A NUMERICAL METHOD FOR THE DETERMINATION OF AN EFFECTIVE MODULUS FOR COATED GLASS FIBERS USED IN PHENOLIC COMPOSITES

V. Nassehi

Chemical Engineering Department, Loughborough University
Loughborough, Leicestershire, LE11 3TU, UK

S. A. Hashemi and M. H. Beheshty

Iran Polymer Institute
P.O. Box 14185/458, Tehran, Iran

Abstract It is well known that the mechanical properties of fiberglass reinforced "phenolic moulding compounds" are significantly enhanced if the glass particles are coated with silane coupling agents before compounding. It has been shown that improvements obtained by using scanning electron microscopy techniques are due to better bonding of phenolic resin to the surface of treated glass fibers. These observations prove that coated glass fibers effectively exhibit properties which are different from those of the glass itself. Thus from a modelling point of view, they can be regarded as materials having moduli different from the modulus of glass. However, considering the very small width of the coating layers used, it cannot be expected that by using direct experimental measurements of relatively large specimens, significantly different moduli for uncoated and coated glass fibers will be found. In this paper, the notion of an effective moduli for coated fibers is introduced. It is shown that such values can be numerically determined using experimentally measured bulk mechanical properties of coated glass filled composites. A trial and error procedure is developed for obtaining optimum moduli for the reinforcing phase. This scheme is based on the comparison of simulation results obtained by a previously validated finite element technique and data collected from flexural tests and fracture surface observations for different types of glass reinforced phenolic composites.

‌‌‌

1. INTRODUCTION

In order to improve the energy absorption properties of polymeric composites under impact loads and enhance their flexural and yield strength it is necessary to prevent the build up of harmful peak stresses at the fiber/matrix interface. This is usually achieved by coating the reinforcing fibers with chemicals which affect the bonding of the fiber and matrix and alter the patterns of stress distribution in reinforced composites. Glass fibers are extensively used in manufacturing of polymeric composites and for the stated reason they are generally coated with a coupling agent to improve matrix/fiber

bonding [1,2,3]. Amongst the most important materials which are used to coat fiberglass reinforcing phases are the silane coupling agents [4-7]. The silane coupling agents significantly improve the bonding between the fillers and polymer matrix. Extensive studies of their properties can be found in the literature [8-12]. The way these coupling agents affect the microscopic behaviour of fiberglass reinforced polymeric composites depends on factors such as the type of the polymer and the shape and size of the reinforcing phase. Due to the excellent mechanical properties and their high electrical and thermal resistivities, phenolic moulding compounds are widely used in various industrially important composites [13].

Detailed experimental work has been carried out to gain insights about the behaviour of phenolic composites. For example the cure reaction of these materials have been determined experimentally to be related to the degree of coupling between the fiberglass and polymer matrix [14]. It is however, very difficult to obtain quantitative data about stress distribution patterns at the fiber/matrix interface for composites under various types of loading by experimental techniques. Such data can be usually found by finite element modelling.

In the present work, bulk flexural modulus of glass reinforced phenolic composites are first determined by experiment. Next, an in-house developed finite element model was used to compute the flexural modulus of the composite under study via simulated stress/strain data [15,16] and to compare the calculated modulus with the experimental results. In the finite element simulations, individual modulus of matrix and reinforcing fibers should be used as input. However, in the case of coated glass fibers ideally one needs to use separately

measured modulus of the glass itself and the layer which coats the glass. The exact experimental measurement of the modulus of the thin coating layer is not possible and the flexural tests of "macroscopic" scale specimens of coated or uncoated glass cannot be expected to yield significantly different results. Therefore, for the coated glass, the calculations start by inserting the measured modulus uncoated glass. Then using the comparison of the computed results for the composite specimens with the bulk experiments as a guide, the modulus of the coated glass is adjusted. This procedure is repeated until an acceptable comparison between experimental and computed results is achieved. It should be noted that due to the small difference between the modulus of coated and uncoated glasses found by macro-scale flexural tests the described procedure can also be carried out by the introduction of the modulus of the coated glass as the initial value in the iterations. Thus we define an effective flexural modulus for coated glass fibers which gives a simulation close to the actual experimental behaviour of the composites. Using the determined effective moduli of coated glass fibers other useful information such as normal stress and strain and Von Mises stress at the fiberglass/polymer matrix interface are found.

2. EXPERIMENTS

Phenolic polymer used in this study was a novolak resin called Leriphen produced by Industrie Chimiche LERI, Italy. The resin was supplied in powder form with a melting point of 110^3C and contained 7-9% curing agent (Hexa). We used chopped glass fibers of 6 mm in length and 12 am in diameter. This kind of fiberglass is very widely used in the production

TABLE 1. Experimental Flexural Strength, Modulus and Strains.

TYpe of fiberglass used	Test Condition	Flexural Strength (MPa)	Flexural Modulus (GPa)	Flexural Stains (%)
As Received (Commercial)	Normal	74.0	8.5	0.84
	Wet	70.4	8.2	0.89
	Dry	67.9	8.5	0.81
Coated with AMEO	Normal	76.1	8.8	0.80
	Wet	74.2	8.6	0.84
	Dry	75.1	8.7	0.81
Coated with AMEO-T	Normal	84.5	9.8	0.74
	Wet	82.0	9.6	0.78
	Dry	82.5	9.7	0.77
Thermally Treated	Normal	39.4	7.7	0.62
	Wet	30.4	4.7	0.76
	Dry	26.1	4.8	0.62

of fiberglass reinforced polyesters. We used Dynasylan AMEO and Dynasylan AMEO-T produced by Dynamite Noble Co. of Germany as the coupling agents. The manufacturer has specified the chemical formula for Dynasylan AMEO as $H_2N(CH_2)_3Si(OC_2H_2)_5$ which is designated as a [-amino- propyltriethoxysilane. AMEO-T is a technical grade of the commercial AMEO coupling agent.

Industrially important phenolic composites contain high volume fractions of reinforcing phase " Therefore composites which contain as much as 50% by weight fiberglass were considered here. Four different kinds of fiberglass were used. These were "as received" chopped glass fibers (containing small amount of an unspecified silane coupling agent), thermally treated glass fibers, thermally treated fibers coated with AMEO silane agent and thermally treated glass fibers coated with AMEO-T silane agent. Compounding the premixed materials was carried out in a two roll mill with a friction ratio of 1.4 at 12 rpm for five minutes at 120yC. The sheet of compound was

then chopped and milled to obtain phenolic moulding composite in the powdered form. The obtained powder was then used to prepare flexural test specimens by compression moulding according to ASTM D-790M. Moulding was carried out at a temperature of 170yC and a pressure of 15.69 MPa for 8 minutes. Composites containing fiberglass coated with silane coupling agents were a lot easier to mould than the type in which thermally treated glass fibers were used. Specimens made using uncoated fiberglass were also sometimes found to contain voids and they had to be discarded. In general, glass fibers coated with silane agents mixed much more readily with other ingredients in a compound. Flexural tests were performed using Instron 6025 universal testing machine with 10 kN load cell. The room temperature during the flexural tests was 23yC. In order to eliminate experimental errors, each test was repeated seven times using identical specimens. Flexural tests were carried out using three types of specimens kept under normal, wet and dry

conditions. Wet specimens were prepared by soaking the samples in boiled distilled water for 4 hours. In order to prepare a dry specimen, first a wet sample was made and then it was thoroughly dried in a vacuum oven. As it is described in the next section the experimentally obtained results for different specimens were treated as the benchmark guide in the developed finite element algorithm.

Scanning electron microscopy using Cambridge S360 microscope was performed to monitor the uniformity and effectiveness of fiber coating and polymer/fiber bounding. Scanning electron micrographs of each specimen after being subjected to a flexural test were also prepared and examined to determine the occurrence and nature of fracture surfaces in the composite.

3. FINITE ELEMENT MODEL

Details of our finite element model have been published elsewhere [15,16] and only a brief account of it will be given in this paper. Our model is based on the finite element solution of the following governing equations:

$$\partial g_{ij}/\partial x_j + f_i = 0 \qquad (1)$$
$$\partial u_j/\partial x_j = 0 \qquad (2)$$

where g_{ij}, f_i and u_i represent components of total stress, body force (load) and displacement, respectively, in the Cartesian co-ordinate system (x_j, $j = 1,2$). In this model the total stress components are defined as:

$$g_{ij} = -PX_{ij} + h_{ij} \qquad (3)$$

where p is the hydrostatic pressure, X_{ij} stands for the components of the unit second order tensor (Kroneker delta) and h_{ij} denotes deviatoric stress components.

Equation 1 represents the equilibrium of internal and body forces acting on composite specimen under a given load and Equation 2 is

the expression of material incompressibility. Equations 1 and 2 can be used to describe the deformation of an elastic solid in penalty finite element schemes [17]. Their solution requires applied loads and/or displacements and the locations of fixed points (i.e. points where displacement is zero) along the geometrical boundaries of the domain of study. In the finite element model used in this work the composite domain of known dimensions is first discretised into a number of nine noded Lagrangian elements. Then a weak variational statement based on the governing equations is derived using continuous penalty Galerkin weighted residuals method. The derived statement is valid for every element. Thus the repeated application of the procedure for all of the elements in the solution domain and subsequent assembly of the elemental equations gives a set of algebraic global finite element equations which describe the deformation of the composite. After the prescription of the boundary conditions the global set of equations becomes determinate and its solution yields the displacement values at all node. The computed displacement field is then used to calculate nodal stresses via a variational recovery method [18].

From a mathematical modelling point of view the problem under study is an inverse problem in which the equations should be solved with respect to the unknown moduli of coated glass fibers. Such a solution however, requires detailed microstructural data about stress/strain and displacements for composites under loading. As it is mentioned earlier it is not possible to obtain this data by direct experimental methods. The procedure which we have developed avoids this problem since we measure bulk deformation behaviour of the

composite specimen and use this data in a trial and error cycle to find optimum effective moduli for coated fibers. In our procedure initially all of the simulations start using typical values of flexural modulus for phenolic resins and uncoated glass fibers. After obtaining the first set of results average stresses along different directions in the solution domain are found and used to calculate the modulus of the composite. Then for each case the calculated value of the modulus is compared with the experimental results. The first guess modulus for the reinforcing phase is then adjusted and a new solution is obtained. This process is repeated until a final value for the modulus of coated fiberglass is found which gives a composite modulus close to the experimentally determined value. The choice of the nodal positions at which average stresses should be used to calculate a composite modulus comparable with the experimental conditions depends on the nature of imposed boundary conditions [15]. The determination of optimum flexural modulus for various types of coated fiberglass enables us to find stress distributions on the fiber/matrix interface and form a judgement about the overall behaviour or particular composites.

Von Mises stresses along the nodes corresponding to fiber/matrix interface are also found using the following equation

$$g_v = \left(g_1^2 + g_2^2 - g_1 g_2 + 3 \, h_{12}^2 \right)^{1/2} \qquad (4)$$

where indices 1 and 2 represent respective Cartesian components of the total and deviatoric stress. In the present work we do not take into account plastic deformations of composites and thus a criteria for their failure by yielding based on a critical value of Von Mises stress at the fiber/matrix interface is considered. This criteria however, may not be appropriate if in practice these composites are found to be very brittle [19]. In this case the predicted normal stress or normal strains at the fiber/matrix interface should be used to analyze their behaviour at the point of failure.

4. RESULTS AND DISCUSSION

Experimental flexural strength and modulus results obtained for normal (moisture content not altered), wet and re-dried composites containing "as received", thermally treated and coated glass fibers are given in Table 1. As expected these results show that composites containing coated fiberglass as the reinforcing agent have high flexural strength and more significantly they retain their flexural strength under wet conditions. Although it is shown that composites containing AMEO-T coated fiberglass have a higher flexural strength than those using AMEO coated or "as received" fillers, nevertheless the results obtained for the latter two categories are good enough to justify the use of either of them in the production of fiberglass reinforced phenolic composites. The flexural modulus of composites reinforced by coated fiberglass under all three conditions are quite high and again those using AMEO-T coated glass fibers give the best results. The flexural modulus of composites which contain coated fillers vary by relatively small amounts for normal, wet and dry conditions. Under normal conditions the composite containing uncoated glass fibers has reasonably high modulus but it is significantly reduced for both wet and dry situations. Therefore despite having relatively high modulus under normal conditions, the use of uncoated glass in polymeric composite is not acceptable since in many cases wet or dry conditions may be present which impairs the bounding properties

TABLE 2. Computed Normal Stresses At Sample Interfacial Nodes A, B and C (Figure 1) And Maximum Von Mises Stress.

| Type of fiberglass used	Test Condition	Normal Stress in X_1 Direction (MPa)			Normal Stress in X_2 Direction (MPa)			Maximum Von Mises Stresses (MPa) Computed
		A	B	C	A	B	C	
As Received (Commercial)	Normal	48	42	39	54	40	43	67.7
	Wet	44	38	32	46	40	35	55.8
	Dry	46	42	39	52	39	43	64.9
Coated with AMEO	Normal	49	44	41	59	43	45	70.7
	Wet	48	41	40	54	41	43	50.0
	Dry	48	43	40	52	42	44	59.6
Coated with AMEO-T	Normal	51	45	43	62	49	47	67.5
	Wet	49	42	41	56	42	45	49.4
	Dry	50	44	42	61	44	43	51.6
Thermally Treated	Normal	37	35	32	47	36	38	65.1
	Wet	29	31	30	27	32	33	57.4
	Dry	20	21	24	28	27	24	60.2
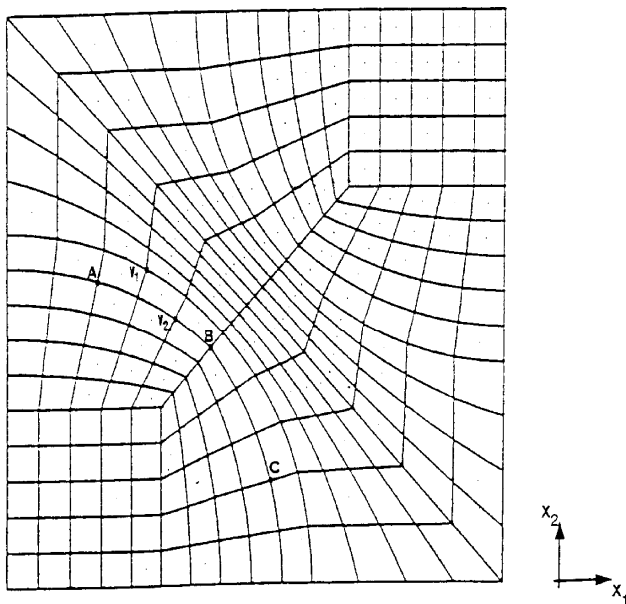
Figure 1. Finite element mesh; A, B and C stress sampling nodes; V1 Position of predicted maximum Von Mises stress using cleaned fibers. V2 Position of predicted maximum Von Mises stress using coated fibers.

of the uncoated glass fillers. Experimentally obtained flexural strain values for all of the cases are also given in Table 1. Maximum strains were found to occur under wet conditions for all types of composites used in this study. This may be due to the plasticising effects of water.

Finite element simulation of the deformation of a typical composite section containing glass fibers was carried out on a mesh shown in Figure 1. Our numerical experiments showed that this mesh gives the optimum results in the analysis of the behaviour of composites used in our study. We have prescribed displacement boundary conditions compatible with the actual deformations observed during the flexural experiments. This can be done by marking the test piece by a fine grid before the application of the flexural load and recording its deformation afterwards. Normal stresses
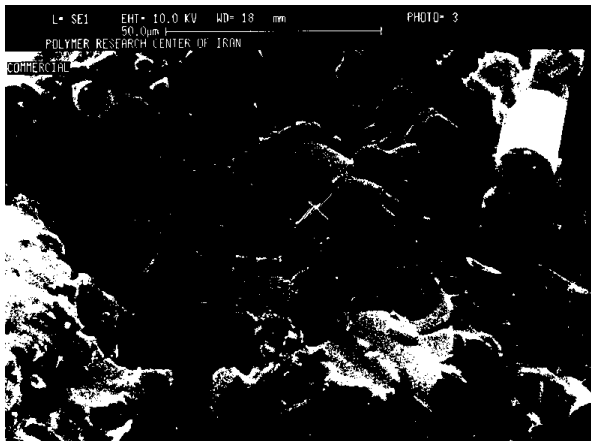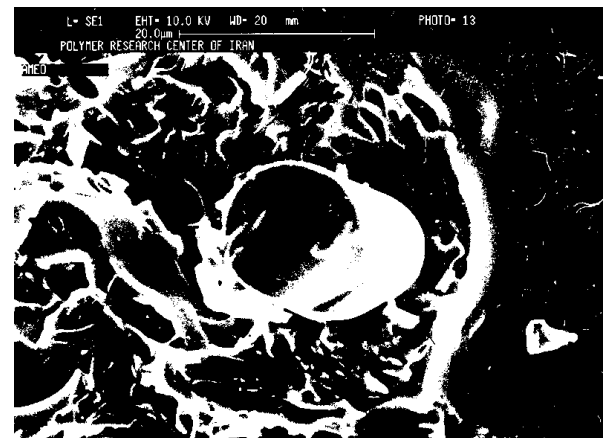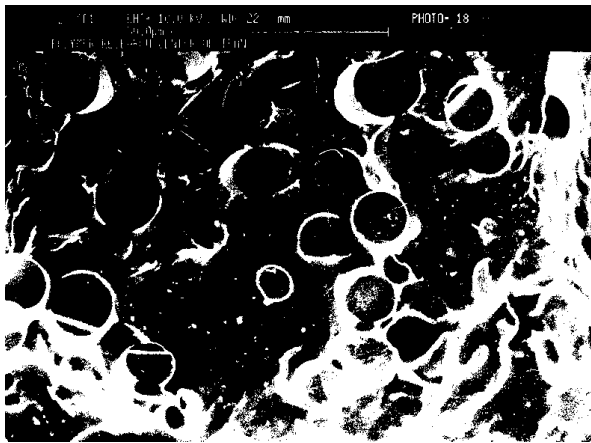
(a)
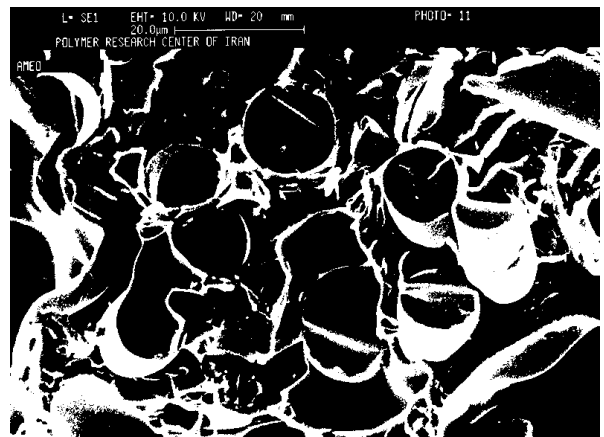
(a)

(b)

(b)

Figure 2. Scanning electron micrograph of fracture surface of composite containing commercial fiberglass: (a) magnification 850 and (b) magnification 1800.

Figure 3. Scanning electron micrograph of fracture surface of composite containing fiberglass coated with AMEO: (a) magnification 600 and (b) magnification 1950.

calculated at three sample nodes (A, B, C, Figure 1) located at the fiber/matrix interface are given in Table 2. These values are based on the use of fiberglass flexural moduli adjusted using the previously described trial and error procedure.
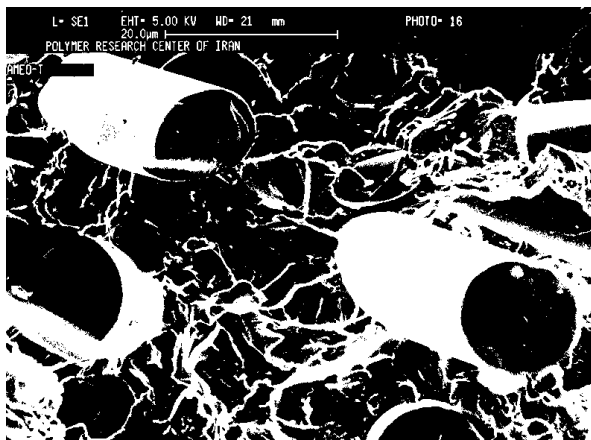
Positions where maximum Von Mises stress under normal conditions for different types of composites are found are also shown in Figure 1. It can be seen that using all three types of coated fiberglass the maximum predicted Von Mises stress occurs at the same node. Computed
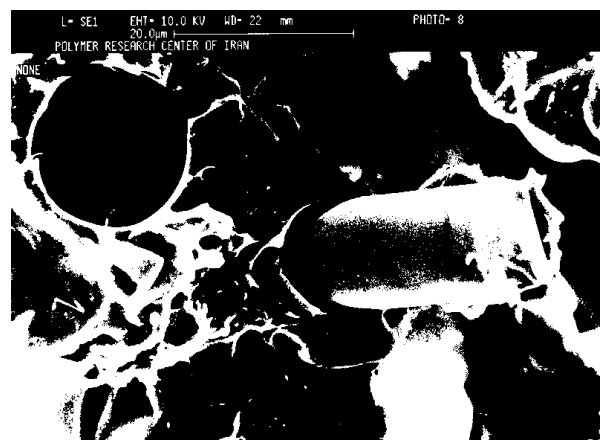
(a)

(b)

Figure 4. Scanning electron micrograph of fracture surface of composite containing fiberglass coated with AMEO-T: (a) magnification 860 and (b) magnification 1700.

(a)

(b)

Figure 5. Scanning electron micrograph of fracture surface of composite containing thermally cleaned fiberglass. (a) magnification 800 and (b) magnification 1800.

maximum Von Mises and normal stresses for different composites are also given in Table 2. The presented finite element results show a large difference between the deformation behaviour of composites containing coated or uncoated fiberglass and by comparison the

difference between the behaviour of composites containing glass fibers coated with different silane coupling agents is not very significant.

Scanning electron micrographs of different specimens after being subjected to the flexural tests are given in Figures 2-5. Figures 2-5 are

the micrographs of composites containing different types of coated fiberglass obtained using specimens subjected to flexural tests. In some cases, as it is shown in Figures 2-4, the bonding between coated fiberglass and polymer matrix is strong enough to remain relatively intact after the application of 10 kN load in the flexural tests.

In contrast, the Figure 5 shows the appearance of fracture surfaces between the cleaned glass fibers and the polymer matrix. This corresponds to the stress distribution patterns predicted by the finite element model.

5. CONCLUSIONS

Our results show that the mechanical behaviour of fiberglass reinforced phenolic composites are clearly affected by the coating of the glass fibers with silane coupling agents prior to compounding. The most significant improvement of these properties is however, achieved after using coated fiberglass instead of uncoated material and in comparison the use of different silanes have a limited effect in this respect.

Results obtained by our finite element analysis of composites containing coated and uncoated fiberglass used in this study also confirm this point. It is shown that a trial and error procedure can be successfully used to determine an effective (optimum) modulus for coated glass fibers which takes into account greater compatibility of the fiber/matrix interface achieved after coating glass particles with silane coupling agents.

6. REFERENCES

1. Lubin, G., "Handbook of Composites", Van Nostrand, New York, pp. 149-155, (1982).
2. Sewymcur, R. B., "Additives for Plastics", Academic Press, New York, pp. 70-98, (1987).
3. Knop, A., and Pilato L. A., "Phenolic Resins, Chemistry, Applications and Performance", Springer Verlag, Berlin, pp. 196-212, (1985).
4. Plueddemann, E. P., "Silane Coupling Agents", Plenum Press, New York, pp. 1-27, and pp. 111-140, (1982).
5. Mani, P., Gupta A. K. and Krishnamoorthy S., "Effect of Silane Coupling Agents on Mechanical and Thermal Properties of Polyester Resin Concrete", *Journal of Materials Science*, Vol. 18, (1983), 1506-1514.
6. Culler, S. R., Gillette P. C., Ishida H. and Koenig J. L., "Factor-analysis Applied to a Silane Coupling Agent on E-glass Fiber System", *Applied Spectroscopy*, Vol. 38, (1984), 495-500.
7. Wu, H. F., Dwight D. W. and Huff N. T., "Effects of Silane Coupling Agents on the Interphase and Performance of Glass-Fiber-Reinforced Polymer Composites", *Composite Science and Technology*, Vol. 57, (1997), 975-983.
8. Pape, P. G., "Silane Coupling Agents: Enhancements of Physical Properties of Plastics", *Engineering Plastics*, Vol. 9, (1996), 109-115.
9. Suzuki, N. and Ishida H., "A Review on the Structure and Characterization Techniques of Silane/Matrix Interphases", *Macromolecular Symposia*, Vol. 108, (1996), 19-53.
10. Yamaguchi, M., Nakamura Y. and Lida T., "Reactivity of Silane Coupling Agent with Surface of Silica Particles", *Polymers and and Polymer Composites*, Vol. 6, (1998), 85-88.
11. Marcinie, B., Krysztafkiewicz A. and Domika A., "Wettability of Silane Films on Silica Fillers", *Colloid and Polymer Science*, Vol. 261, (1983), 306-311.
12. Soderholm, K. J. M., "Influence of Silane Treatment and Filler Fraction on Thermal-Expansion of Composite Resins", *Journal of Dental Research*, Vol. 63, (1984), 1321-1326.
13. Hong, S. G., Lin J. J., "The Effects of Glass Beads and Silane Treatment on the Curing Behaviour of a Brominated Epoxy Resin: DSC Analysis", *Journal of Polymer Science, Part B - Polymer Physics*, Vol. 35, (1997), 2063-2071.
14. Graf, R. T., Koenig J. L. and Ishida H., "Reaction-Rates of Silane Coupling Agents in E-Glass Systems", *Modern Plastics*, Vol. 61, (1984), 116 et seq.
15. Nassehi, V., Kinsella M. and Mascia L., "Finite Element Modelling of the Stress Distribution in Polymer Composites with Coated Fiber Interlayers", *Journal of Composite Materials*, Vol. 27, (1993), 195-214.

16. Nassehi, V., Dhillon J. and Mascia L., "Finite Element Simulation of the Micromechanics of Interlayered Polymer/Fiber Composites: A Study of the Interactions between the Reinforcing Phases", *Composite Science and Technology* Vol. 47, (1993), 349-358.

17. Hughes, T. J. R., "The Finite Element Method", Prentice-Hall, Englewood Cliffs N.J., (1987).

18. Zienkiewicz, O. C., "The Finite Element Method", 3rd Ed., MacGraw-Hill London, (1977).

19. Malvern, L. E., "Introduction to the Mechanics of a Continuous Medium", Prentice-Hall, (1969).