

Mechanical Properties of Glass Fabric/Polyester Composites: Effect of Silicone Coatings on the Fabrics

S. Pavlidou, S. Mai, T. Zorbas, C. D. Papaspyrides

Laboratory of Polymer Technology, Department of Chemical Engineering, National Technical University of Athens, Zographou, Athens 157 80, Greece

Received 31 October 2002; accepted 17 June 2003

ABSTRACT: An experimental investigation was carried out to study the effect of a silicone coating on the mechanical properties of polyester/woven glass fabric composites, fabricated by resin transfer molding. E-glass woven fabrics were coated with a silicone elastomer by solution dip coating. The effect of variation of silicone amounts on the impact resistance, toughness, and mechanical properties of the composite was determined. Short beam shear tests were performed to assess the effect of coating on the adhesion of the fiber to the matrix. The coated specimens exhibited worse interlaminar shear strength over that of uncoated fabrics. Three-point bending tests were also performed to investigate the effect of the coating on flexural properties. Whereas

flexural strength and Young's modulus decreased with increasing amount of coating, the toughness, represented by the area under the stress-strain curve, presented a maximum. Finally, notched Izod impact tests were carried out and the curve for the energy absorbed during impact versus the amount of coating also appeared to have a maximum, indicating an interesting slot for optimum impact performance. © 2003 Wiley Periodicals, Inc. *J Appl Polym Sci* 91: 1300–1308, 2004

Key words: glass fibers; mechanical properties; polyester; silicone; toughness

INTRODUCTION

In composite materials stress transfer in the fiber/matrix interface requires a strong interfacial bond between the two components. However, for the most part, an improvement of the coupling often causes a decrease in impact strength, given that a direct linkage between fiber and matrix gives rise to a rigid, low impact resistance material.^{1,2} In other words, a strong interface favors a brittle fracture mode with relatively low energy absorption, whereas a weak interface favors a multiple shear mode with high energy absorption.³ This effect is related to the ease of debonding and pull-out of fibers from the matrix during crack propagation.⁴ For example, the only reason that brittle fibers in a brittle matrix can have any appreciable toughness at all is that cracks become diverted along the fiber/matrix interface.⁵ Therefore, optimization of the interfacial adhesion is required to obtain excellent interfacial strength and impact properties simultaneously.^{3,6}

Modification of the fiber/matrix interface is possible by coating the fibers by a polymer, which becomes the interphase between fiber and resin in the composite. Different technologies are used, such as solution dip-coating and interfacial polycondensation.² Polymers

used to provide a flexible interlayer at the filler surface have various natures depending on the mode of deposition.⁷ Their thickness and characteristics (such as glass-transition temperature and modulus) are defined by the properties required for the composite material (fatigue behavior or enhanced impact strength).⁸ According to Kardos, the concept of reducing stress concentration at the interface between a brittle matrix and glass fibers by applying a “rubber bumper” interlayer on the glass was first described by Lavengood and Michno in 1975.⁹ This technique has several advantages over others to increase composite toughness. For example, in early studies, Xanthos and Woodhams showed that there is an advantage in locating an energy-absorbing layer at the fiber/matrix interface rather than randomly in the matrix. Impact resistance was found to improve more when an elastomeric phase was at the interface, whereas little or no improvement was achieved when isolated from the interface for the same amount of elastomer.^{10,11}

The advantages of using an elastomeric coating can be summarized as follows:

1. A reduction of the stress concentration in the matrix in the vicinity of the fibers.
2. A reduction of residual stresses caused by differential thermal contraction as the composite cools from processing temperatures.
3. Its action as a spacer preventing fiber/fiber contacts during processing, which are sources of

Correspondence to: C. Papaspyrides (kp@softlab.ece.ntua.gr).

very high stress concentrations in the final composite⁹

Moreover, an elastomeric interlayer acts as an energy absorber, stress delocalizer, and crack arrestor.¹⁰ A direct consequence of these advantages is the increase in the impact strength of the composite. The effect of the coating on interlaminar shear strength (ILSS) and transverse tensile strength (TTS) is still a matter of debate.⁹ For example, Speri and Jenkins in their investigation of the effect of fiber–matrix adhesion on the properties of ABS, concluded that the composite's impact strength varied inversely to the fiber–matrix adhesion and that the TTS decreased as the adhesion between the two phases decreased.¹⁰

Many coating materials have been studied to modify the interfacial properties and eventually to improve the fracture toughness. Some points of generalization can be drawn with regard to the conditions, which determine a good coating for improving the toughness of composites without loss of strength⁶:

1. If the coating remains fluid or rubbery at the interface after cure a high viscosity coating is preferred because it can increase the frictional shear work when the fibers are being pulled out.
2. If the coating becomes a rigid interlayer after cure it should be more ductile and compliant than the matrix and should provide weak bonding at the interface while retaining sufficiently high frictional bonding.
3. The thickness of the various coatings, which are most commonly applied on the glass surface by dipping or spraying, depends on such variables as solution concentration, solution viscosity, and solvent evaporation rate. As noted by Kardos et al., the thickness of the interlayer has a pronounced effect on composite properties.¹⁰ Thickness of the coating should be kept as small as possible to eliminate the possibility of reduction in composite strength and modulus. Systematic decreases in flexural strength and ILSS with increasing coating thickness [e.g., silicone rubber coating and polyvinyl acetate (PVA) coating] have been noted. Thicker coatings also reduce the maximum V_f allowable for maximum composite strength without contact between neighboring fibers.
4. There are different views concerning the reactivity and miscibility of the coating with the resin matrix during curing. Sung et al. suggested that the coating should form and remain in a discrete layer at the interface without reaction with the composite constituents. However, a certain degree of chemical reaction between the coating and matrix may increase the frictional shear stress.

The objective of the present study was to investigate the effect of a glass-fabric surface treatment on the impact properties of woven-glass-fabric/polyester composites by using polydimethylsiloxane (PDMS) as surface modifier for the glass fabric. We investigated the impact behavior of composites treated with various amounts of coating and explored the relationship between the interfacial adhesion strength and the composite flexural and impact properties.

EXPERIMENTAL

Materials

The E-glass cloth (HK WR 500-A, C. Chronis SA, Athens, Greece) used was in the form of a plain-woven fabric, with 1/1 warp/weft strands. Each strand consisted of filaments of 22 μm in diameter, whereas the linear density of glass was 1150 tex. The matrix material was an unsaturated polyester resin (Norpol 410-900, C. Chronis SA), which was cured with 1% w/v methyl ethyl ketone peroxide. Polydimethylsiloxane (Silopren C-70, Bayer AG, Leverkusen, Germany) was used as the coating material. It was crosslinked by addition of a crosslinking agent (blend of alkoxisilanes and tin catalysts, 1% v/w), forming an elastomer with a three-dimensional network structure.

Deposition of coating

The surface treatment involved first pyrolyzing the size. The E-glass fibers were coated with a proprietary organic size at the time of manufacture to protect them from abrasion damage during production. Before the deposition of the coating material the fabrics were desized at 600°C for 2 h. It was found in the literature that this "heat-cleaning" treatment is sufficient to remove presizing and organic impurities from the glass-fiber surface.^{8,12}

The deposition was performed by the dip-coating technique, using toluene as solvent. The fabric was fixed on a frame to avoid deformation and immersed into the elastomeric solution at room temperature. After removing the cloth, which dipped up a quantity of the solution, the cloth was hung until the excess of the solution finished dripping, and was dried in an oven (120°C, 10 min) to effect solvent evaporation. Solution concentration permitted control of the thickness of the interlayer. In this case, four different concentrations were used (0.25, 0.5, 1, and 4% w/v).

Fabrication of composites

Woven E-glass fabric/polyester composites were fabricated by resin-transfer molding (Isojet Equipment, CUVF RTM, France). After placing 20 cloth pieces in the mold and degassing the resin to avoid air entrap-

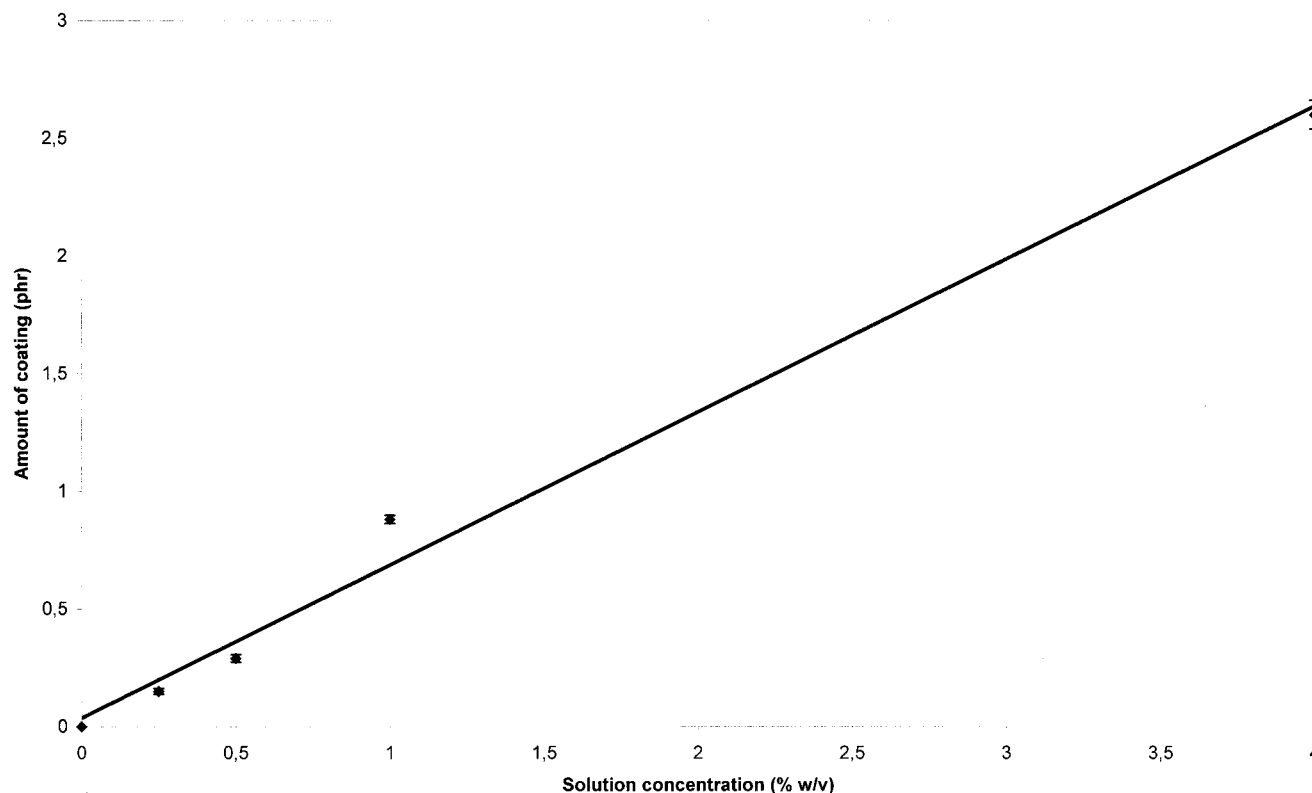


Figure 1 Amount of coating on the fabrics versus solution concentration.

ment in the composite, the mold (diameter: 32 cm, thickness: 9 mm) was closed with two flat metal plates. All injections were carried out under a pressure of 1 bar. After curing for 24 h at room temperature, specimens for the mechanical tests were cut from the laminate using a water-cooled rotary diamond-impregnated wheel. They were fully postcured at 60°C for 4 h and 80°C for 4 h.

Characterization of composites

The matrix burn-off technique was used for the determination of the composites' fiber content. The samples were pyrolyzed in a furnace by gradually increasing the temperature to 600°C and maintaining them at that temperature for 3 h. The amount of PDMS deposited was determined gravimetrically.

Mechanical testing

Short-beam shear test

The interlaminar shear strength of the glass-fabric/polyester composites was determined according to the ASTM D2344 standard on an Instron testing machine (Model 4466; Instron, Canton, MA). Specimens were of dimensions 70 × 6.35 × 10 mm, with a support span of 50 mm, resulting in a span-to-depth ratio of 5, and

the crosshead speed was 1.3 mm/min. At least 10 specimens were tested.

Izod impact test

The impact resistance of the composites was evaluated by means of Izod tests. A short-beam specimen [70 × 10 × 10 mm (length × width × thickness)] was fixed in an Izod impact tester (Instron Wolpert PW5) with the fabrics perpendicular to the direction of blow. A notch was milled across the specimen width to provide an area of stress concentration and initiate failure. The specimen was positioned with the notch on the striking surface. The length between the impact point and the fixture was set at 22 mm. The initial potential energy of the pendulum was 19.4 J. At least 10 specimens were tested.

Three-point bending test

Flexural tests were also performed on the Instron testing machine (Model 4466) using a three-point bending fixture on 190 × 13-mm (length × width) specimens, in accordance with ASTM D790 standard at a constant span-to-depth ratio of 15, which resulted in a support span of 150 mm. The rate of center loading was 4.1 mm/min. At least five specimens were tested.

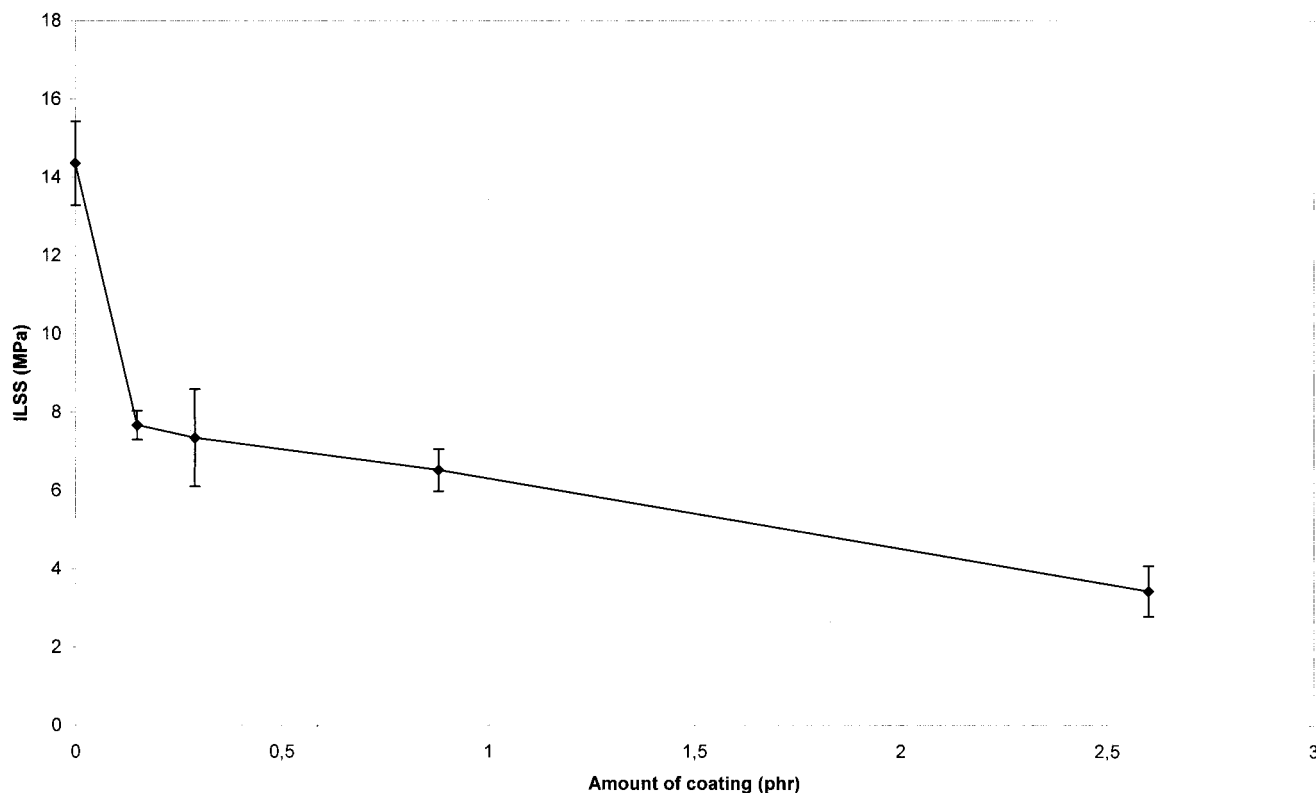


Figure 2 Interlaminar shear strength versus amount of coating.

RESULTS AND DISCUSSION

Characterization of composites

The weight fraction of the fibers, as determined by the resin burn-off technique, was approximately 55%.

As expected, the amount of coating increases as the PDMS concentration increases. It is worth noting that the increase is linear (coefficient of deviation, $R^2 = 0.99$), at least within the range of the solution concentrations examined here (Fig. 1).

Mechanical properties

Short-beam shear test

The short-beam shear test was used to estimate the interlaminar shear strength. It is based on elementary beam theory and involves a three-point flexure specimen with a span-to-depth ratio chosen to produce interlaminar shear failure.¹³

In Figure 2, the ILSS values are presented versus the amount of PDMS elastomer deposited on the fibers. The application of coating reduces the ILSS value. In fact, a significant decrease in the ILSS value is obtained for only 0.15 phr of coating, whereas the reduction rate decreases with further increases of the amount of coating. As mentioned in the introductory remarks these results are in agreement with those of Kim et al.,⁶ who claimed that the coating thickness

must be as small as possible to avoid systematic decreases of ILSS and impact strength.

Thus, the short-beam shear test indicates a "lubricating" character of the coating in relation to the matrix, which can be analyzed using the surface energies of the resin over the silicone-coated fiber. It is a well known fact that for a liquid resin to wet or spread over a substrate completely, the surface tension of the liquid resin must be less than that of the substrate itself.¹¹ In reverse conditions, there would be poor wetting of the liquid resin and consequently poor adhesion between the two components, that is, in our case matrix and coated fiber. The surface tension of polydimethylsiloxane is 24 mJ/m^2 .¹⁴ Only fluorinated compounds show lower surface tension than this value. Most organic polymers, like the polyester matrix, have surface tension between 30 and 45 mJ/m^2 .¹¹ Consequently, in our case, the polyester matrix with a surface tension higher than that of the silicone-coated fiber does not adhere to that surface and this may explain the behavior encountered.

Another possible reason for the deterioration of adhesion in the presence of the PDMS coating might be, apart from the bad affinity between PDMS elastomer and polyester resin, that the wetting of the inner fibers of the glass fabric and the ability of the polyester resin to penetrate through the fabric are hindered. The same behavior has been observed in previous studies for

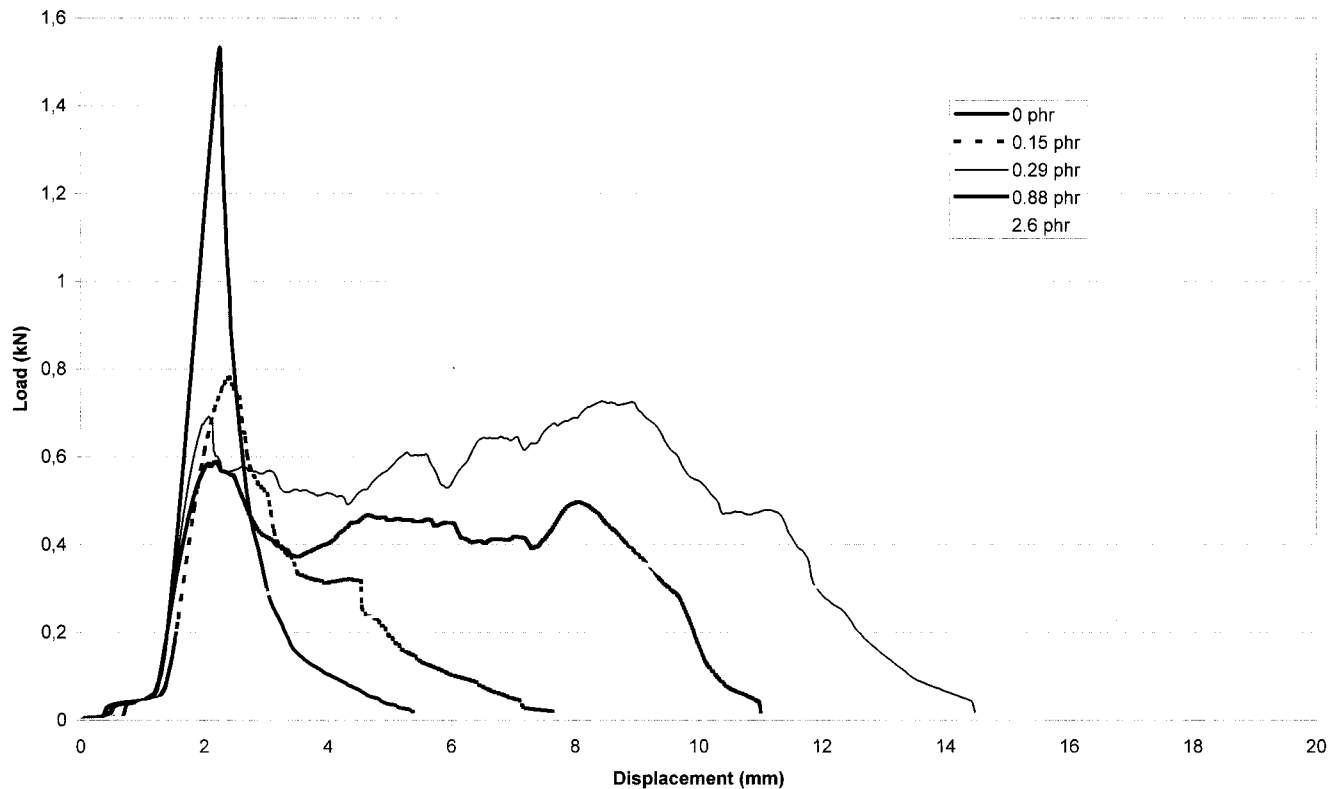


Figure 3 Typical load/displacement curves recorded during short beam shear tests for different coating conditions (data based on PDMS concentration).

polyamide-coated glass and Kevlar fabrics embedded in polyester and epoxy resin, respectively.¹⁵

The shape of the load versus displacement curves recorded during the short-beam shear tests (Fig. 3) is worth noting. It is readily observed from these curves that the presence of an elastomeric interlayer leads to different deformation and failure behavior. In particular, the maximum load supported by the specimen decreases gradually with the application of the PDMS elastomer on the glass fabric, this effect being accompanied by an increase of the maximum displacement. In the case of the uncoated specimens, the corresponding curve indicates that failure occurred in a rather brittle tensile mode during the short-beam bending test. This was also observed macroscopically during testing. On applying the elastomeric coating, the failure mode changed to pure shear and the coated specimens continued to deform after the first rupture. This phenomenon is in harmony with the study of Labronici et al. for the case of carbon fiber-reinforced polyimide composites, where a silicone interlayer was inserted between matrix and fibers.¹¹

Izod impact test

Damage resistance and damage tolerance under impact loading are the most important characteristics of

fiber-reinforced composites because they are vulnerable to accidental impact loading of various kinds during the manufacturing process and in service. The fiber/matrix interphase properties, which are affected by fiber surface treatment, play an important role in determining the failure mechanism, the extent of damage, and the threshold energy required for failure of the composite.¹⁶

In our study, a short-beam Izod impact test was used to study the effect of the interlayer on impact resistance of the composites. The height of impact point from the fixture of the sample (L) has a substantial effect on the failure mode of short-beam specimens. A smaller value of L raises the shear stress in the specimen and results in a shear mode fracture, whereas a specimen is broken in the bending mode when L is larger.¹¹ Here, $L = 22$ mm was used for the impact test. The control specimen was broken in the bending mode, but as the interlayer thickness increased, the failure mode clearly changed to shear.

The energy absorbed, expressed by per cross-sectional area of the specimen, is plotted in Figure 4 versus the amount of silicone coating. As can be seen, the behavior of the material changes dramatically as the amount of silicone coating increases from about 0.2 to 0.5 phr. Within our experimental conditions (i.e.,

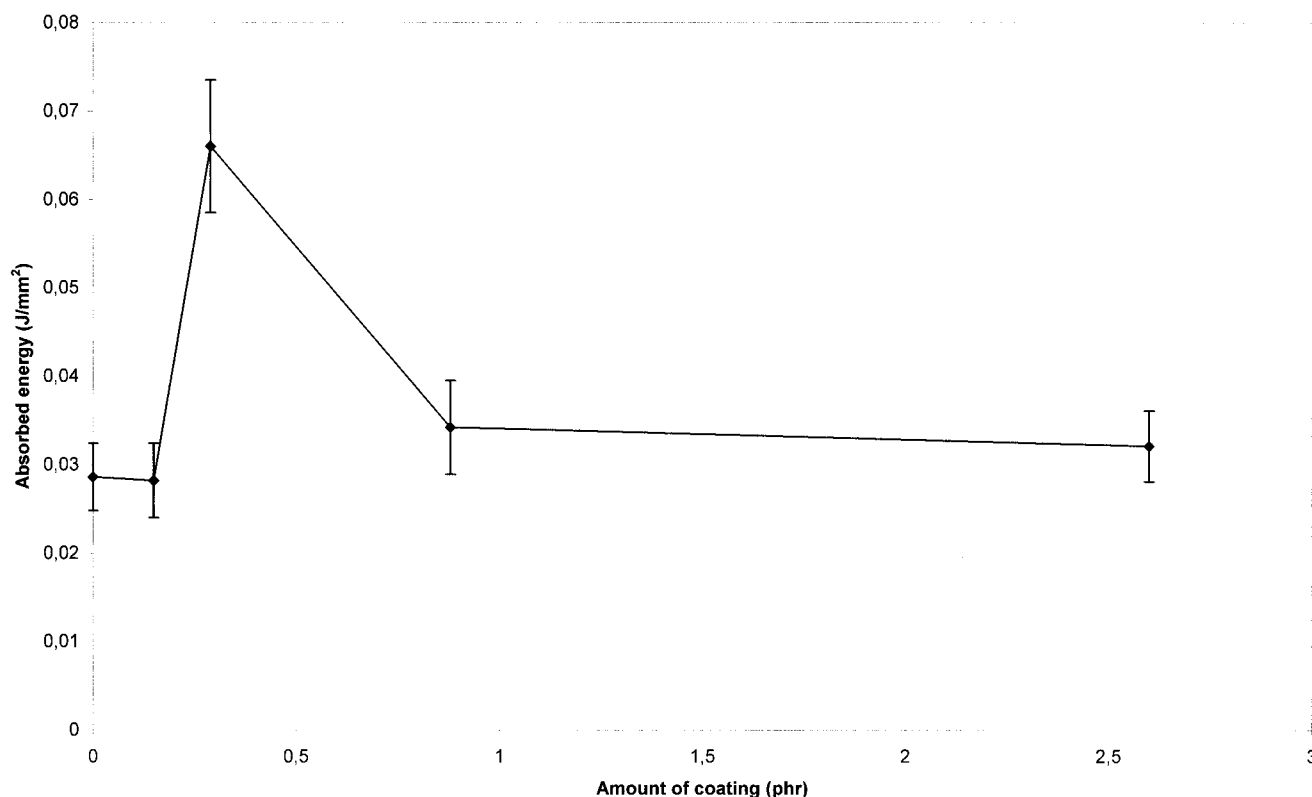


Figure 4 Absorbed energy during impact versus amount of coating.

having one experimental point in this area), the absorbed energy seems to pass through a maximum.

A similar behavior was previously reported in the literature. For example, Peiffer and Nielsen showed that there was a relation between impact toughness and number of latex monolayers in the epoxy matrix/glass fibers coated with acrylic latex composite materials. The impact strength passed through a maximum for a thickness of coating corresponding to two monolayers.⁷ Furthermore, Labronici and Ishida showed that the deposition of PDMS elastomer on carbon fibers embedded in PMR-15 polyimide matrix leads to an increase of impact strength up to a certain coating thickness. Above that optimum thickness impact strength decreased again.¹¹

Enhancement of the impact strength of the composites by the introduction of a soft interlayer can be explained by using a complex combination of mechanisms, as reported in the literature. For example the interlayer may act as an energy absorber, a crack arrester, and a stress delocalizer.¹¹ In fact, on model composites based on a single elastomer-coated glass fiber embedded in an epoxy matrix and tested in tension (fragmentation test), Ahlstrom demonstrated that the presence of a low-modulus interphase leads to a modification of the stress field around the coated fiber.⁸

The progressive reduction in impact strength beyond the optimum thickness may be attributable to severe fiber sticking and nonuniform distribution of the polyester resin between coated fibers.¹¹

Three-point bending test

Bending test methods are highly versatile regarding the possibility of measuring a wide spectrum of mechanical properties.¹⁷ In the present study a three-point bending test was used to assess the effect of PDMS coating on flexural strength, Young's modulus, and fracture toughness of woven-glass-fabric/polyester composites.

Here, both flexural strength and modulus of composites tend to decrease as the amount of PDMS deposited increases (Fig. 5).

Representative stress/strain curves recorded during the three-point bending test of the materials studied are presented in Figure 6. As in the case of short-beam shear tests, the elastomeric interphase modifies the failure behavior. Thus, the coated fabric composites show a curve typical of a toughened sample with increased strain to failure. An "unstable" mode of crack growth predominates, where the crack propagation occurs intermittently in a stick-slip manner. In contrast, the uncoated composites present a rather

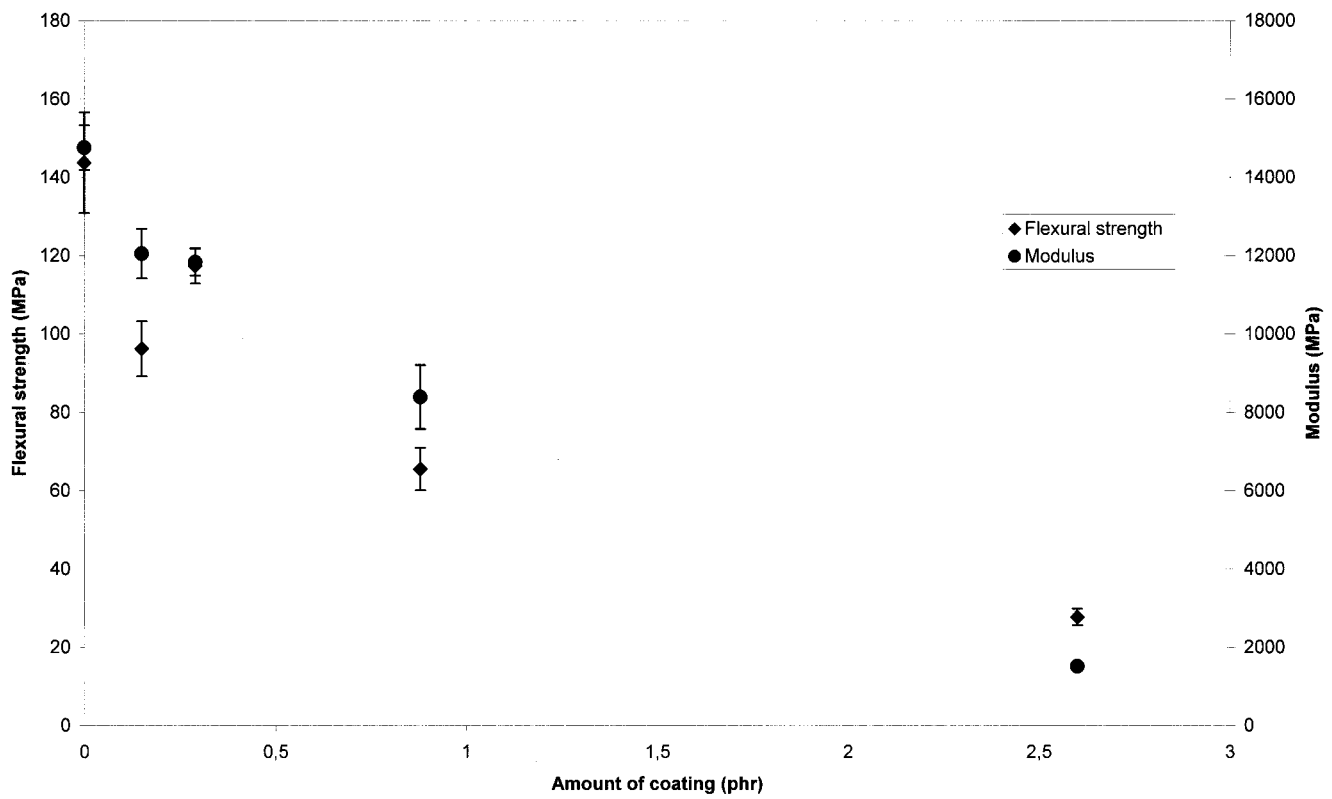


Figure 5 Flexural strength and modulus versus amount of coating.

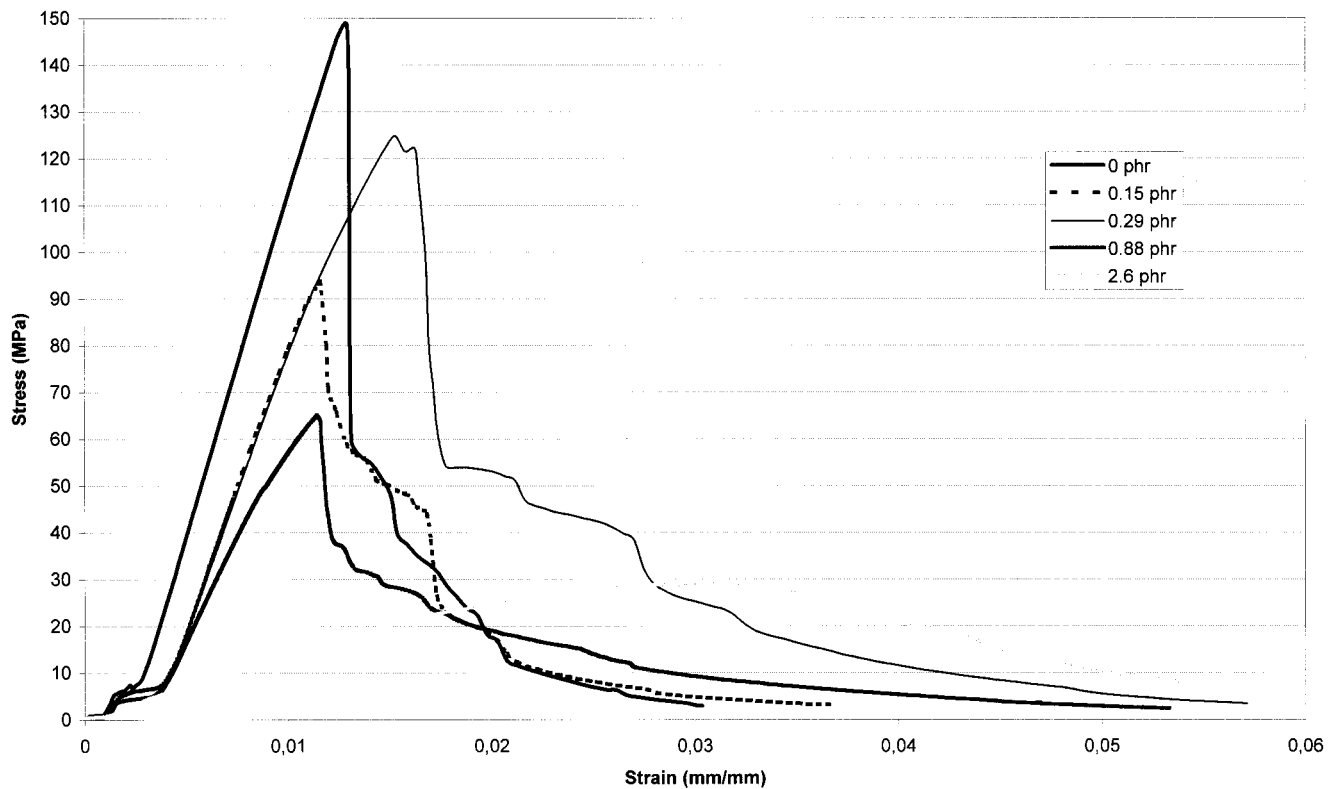


Figure 6 Typical stress/strain curves recorded during three-point bending tests for different coating conditions (data based on PDMS concentration).

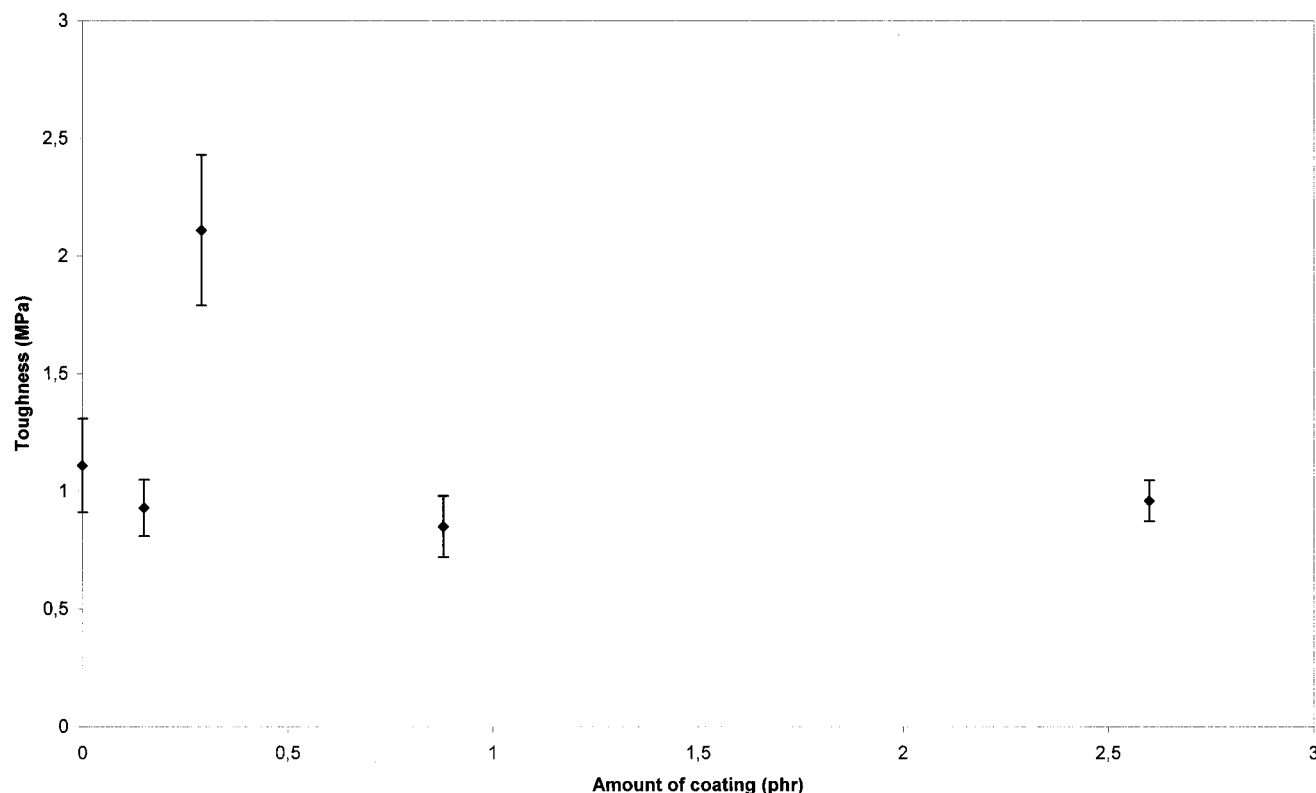


Figure 7 Toughness versus amount of coating.

brittle behavior, in agreement with findings from the literature.¹¹ It should be emphasized that when the fabrics are coated with the elastomer, a ductile reversible deformation is displayed. This is of critical importance for enhancing fatigue properties.⁷

The "toughness" of composites, a broadly accepted mathematical definition of which is the work done in breaking a specimen, was derived from the stress versus strain graph by computing the area under the curve, given that this integrates all the units of stress \times strain to give the total work—that is, the toughness.^{12,18} Results are presented in Figure 7. Compared with the untreated composite, increased toughness was observed for fabrics treated with 0.29 phr of PDMS elastomer, but higher PDMS amounts decrease the toughness. This is attributed to the very low flexural strengths recorded for high amounts of coating.

It is worth noting that, despite the differences in the fracture modes between a "slow" three-point bending test and an Izod (cantilever) impact test, the silicone interlayer seems to affect the toughness of the composite in a similar way.

CONCLUSIONS

Coatings in general, and the PDMS coating in particular, can serve as useful tools in the design of composite structures and in providing a means to tailor

the composite properties depending on the specific application. However, the enhancement in toughness, which was basically attempted here, is usually obtained at the expense of the flexural and interlaminar shear strength. In the present study a significant improvement in impact strength was achieved by the deposition of 0.29 phr of PDMS elastomer on woven glass fabrics embedded in polyester matrix, whereas, for that amount of coating, decreases in interlaminar shear strength and flexural strength were recorded. Higher amounts of coating result in reduction of the impact strength.

The authors thank Dr. Nikos Pantelelis and the Ph.D. student Thomas Vrouvakis for their support in manufacture of composites. We also thank Mr. Mavromatis (Dr. D. A. Delis AG) and Mr. Prantsidis for providing us the polydimethylsiloxane resin.

References

1. Ehrburger, P.; Donnet, J. B. *Philos Trans R Soc Lond A* 1980, 294, 495.
2. Varelidis, P. C.; McCullough, R. L.; Papaspyrides, C. D. *Compos Sci Technol* 1999, 59, 1813.
3. Park, R.; Jang, J. *Compos Sci Technol* 1998, 58, 979.
4. Hull, D. *An Introduction to Composite Materials*; Cambridge Solid State Science Series: Cambridge, UK, 1987; Chapter 3, p. 37.

5. Dorey, G. *Advanced Composites*; Elsevier Science: London, 1989; Chapter 11, p. 374.
6. Kim, J. K.; Mai, Y. W. *Compos Sci Technol* 1991, 41, 333.
7. Gerard, J. F. *Polym Eng Sci* 1988, 28, 568.
8. Tillie, M. N.; Lam, T. M.; Gerard, J. F. *Compos Sci Technol* 1995, 58, 659.
9. Podgaiz, R. H.; Williams, R. J. J. *Compos Sci Technol* 1997, 57, 1071.
10. Peiffer, D. G.; Nielsen, L. *J Appl Polym Sci* 1979, 23, 2253.
11. Labronici, M.; Ishida, H. *Compos Interfaces* 1997, 5, 87.
12. Larena, A.; Matias, M. C.; Urreaga, J. M. *Spectrosc Lett* 1992, 25, 1121.
13. Herrera-Franco, P. J.; Drzal, L. T. *Composites* 1992, 23, 2.
14. Shafrin, E. G. In: *Polymer Handbook*; Brandrup, J.; Immergut, E. H., eds.; Wiley: New York, 1974; pp III, 225.
15. Varelidis, P. C.; Papakostopoulos, D. G.; Pandazis, C. I.; Paspaspyrides, C. D. *Composites Part A* 2000, 31, 549.
16. Hirai, Y.; Hamada, H.; Kim, J. K. *Compos Sci Technol* 1998, 58, 91.
17. Rosensaft, M.; Marom, G. *J Compos Technol Res* 1985, 7, 12.
18. Brown, R. P. *Handbook of Plastics Test Methods*, 2nd ed.; George Godwin: London, 1981; Chapter 8, p. 153.