Available online at www.sciencedirect.com
SCIENCE DIRECT
Polymer 46 (2005) 7478–7484
polymer
www.elsevier.com/locate/polymer

Micromechanical modeling of hybrid composites

Prem E.J. Babu, S. Savithri, U.T.S. Pillai*, B.C. Pai

Materials and Minerals Division, Regional Research Laboratory (CSIR), Industrial Estate PO, Pappanamcode, Trivandrum, Kerala 695019, India

Received 3 January 2005; received in revised form 30 May 2005; accepted 30 May 2005
Available online 1 July 2005

Abstract

The main aim of this work is to study the effective elastic modulus of hybrid composites through micromechanical modeling. The micromechanical framework based on the generalized method of cells has been employed for this study. The predictions based on the present model are compared with an assortment of experimental and other theoretical predictions. The effect of two types; sequential mode and mixed mode of filler additions on the effective elastic modulus of the hybrid composite are studied. Moreover, the effect of other microstructural parameters such as the concentration, shape and aspect ratio of fillers in altering the hybridization effects are also investigated.

Keywords: Hybrid composites; Theoretical model; Elastic modulus

1. Introduction

The development of composite materials is one of the major advancement in the field of science and engineering. Composites of varying types and magnitudes based on diverse materials have been developed during the ages of its evolution. Composites based on polymers [1–28] have become one of the most significant advanced materials used in the areas of aerospace, automotive, defense and other broad-spectrum engineering applications. These composites possess scores of superior properties such as high specific strength and stiffness, increased thermo-oxidative stability, and enhanced high temperature performance and improvement in other thermal and mechanical properties than those of base matrices. The conventional composites normally possess only one type of reinforcement and are termed as monocomposites. The naissance of hybrid composites, wherein more than one type, kind, shape and size of reinforcements are used, bestow synergistic properties of the fillers and matrix chosen. Studies on hybrid composites have been started recently and the trend shows it as one of the potential materials of future with diversified material characteristics.

Furthermore hybrid composites are becoming more and more commercially significant in their own right for a number of advantages. First, there are economic advantages in diluting a more expensive reinforcement or filler with cheaper materials. Second, a wider spectrum of physical and mechanical properties is possible, facilitating the design of materials with specific characteristics. Third, hybrids are used to achieve synergistic effects and improvement in mechanical and functional properties. The properties of particulate-filled polymers are determined by several factors, such as the component properties (matrix and filler), composition, and structure. The effect of structure of fillers usually depends greatly on their shape, particle size and particle size distribution. There are five major types of particle shapes of mineral fillers: sphere, cube, block, flake and fibrous. For example, talc and kaolin are platelet-type particles, whereas $CaCO_3$ shape will be normally uneven [29]. Fibrous filler can usually improve the tensile strength. A sheet like or plate like filler can improve rigidity, and the improvement depends on the aspect ratio of the filler [30]. The specific surface area is one of the most important characteristics of fillers that in turn controlled by the size of the fillers. It determines the amount of surface contact between the polymer matrix and the filler. Fillers with

* Corresponding author. Tel.: +91 471 2515251; fax: +91 471 2491712.
E-mail address: utspillai@rediffmail.com (U.T.S. Pillai).

0032-3861/$ - see front matter © 2005 Elsevier Ltd. All rights reserved.
doi:10.1016/j.polymer.2005.05.120

higher surface areas will contribute to more surface contact between the filler and matrix, thus increasing the mechanical properties of the composite. Fillers with fine or small particles have higher surface areas than fillers with big particles. However, the finer the particles are, the greater their tendency is to agglomerate, and this can cause an adverse effect on mechanical properties, especially the impact resistance of composites. The same is true for fillers with bigger sized particles, which may act as stress concentration points or points of discontinuity in composites, thereby promoting crack initiation and propagation. Hence neither too finer nor too big particles are preferred in improving the mechanical properties of composites, and it is true for hybrid composites also.

However, studies on the effect of filler shape, filler orientation and aspect ratio in improving the overall mechanical properties of hybrid composites are very few. In this paper, an attempt has been made to examine the effect of filler concentrations, filler shape and aspect ratio on the effective elastic properties of polymer based hybrid composites. In addition, the effects of the different modes of filler addition, namely the sequential and mixed mode, on the effective elastic modulus of hybrid composites are also investigated. For this purpose, a micromechanical framework based on the generalized method of cells (GMC) [31] has been employed.

The generalized method of cells (GMC) [31] is a semi-analytical method to determine the effective properties of composites. In this method, a representative volume element (RVE) of the composite under consideration is discretized into a regular grid of subcells. Equilibrium and compatibility are satisfied on an average basis across subcells using integrals over subcell boundaries. GMC generates a matrix of algebraic expressions containing information about subcell material properties. The effective stiffness of the composite can be obtained by inverting this matrix. One advantage of GMC over other numerical techniques is that the full set of effective elastic properties of a composite can be calculated in one step instead of solving a number of boundary value problems with different boundary conditions. GMC has also been found to be more computationally efficient than the finite element calculations for fiber reinforced composites [32], since far fewer GMC subcells than the finite elements are necessary to obtain the same degree of accuracy. The problem of discretization is also minimized since a regular rectangular grid is used in GMC. The formulation of GMC is given elsewhere [33] where the applicability of GMC for prediction of mechanical properties of various particulate reinforced composites is established.

Most importantly, GMC results in closed form constitutive equations for the composite, which, combined with its efficiency, makes the model ideal for inclusion within larger structural analysis approaches to simulate the composite behavior at a material point.

2. Methodology

The above-discussed 3D GMC formulation is applied to predict the effective elastic properties of hybrid composites. Two methodologies are used in this regard. The first one is the approach of sequential reinforcing, wherein the reinforcements are added one by one in the base matrix material to make the hybrid composite, and a schematic of one such system is shown in Fig. 1. For modeling such sequential reinforcing technique through GMC, the following steps are adopted. Using the formulation for single filler reinforced composite, the unit cell is designed to have a single reinforcement in the base matrix and the effective properties of the monocomposite is determined. This monocomposite is then treated as the matrix material and then the second filler is reinforced in this matrix. Now, once again employing the GMC technique, the effective properties for this system are predicted, and this gives the overall effective properties of the hybrid composite.

The second approach is the mixed mode reinforcing technique, in which, both the fillers are arranged in some fashion, and the overall effective properties of the hybrid composite are predicted in a single step. The unit cells taken for the analyses are explained clearly in the sections wherever used.

3. Results and discussion

In order to verify and illustrate some of the unique features of the presented GMC formulation, the following results have been generated using the formulation as implemented within a computer code. First, predictions for the effective elastic modulus of a polypropylene (PP)–ethylene propylene rubber (EPR) particles–short glass fiber (SGF) hybrid composite are compared with the well known experimental results of Zebarjad et al. [34]. Next, predictions are made for a three-phase composite reinforced with continuous cylindrical fibers and isotropic spheroids, and the GMC results are compared with the theoretical predictions of Kanaun and Jeulin [35] for the same composite. Results are also presented for a hybrid particle–short fiber–polymer composite and are compared with the results of Fu et al. [36]. Thus the results of the succeeding validation results section serves to authenticate the present theory for cases, where literature data exists. Furthermore the effect of the two type of processing: sequential and mixed mode filler additions, on the effective elastic modulus of hybrid composites are also analyzed and are compared with the results of Kanaun and Jeulin [35].

Subsequently, after performing such extensive comparisons to validate the proposed formulation in this paper, a study has been conducted, on the variations in effective elastic modulus of hybrid composites with respect to the different filler shapes and aspect ratios. For analyzing the effect of filler shape, two filler shapes are considered; cubic

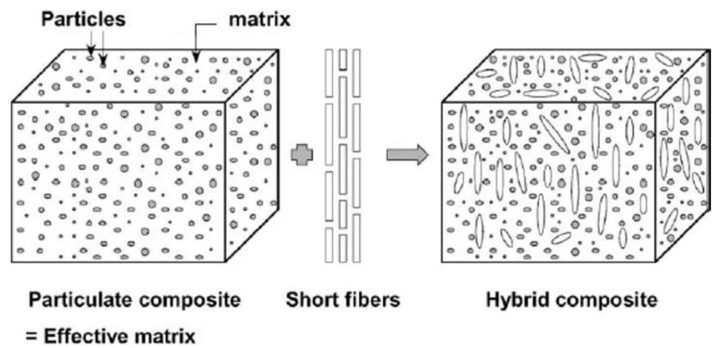

Fig. 1. Illustration of a sequential reinforcing method (one by one addition) of a hybrid composite having particulate and short-fiber fillers.

and rectangular parallelepiped. These two typical filler shapes were chosen, since in many discontinuous filler composites, the fillers have flake-like or arbitrary shapes containing corners. Moreover, the cubic and parallelepiped shapes can hypothetically represent a particle and short-fiber filler. The effect of aspect ratio is analyzed by varying the dimensions of the parallelepiped.

3.1. Validation results

The efficiency of the present theoretical formulation in predicting the effective elastic properties of hybrid composites is validated by extensive comparisons with the available literature results. As a first case, the polypropylene based hybrid composite filled with EPR particles and short glass fibers (SGF) is modeled. Note that, for in this case, the sequential reinforcing method (SRM), as described above is employed. For this estimation, the effective elastic properties of the PP–SGF monocomposite system are first found out using the above described 3D GMC formulation. A 3 by 3 by 3 subcelled unit cell has been taken for the analysis, in which the centre (2 by 2 by 2) subcell is allotted for the short fiber. The dimensions chosen for the short fiber subcell is $a \times a \times 2a$, where, the characteristic dimension 'a' is calculated based on the short fiber volume fraction. These effective properties of this PP–SGF monocomposite are substituted for the matrix properties in the same 3D GMC framework, where EPR particles are the fillers. A same 3 by 3 by 3 subcelled unit cell is taken for this analysis too. However, the dimensions of the centre (2 by 2 by 2) subcell that is allotted for the particle is $a \times a \times a$. Here 'a' is calculated based on the volume fraction of the particles. Experimental results for the effective elastic modulus of this hybrid system were presented by Zebarjad et al. [34] and this result is chosen for the comparison purpose.

The elastic properties for the PP matrix, EPR particles and CGF are given in Table 1. The prediction for the elastic modulus of this hybrid composite is shown in Fig. 2, along with the available experimental data. Clearly, the predictions of the present theory agree well with the experimental data of Zebarjad et al. [34]. Succeeding comparisons in this section explicitly demonstrate the preeminence of the present analytical framework over the other available theories for hybrid composites in the literature.

Kanaun and Jeulin [35] proposed an effective field approach (EFA) for predicting the elastic properties of hybrid composites. There predictions are for a three-phase composite having an isotropic matrix, a set of infinite unidirectional cylindrical fibers and a set of spheroids. The elastic properties used for the three phases are given in Table 2. They have conducted a study to understand the effect of different modes of filler addition on the effective elastic properties of the hybrid composites. In one method they have generated a 2D random distribution of cylinders first and then added particles and then in the second method they have generated particle first and then cylinders. Hence to validate our model with their results two schemes are proposed in this work. We have chosen a 2D unit cell, which is then divided into 8 by 8 subcells. Using a random number generator the material properties are then assigned. In scheme 1 depending upon the volume fraction of cylindrical fibers the number of subcells are calculated and then they are placed randomly. The effective properties of this composite are first determined. Then these properties are chosen as the matrix properties. After that depending on the volume fraction of particles the no of subcells are calculated and their locations are assigned randomly. In scheme 2, the above method is reversed i.e. particles are added first and the fibers second. The random distributions of the filler subcells in the unit cell are generated using a random number generator program.

The predictions for the axial and transverse elastic modulus of the hybrid composite using the two modes of filler addition are shown in Fig. 3(a) and (b), respectively.

Table 1
Elastic properties of the phases in PP–EPR–CGF hybrid composite

Mechanical properties	Material type		
	PP	EPR	CGF
Young's modulus E (GPa)	1.25	3.0	70
Poisson ratio, ν	0.42	0.42	0.23

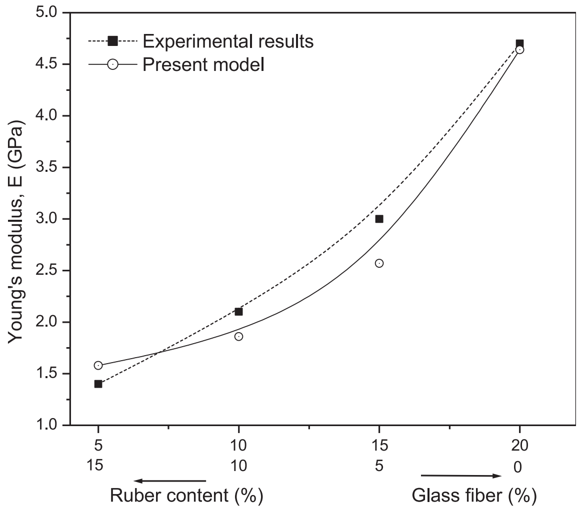

Fig. 2. Comparison for the elastic modulus of PP–EPR–SGF hybrid composite.

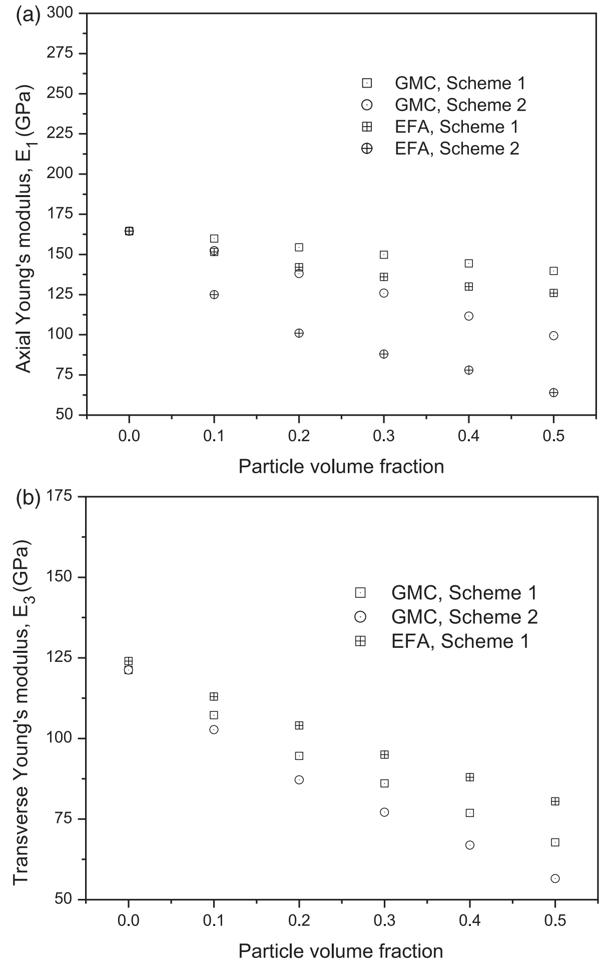

Fig. 3. Elastic modulus predicted by various GMC schemes (a) axial (b) transverse.

It can be clearly seen from the figures that both axial and transverse modulus of the hybrid composite varies much with the different modes of filler additions. The GMC analyses are carried out using 2D analysis, 8 by 8 subcelled array and random distribution. For these schemes, higher values are observed for the one where particles are filled first and then followed by fibers followed by the one where fibers are filled first and then followed by particles and is matching well with the trend observed in the EFA results of Kanaun and Jeulin [35]. This clearly proves that the modes of addition of fillers have a strong effect on the effective elastic properties of the hybrid composites, mainly due to the different interaction effects that occur during addition of fillers in the matrix. In his extensive studies on aluminum based hybrid composites, Rajan [37] has confirmed this fact experimentally. The results of his investigation concluded that the order of filler addition in the matrix influences the microstructure of hybrid composites and in turn varies their mechanical properties.

The next validation study is performed for a hybrid particle–short fiber–polymer composite. Fu et al. [36] predicted the effective elastic modulus of this hybrid composite using the rule of hybrid mixtures (ROHM) and the laminate analogy approach (LAA). The elastic properties used for the phases are shown in Table 3. In the LAA, particle filled polymer is regarded as the monocomposite, in which the short fibers are reinforced. It has been suggested by Fu et al. [36] that the LAA technique is more suitable than the ROHM for hybrid composites owing to the fact that results of LAA agree well with the experimental results than the ROHM results. Hence the results of LAA are taken to compare with the predictions of the present model.

Fig. 4 compares the present model predictions with the results of LAA for the effective elastic modulus. The hybrid composite with fiber volume percent is varied from 0 to 50 while maintaining a total filler volume percent of 50 in the composite (Particle + short fiber volume percent = 50 at all times). It is noticed from the figure that GMC-scheme 2

Table 2
Elastic properties of the phases in the three-phase composite having an isotropic matrix, a set of infinite unidirectional cylindrical fibers and a set of spheroids

Mechanical properties	Material type		
	Matrix	Cylinders	Spheroids
Young's modulus E (GPa)	96.5	431.0	34.4
Poisson ratio, ν	0.3005	0.2529	0.2028

Table 3
Elastic properties of the phases in polymer–particle–short fiber hybrid composite

Mechanical properties	Material type		
	Polymer matrix	Particle	Short fiber
Young's modulus E (GPa)	2.39	8.365	75
Poisson ratio, ν	0.35	0.25	0.25

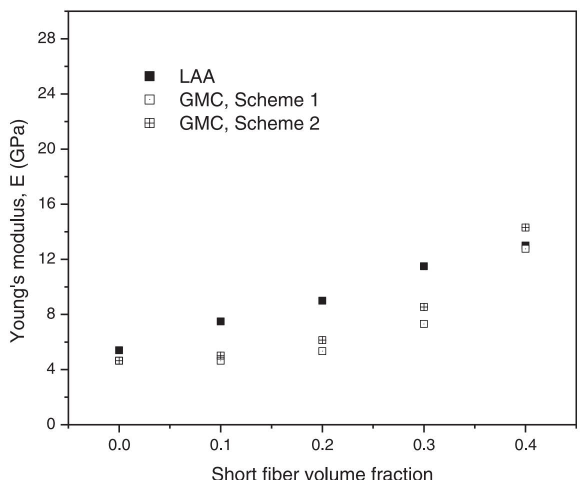

Fig. 4. Elastic modulus predicted by various GMC schemes and the LAA.

agrees well with the LAA results than the GMC-scheme 1, mainly due to the regular arrangement pattern used in the GMC-scheme 2. This is the advantage of the present formulation over the other models, i.e. its capability to accommodate any combination of filler arrangements in the unit cell, depends upon the microstructure. Good agreement between the present model predictions and the literature results in all the validation tests exemplify the applicability and usage of the present formulation in predicting the effective elastic modulus of hybrid composites.

3.2. Unique results

In fact, the predictions of the present theory agree well with the literature data for the effective elastic modulus of hybrid composites as seen from the previous section. Moreover, the effect of various volume fractions and its proportions on the effective elastic modulus can be referred from those comparisons. The variation of elastic properties with filler volume content seems to be non-linear and represents a typical composite behavior. Now, illustrating the new capabilities of the theory, the effects of filler shapes and aspect ratios on the effective elastic modulus of hybrid composites are studied. It should be noted that the results presented in this section are intended to display the theory's unique capabilities as opposed to addressing a practical structural design problem. Future work will involve comparison to appropriate experimental data for such composites when it becomes available.

3.2.1. Effect of filler shape

In this study, the effects of particle shape on the effective elastic modulus of hybrid composites are examined. The particle shapes considered for this study are cubic and rectangular parallelepiped, owing to the fact that most discontinuous fillers have flake-like or arbitrary shapes containing corners. Moreover these shapes can be compared to the particles and short-fiber fillers due to the unit aspect ratio of cube and an aspect ratio greater than unity for the parallelepiped. The constituent properties used for analyzing the effect of filler shape are $E = 2.39$ GPa and a Poisson ratio of 0.35 for the matrix and an identical elastic modulus of $E = 75$ GPa and a Poisson ratio of 0.25 is taken for both the short fiber and the particulate fillers.

The effect of particle shape is analyzed by predicting the effective elastic modulus of the hybrid composite for the following cases: varying the fiber volume while keeping the particle volume constant and vice versa. The results for both the cases for one fixed filler volume (either particle or short fiber) of 10% with varying other filler volume from 0 to 50% are plotted in Fig. 5. It can be noted from the figure that, in the initial stages, up to a second filler volume fraction of around 10%, the elastic modulus for the monocomposite having short fibers is found to be dominating over the other, beyond that the monocomposite having particles is outstripping the other. This may be primarily due to the supremacy of short fiber over the particle in improving the modulus of the composites for all the volume fractions studied. Thus, it can be concluded that the reinforcing efficiency of short fibers or the fillers having an aspect ratio greater than unity is comparatively more, when compared to unit aspect ratio particulate fillers. It will be interesting now to cotton on, the effects of varying aspect ratios of fillers on the effective elastic modulus of hybrid composites. Thus the following section is devoted to analyze the effect of filler aspect ratio in improving the effective modulus of hybrid composites, by maintaining same material properties for the constituent phases throughout.

3.2.2. Effect of filler aspect ratio

The study of Fu et al. [36] reveals that the effective elastic modulus of hybrid composite is having a reduced dependency on fiber length compared to the fiber volume fraction. This focus of this section is not to compare such parameters, but to predict the variation in effective elastic modulus of the hybrid composite with respect to varying

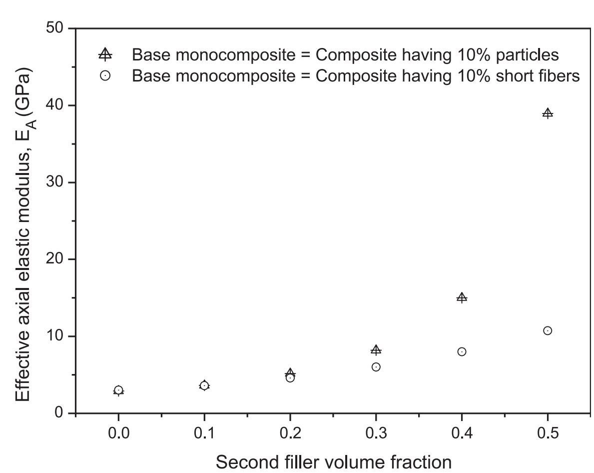

Fig. 5. Variation of elastic modulus with filler shapes (cubic, parallelepiped).

aspect ratios of the fillers. The prior results in this work pointed out an improvement in the effective elastic modulus of the hybrid composite, when the fillers are having an aspect ratio greater than unity, when compared to the composite having fillers in the region of unit aspect ratio. Hence the effective elastic modulus of the hybrid composites having aspect ratio of fillers ranging from 0.3 to 2.0 are predicted and presented in Fig. 6. It can be clearly deduced from the figure that the effective elastic modulus increases with the filler aspect ratio.

4. General discussion

The composite unit cells are considered as phenomenological objects whose behavior is derived mainly or partly from macroscopic behavior of constituent materials. Hence, the unit cell as material element that should contain sufficient information for predicting macroscopic behavior of a material and, at the same time, should be based on physical concepts without enlisting macroscopic notions, can then be regarded as a vital problem in today's material science. Such a composite unit cell can be unequivocally modeled using the present formulation than the other models available for hybrid composites in the literature. For the composite unit cells analyzed, the results predicted using the present model agrees well with the available literature results for any combination of hybrids.

The significant advantage of the present formulation is its ability to accommodate any combination of *n*-number of phases at a time. This advantage helps to analyze the effect of different filler additions on the effective material properties of hybrid composites. The analysis carried out for different filler addition modes clearly proves that the effective elastic modulus vary with different modes of filler additions. The study conducted on the effect of phase concentrations evidently show that the improvement in modulus values is not linear with phase concentrations and represents the typical composite behavior. For analyzing the effect of particle shape on the effective elastic modulus, cubic and parallelepiped particles have been considered, due to the piece of evidence that most discontinuous composites possess flake-like or arbitrary shapes containing corners. It has been further noticed that fillers having an aspect ratio greater than unity improves the effective modulus than the fillers having unit aspect ratio. Results of the investigation on the aspect ratios ranging from 0.3 to 2.0 confirm the improvement in elastic modulus with increasing aspect ratios.

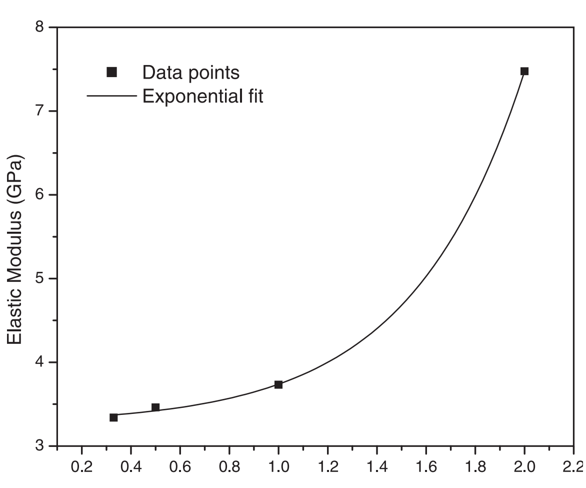

Fig. 6. Elastic modulus variation with varying aspect ratio of fillers in the composite.

5. Conclusions

The effective elastic properties of hybrid composites are predicted through a micromechanical theory. The theory employs the generalized method of cells for this purpose. Extensive comparisons that are made with the model predictions and the available literature results prove the supremacy of the present model in efficiently predicting the elastic properties of hybrid composites. The predictions for the effective properties of such hybrid composites form a base for analyzing their overall behavior in a macro-scale.

Acknowledgement

The first author wishes to acknowledge the Council of Scientific and Industrial Research, Govt. of India, for the award of Senior Research Fellowship. Moreover, the valuable help rendered by Ms. Sobhi Daniel of Chemical Sciences Division, Regional Laboratory, Trivandrum in preparing this manuscript is greatly acknowledged.

References

[1] Khunova V, Hurst J, Janigova I, Janigova V. Polym Test 1999;18:501.
[2] Rubin II. Handbook of plastic materials and technology. New York: Wiley; 1990. p. 693.
[3] Huang C, Li RKY, Wu CML, Duan Z. J Mater Process Tech 1999;96:48.
[4] Thomason JL, Vlug MA. Composites A 1997;28:277.
[5] Zafeiropoulos NE, Williams DR, Baillie CA, Matthews FL. Composites A 2002;33:1083.
[6] Gassan J, Bledski AK. Composites A 1997;28:1001.
[7] Fuad MYA. PhD Thesis, Universiti Sains Malaysia; 1994.
[8] Pukansky B. In: Karger-Kocsis J, editor. Polypropylene structure, blends and composites. London: Chapman & Hall; 1995. p. 1 [Chapter 3].
[9] Kim KJ, White JL. J Non-Newtonian Fluid Mech 1996;66:257.
[10] Zuiderduin WCJ, Westzaan C, Huetink J, Gaymans RJ. Polymer 2003;44:261.
[11] Thio YS, Argon AS, Cohen RE, Weinberg M. Polymer 2002;43:3661.
[12] Ferrage E, Martin F, Boudet A, Petit S, Fourty G, Jouffret F, Micoud P, De Parseval P, Salvi S, Bourgerette C, Ferret J, Saint-Gaeard Y, Buratto S, Fortune PJ. J Mater Sci 2002;37:1561.

[13] Alonso M, Velasco JL, De Saja AJ. Eur Polym J 1997;33:255.
[14] Collar EP, Laguna O, Areso S, Garcia-Martinez JM. Eur Polym J 2003;39:157.
[15] Mareri P, Bastide S, Binda N, Crespy A. Compos Sci Tech 1998;58: 747.
[16] Guerrica-Echevarria G, Eguiazabal JI, Nazabal J. Eur Polym J 1998; 34:1213.
[17] Avella M, Martuscelli E, Raimo M, Partch R, Gangolli SG, Pascucci BJ. J Mater Sci 1997;32:2411.
[18] Tjong SC, Meng YZ. Polymer 1998;39:5461.
[19] Tjong SC, Meng YZ. Polymer 1999;40:1109.
[20] Gupta VB, Mittal RK, Sharma PK. Polym Compos 1989;10:16.
[21] Joshi M, Maiti SN, Misra A. Polym Compos 1994;15:349.
[22] Kannan K, Misra A. Int Polym Process 1994;11:184.
[23] Ulrych F, Sova M, Vokrouhlecky J, Turcic B. Polym Compos 1993; 14:229.
[24] Reuda LI, Anton CC, Rodriguez MCT. Polym Compos 1989;9:199.
[25] Pande SJ, Sharma DK. Fibre Sci Technol 1984;20:235.
[26] Yilmazer U. Compos Sci Technol 1992;44:119.
[27] Hargarter N, Friedrich K, Catsman P. Compos Sci Technol 1993;46: 229.
[28] Fu S-Y, Lauke B. Composites A 1998;29:575.
[29] Leong YW, Mohd. Ishak ZA, Ariffin A. J Appl Polym Sci 2004;91: 3327.
[30] Jarvela PK. J Mater Sci 1996;31:3853.
[31] Aboudi J. Compos Eng 1995;5:839.
[32] Wilt TE. Technical Report NASA-CR-195451, (1995), National Aeronautics and Space Administration, Lewis Research Center, USA.
[33] Babu PEJ, Savithri S, Pillai UTS, Pai BC. Metall Mater Trans B 2004; 35B:1029.
[34] Zebarjad SM, Bagheri R, Lazzeri A. Plast, Rubber Compos 2001;30: 370.
[35] Kanaun SK, Jeulin D. J Mech Phys Solids 2001;49:2339.
[36] Fu S-Y, Xu G, Mai Y-W. Composites B 2002;33:291.
[37] Rajan TPD. PhD Thesis, Kerala University; 2002.