relations (Jones, 1999) the Young's modulus and Poisson's ratio can be calculated. Once these two bounds are calculated, the effective properties of the melt-blended matrix are completely defined and the pre-homogenization procedure is over.

2.2 Post-homogenization procedure

Once the melt-blended matrix effective properties are defined, the resulting matrix is applied to virgin unidirectional fibers to obtain laminated PMC. Virgin fibers are used in our case due to the lack of information concerning the performance of recycled fibers. Eriksson *et al.* (1996) point out that during the recycling process the fibers may suffer severe damage as a result of too intensive processing or excessive use of reground material. The cumulative effect of regrinding and remodeling can cause a significant reduction in most strength parameters. However, a final conclusion about such relationship is not completed formulate yet.

It is important to mention that we are dealing with two sets of interfaces. The first one occurs on the pre-homogenization procedure and it is matrix/matrix interface. The second is a fiber/matrix interface, and it appears on the post-homogenization procedure.

The overall composite effective properties are calculated by applying the mutation ratio to each composite constituents and using the variation of the composite cylinder assemblage model proposed by Avila (1999). Recalling the linear functional properties (Szabo & Babuska, 1991) the melt-blended matrix mutation ratio can be calculated as:

$$\Psi_m^* = v_1\Psi_1 + v_2\Psi_2 \quad (9)$$

where the effective mutation ratio of the melt-blended matrix is designed by Ψ_m^* . As we are considering only virgin fibers, the effective mutation ratio for the fibers is equal to the unity.

The entire composite is assumed to be transversely isotropic, and due to this assumption, only five constants are needed to describe the composite behavior. The new expression for the composite effective bulk modulus is given by,

$$K^* = \Psi_m^* k_m^* + \frac{v_f}{\frac{1}{\Psi_m^*} \left(\frac{1}{k_e / \Psi_m^* - k_m^*} + \frac{v_m}{(k_m^* + G_m^*)} \right)} \quad (10)$$

where

$$k_e = \frac{k_f}{1 + \frac{2k_f h}{b\Psi_i(K_i + G_i)}} \quad (11)$$

where the subscript i represent the fiber/matrix interface, h the interface thickness, b the fiber diameter, and the subscripts f and m the fiber and the melt-blended matrix properties, respectively.

The effective axial Young's modulus and the axial Poisson's ratio expressions have the same shape as in Avila (1998) or in Hashin (1992), and for conciseness will not be shown. However, the effective axial shear modulus is defined by the following new expression:

$$G_A^* = \Psi_m^* G_m^* + \frac{v_f}{\frac{b\Psi_i G_i + G_f h}{\Psi_i G_f G_i - \Psi_m^* (bG_i + hG_f)} + \frac{v_m}{2\Psi_m^* G_m^*}} \quad (12)$$

Following Avila (1998), the effective transverse shear modulus must be calculated by applying the generalized self consistent scheme (GSCS). By applying the GSCS we obtain a 8 by 8 determinant equation as,

$$\begin{bmatrix} 1 & -1 & 1 & 1 & 1 & 1 & 0 & 0 \\ 1 & 1 & \frac{2+\eta_m}{1-\eta_m} & 1 & \frac{\eta_m}{1+\eta_m} & -1 & 0 & 0 \\ g^* & 3g^* & 0 & 1 & -\frac{2}{1+\eta_m} & -3 & 0 & 0 \\ g^* & -3g^* & \frac{3}{1-\eta_m} & 1 & \frac{1}{1+\eta_m} & 3 & 0 & 0 \\ 0 & 0 & 0 & 1 & -\frac{2}{(1+\eta_m)v_f} & -\frac{3}{v_f^2} & 0 & -g \\ 0 & 0 & \frac{3v_f}{1-\eta_m} & 1 & \frac{1}{(1+\eta_m)v_f} & \frac{3}{v_f^2} & -\frac{3gv_f}{1-\eta_f} & -g \\ 0 & 0 & v_f & 1 & \frac{1}{v_f} & \frac{1}{v_f^2} & -v_f & -(p+1) \\ 0 & 0 & \frac{(2+\eta_m)v_f}{1-\eta_m} & 1 & \frac{\eta_m}{(1+\eta_m)v_f} & -\frac{1}{v_f^2} & -\frac{(3q+2+\eta_f)}{1-\eta_f} & -(q+1) \end{bmatrix} = 0 \quad (13)$$

where η represents the ratio between the phase transverse shear modulus and the bulk modulus, g is the ratio between the fiber and the matrix transverse shear moduli. The other constants are defined as,

$$g^* = \frac{G_T^*}{\psi_m^* G_m^*} \quad p = \frac{G_f h(1-2\nu_i)}{\psi_i b(1-\nu_i)} \quad q = \frac{2hG_f}{\psi_i bG_i} \quad (14)$$

It is important to notice that Eqn. (14) is used in the particular case of isotropic interface. Hashin (1992) points out that the determinant of Eqn. (13) is a quadratic expression in g^* .

The effective transverse Young's modulus and transverse Poisson's ratio can be obtained by the transverse isotropy relations as cited in Jones (1999). For conciseness, these expressions will not be shown in this paper. Once all effective properties are completely described by a set of algebraic equations the post-homogenization procedure is over.

3. INTERFACE EFFECTS ON THE EFFECTIVE PROPERTIES

A laminated $[\pm 45]_s$ PET/HDPE-E glass transversely isotropic composite is proposed, and the interface effects on the overall composite behavior is studied. In our case, a group of HDPE spherical inclusions with an average diameter of 5 μm is diluted into a PET suspension. The volume fraction ratio between the suspension and the inclusion is 80/20. The E-glass fibers volume fraction is 0.30 and its average diameter is 10 μm . The fibers and the HDPE inclusions are considered virgin materials, the PET suspension is a recycled material. The material properties listed in Table 1 are from Cheremisinoff and Cheremisinoff (1996). The reader must notice that the material properties shown in Table 1 are for virgin materials. The transformation functional must be applied to artificially change the mechanical properties of the recycled materials.

Figure 3 shows the influence of the interface condition on the effective moduli. As it is expected the weak interface condition causes a decrease on the overall effective moduli. However, there is an increase on the bulk modulus due to the weak interface condition. The bulk modulus behavior can be explained by the use of the modified rule of mixtures for the interface. Figure 4 shows the Poisson's ratio behavior for the perfect and weak interface conditions. It is also observed an inversion on the transverse Poisson's ratio behavior as a consequence of the bulk modulus inverse behavior. It is important to emphasize that the axial Young's modulus presents a very straightforward behavior and it is not shown in this paper for conciseness. For the perfect interface condition the suspension matrix variation is dominant, i.e., the effective moduli behavior follows the same pattern that one of the suspension matrix. When the weak interface condition is considered there is a change in this pattern due to the interface influence.

Table 1- Material Properties

Material	E [GPa]	K [GPa]	G [GPa]	ν
HDPE	0.84	0.70	0.32	0.30
PET	3.10	2.58	1.19	0.30
E-glass	72.40	43.10	29.67	0.22

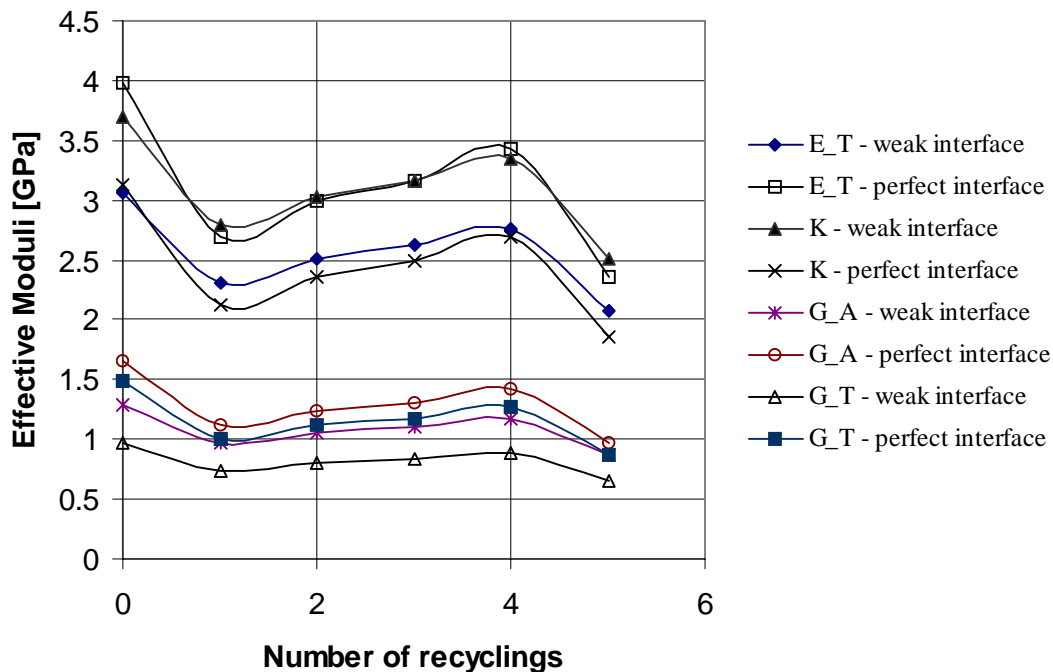


Figure 3: Results: weak x perfect interface condition

The influence of the interface condition on the overall effective moduli is also studied. To be able to study how the two different interfaces, matrix/matrix and fiber/matrix, affect the overall composite effective moduli, it is defined two interface parameters: the first one is the ratio between the inclusion radius and the matrix/matrix interface thickness. This parameter is designated by the Greek letter ϕ . The second interface parameter is the ratio between the fiber radius and the interface fiber/matrix thickness, and it is denoted by ξ .

In our analysis ϕ is changing while ξ is kept fixed. The results are shown on Figures 5 and 6. As ϕ goes to infinity, the results are close to the perfect interface condition, as expected. It seems that there is a direct influence of ϕ on the overall composite effective moduli.

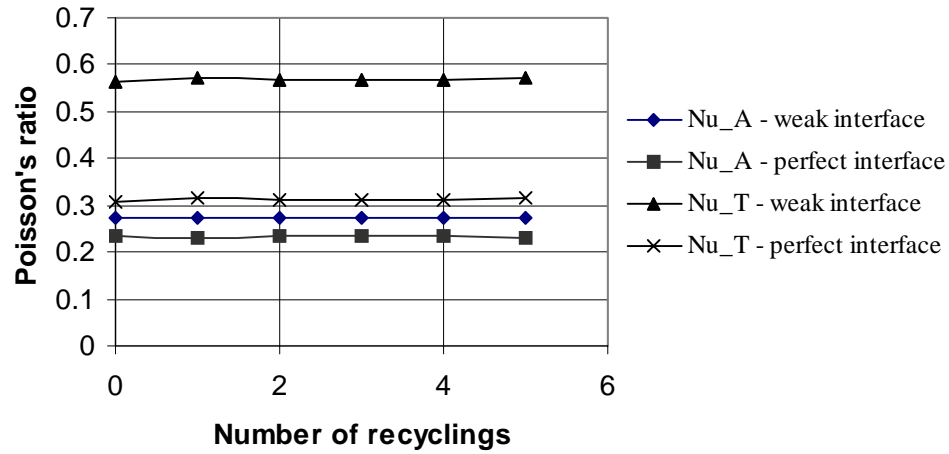


Figure 4: Poisson's ratio – weak x perfect interface condition

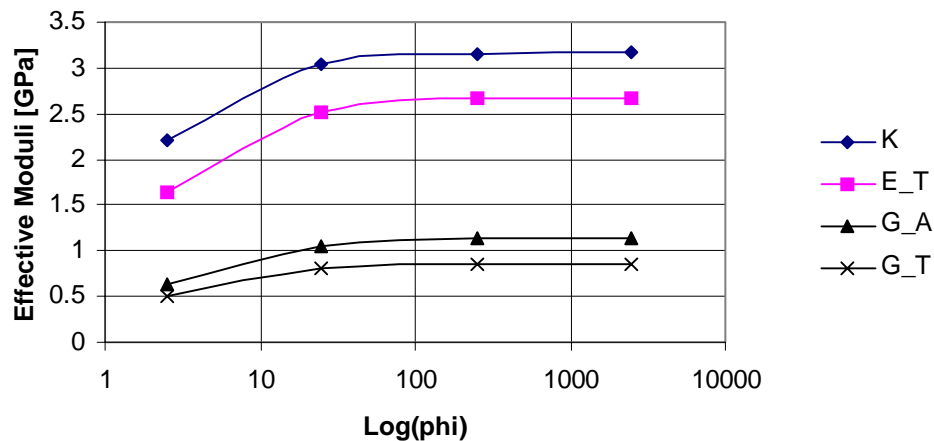


Figure 5: Interface matrix/matrix influence on the effective moduli

The influence of the interface fiber/matrix on the overall composite effective moduli is also studied. For this case the interface parameter ϕ is kept constant while ξ is changing. The results are shown on Figures 7 and 8. The axial shear modulus is practically constant with the interface fiber/matrix changes. This behavior could be caused by the way that the interface properties are calculated. For the axial shear modulus the modified rule of mixtures is close to the rule of mixtures. The same fact is observed on the axial Poisson's ratio. One possible explanation for this behavior is the cancellation of such effects on the ν_A calculation. It is significant to mention that the elasticity theory is used for the ν_A calculation.

4. CONCLUDING REMARKS

The double homogenization procedure proposed is a promising technique to describe the effective moduli of recycled polymeric matrix composites. This procedure is a phenomenological dependent homogenization technique, and it can be applied only for a

certain class of PMCs. However, it seems to capture the material properties transformations during the recycling process. The weak interface condition is a crucial feature of the double homogenization procedure. More investigation must be done to describe the interface properties with more accuracy. After all the interface mechanisms of the loading transferring and the interface properties itself is not clear defined yet

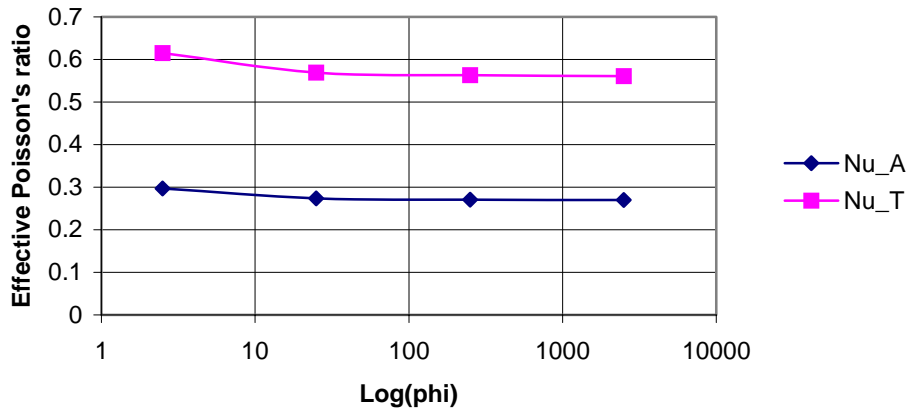


Figure 6: Interface matrix/matrix influence on the Poisson's ratios

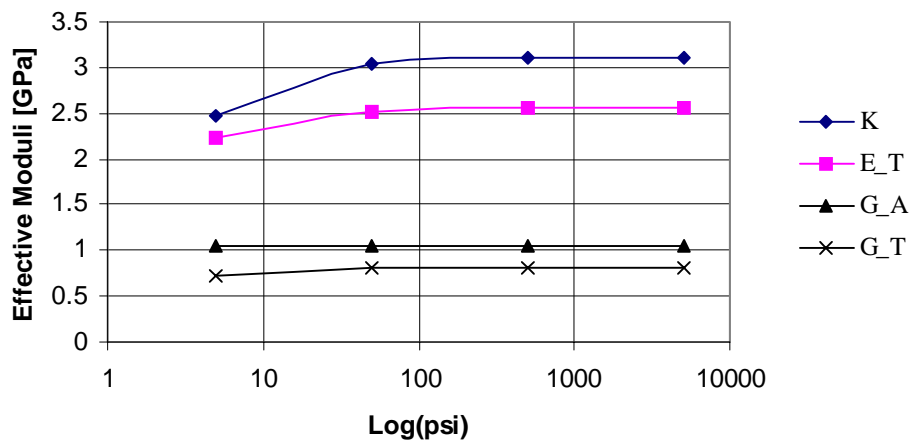


Figure 7: Interface fiber/matrix influence on the effective moduli

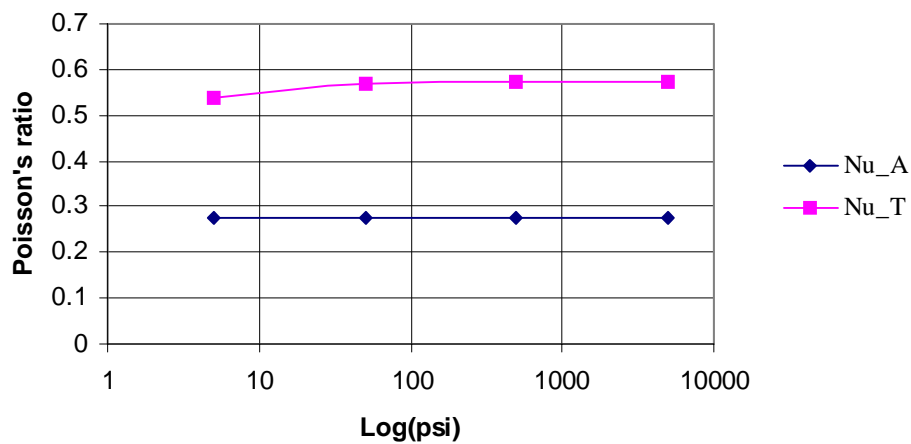


Figure 8: Interface fiber/matrix influence on the Poisson's ratios

5. ACKNOWLEDGMENTS

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