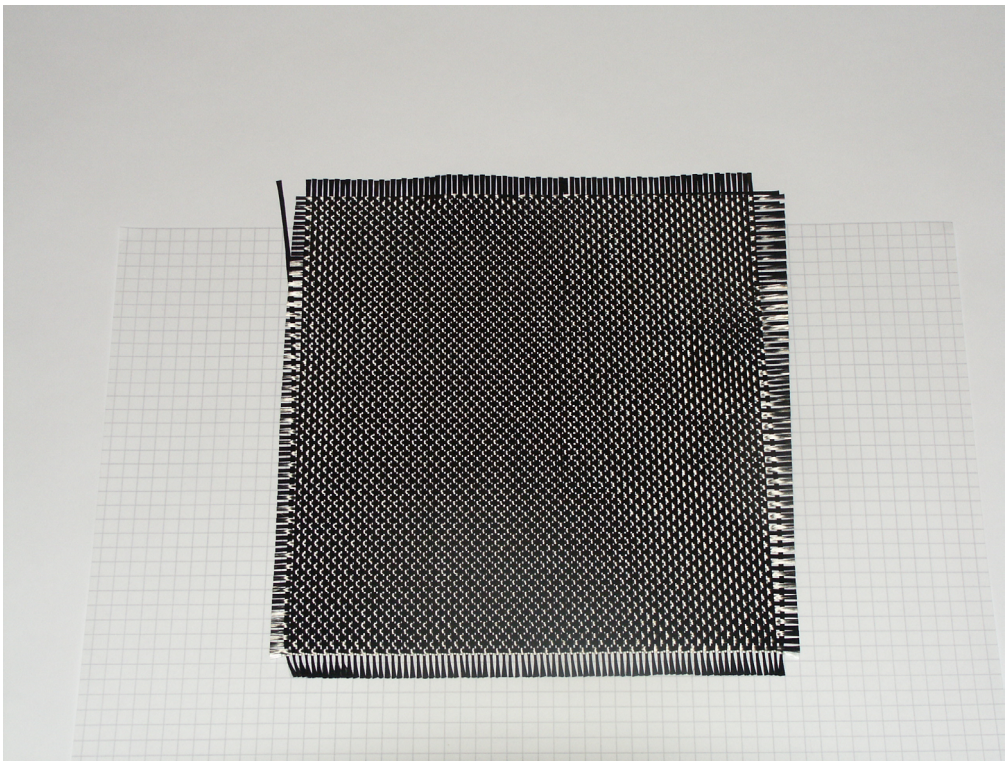
FOI-R--1122--SE
December 2003
ISSN 1650-1942
Technical report

S.J. Savage, F. Larsson, L. Svensson

Isostatic pressing carbon fibre composites



Woven carbon fibre before infiltration with epoxy resin

Sensor Technology
SE-581 11 Linköping

SWEDISH DEFENCE RESEARCH AGENCY

Sensor Technology
P.O. Box 1165
SE-581 11 Linköping

FOI-R--1122--SE

December 2003

ISSN 1650-1942

Technical report

S.J. Savage, F. Larsson, L. Svensson

Isostatic pressing carbon fibre composites

Issuing organization	Report number, ISRN	Report type
FOI – Swedish Defence Research Agency Sensor Technology P.O. Box 1165 SE-581 11 Linköping	FOI-R--1122--SE	Technical report
	Research area code 7. Vehicles	
	Month year December 2003	**Project no.** I6001/E3037
	Customers code 5. Commissioned Research	
	Sub area code 74 Materials Technology	

Author/s (editor/s)	Project manager
S.J. Savage F. Larsson L. Svensson	S.J. Savage
	Approved by
	Sponsoring agency Armed Forces
	Scientifically and technically responsible

Report title

Isostatic pressing carbon fibre composites

Abstract (not more than 200 words)

This report documents the experiments made and results obtained in a study to investigate the effects of hardening epoxy-carbon fibre composites under hydrostatic pressure of 100 bar.

A method has been developed for hardening fibre composites under high pressures, and the method has been successfully applied to processing small samples. These samples have been mechanically tested and compared to similar materials hardened under conventional pressures.

High-pressure hardened materials show reduced porosity and lower levels of inter-laminar matrix. The interlaminar shear strength (ILSS) is only slightly improved, but it is noteworthy that scatter was reduced by 50%. However, an insufficient number of samples were tested.

It appears that hardening under high pressure does lead to some improvement in strength of carbon-fibre composites, which may be useful in military applications.

Keywords

carbon fibre, composites, isostatic pressing

Further bibliographic information	Language English
ISSN 1650-1942	**Pages** 12 p.
	Price acc. to pricelist

Utgivare Totalförsvarets Forskningsinstitut - FOI Sensorteknik Box 1165 581 11 Linköping	**Rapportnummer, ISRN** FOI-R--1122--SE	**Klassificering** Teknisk rapport
	Forskningsområde 7. Farkoster	
	Månad, år December 2003	**Projektnummer** I6001/E3037
	Verksamhetsgren 5. Uppdragsfinansierad verksamhet	
	Delområde 74 Materialteknik	
Författare/redaktör S.J. Savage F. Larsson L. Svensson	**Projektledare** S.J. Savage	
	Godkänd av	
	Uppdragsgivare/kundbeteckning FM	
	Tekniskt och/eller vetenskapligt ansvarig	
Rapportens titel (i översättning) Isostatpressning av polymermatriskompositer		

Sammanfattning (högst 200 ord)

Denna rapport beskriver de försök som gjordes och resultat av en undersökning av tryckets inverkan på härdning av epoxi-kolfiber kompositer vid en hydrostatiska tryck av 100 bar.

En metod har utvecklats för härdning av kompositer under höga tryck, och metoden har tillämpats på små prover. Dessa prover har sedan karakteriserats m a mekaniska hållfasthet, d v s interlaminära hållfastheten (ILSS). Egenskaperna har sedan jämförts med liknande prover härdad under konventionella betingelser.

Materialen som härdats under högtryck visar minskade porositet och mindre nivåer av interlaminära matrismaterial. ILSS var något förbättrade, men spridning i ILSS minskades med 50%. Dock bör det påpekas att ett otillräckliga antal prover undersöktes.

Det konstateras att härdning av fiberkompositer kan ge upphov till en förbättring av ILSS i kolfiberkompositer, och därmed potentiell försvarsnytta.

Nyckelord kolfiber, kompositer, isostatpressning	
Övriga bibliografiska uppgifter	**Språk** Engelska
ISSN 1650-1942	**Antal sidor:** 12 s.
Distribution enligt missiv	**Pris: Enligt prislista**

CONTENTS

INTRODUCTION

Our hypothesis is that porosity, which is a significant problem and has a negative effect on the mechanical properties of fibre composites, particularly interlaminar strength, can be reduced by applying a pressure much higher than those conventionally used in composite production. This is by analogy with the technique of Hot Isostatic Pressing (HIP) now commonly used on a commercial scale to eliminate porosity in cast titanium and other products where predictability of properties and performance are critical, such as in aerospace and biomedical prostheses.

OBJECTIVE

To investigate if the application of a high (up to 100 MPa) hydrostatic pressure on a carbon fibre reinforced epoxy composite during hardening can reduce the occurrence of porosity and thereby improve the mechanical properties of the material

BACKGROUND

A common problem seen in many fibre reinforced polymers (e.g. carbon fibre composites) is that of porosity, which can be as high as several volume percent of the composite material. This porosity leads to mechanical property degradation and reduced predictability of the composite during service. A consequence is that components (which are frequently used in critical load-bearing applications in aerospace) must be overdesigned, leading to sub-optimization and reduced performance.

It is hypothesized that application of a high pressure during hardening of the polymer matrix can lead to improved mechanical properties. The origin of this hypothesis derives from analogy with the now commonplace practice of hot isostatic pressing (HIPing) of critical metal castings or powder metallurgy components, such as are used in aerospace and oil extraction industries [1]. By HIPing at high temperature the flow strength of the metal can be reduced sufficiently that deformation and pore closure occurs. The porosity may be completely removed (if the voids do not contain an insolube gas) or substantially reduced in size (if an insoluble gas is present).

While HIPing is not appropriate for polymer-based materials, cold isostatic pressing (CIPing) may be a beneficial technique. It can be noted that autoclave pressing at lower pressures, up to about 1 MPa, is commonly used during the manufacture of composite components[2].

The origins of porosity in fibre reinforced polymers are not completely understood, and a number of factors are undoubtably responsible. Campbell et al have published an overview which considers what are probably the main causes, which are related to production of gases and vapours during the hardening (polymerization) process. This overview is based on a series of studies performed under contract to the US Air Force from about 1980 onwards.

ORIGINS OF POROSITY

Several mechanisms are known to lead to porosity in carbon fibre composites, some of which have been reviewed by Campbell et al. [3].

During production and storage, both the reinforcing carbon fibre and the resin matrix are exposed to atmospheric humidity, which may be both adsorbed and absorbed. This can be retained even after degassing vacuum treatment, even when the fibre and resin are combined into a pre-impregnated material (pre-preg). When the pre-preg is subsequently laid up in the mould before heating and pressing this absorbed water is not easily removed. Additional air bubbles can be incorporated into the pre-preg during the process of coating the fibres with resin.

Volatile substances such as water and alcohols can be produced by the polymerization (hardening) reaction itself, which occurs in resins that polymerize by condensation. These include common resins such as phenolics, polyamides, epoxies and bismaleimides. Polymers that harden by addition reactions are not affected. During the autoclaving process, which is performed at temperatures typically in the range 200 to 370 °C, the vapour pressure of volatiles may exceed that of the external (autoclave) pressure, leading to void formation. As noted earlier, autoclave pressures of up to about 1 MPa are common, and it may seem unlikely that vapour pressures will exceed this level. However, the actual pressure within the fibre composite may be considerably lower than the autoclave pressure due to shielding by the fibre reinforcement itself, and as a result of "bleeding" off excess matrix. [3].

Other sources of porosity include cracking due to inhomogeneous thermal shrinkage during cooling from the autoclave temperature, and air trapped during the lay-up process. Paradoxically, this appears to be a more serious problem when using pre-pregs with better (i.e. smoother) surfaces than those with surface irregularities. Internal stresses caused by rapid cooling (necessary to reduce production cycle times for economic reasons) also contribute to void and micro-crack formation [4].

EXPERIMENTAL DETAILS

An experiment was designed to test the hypothesis. A carbon fibre reinforced epoxy composite was manufactured and allowed to harden under (a) normal pressure and (b) at 100 MPa. The mechanical properties of the composite were then measured, and the microstructure examined. Compared with conventional processing, the only significant difference is the external pressure. A normal autoclave pressure is about 1 MPa.

The equipment used consisted of a locally available cold isostatic press (CIP), (Olin Monostatic powder press) with a cylindrical pressure chamber 75 mm diameter and 250 mm high. The pressure transmitting fluid was water containing a corrosion inhibitor. Pressures up to approximately 100 MPa (1000 bar) are achieved by a compressed air pump.

Materials production

A number of unsuccessful experiments were made before the following procedure was developed. It is important that air be evacuated from the sample during impregnation, and that the sample package does not leak unhardened epoxy into the isostatic press. Epoxy in the valves or pipes of the press would have disastrous consequences.

A shown in the diagram below a number of pieces of carbon fibre weave were cut and stacked on top of each other,. A conventional carbon fibre: T300 was used, with a 0, 90° orientation in the stack. A piece of 0,5 mm thick polycarbonate was placed at the top and bottom of the stack, to give rigidity to the material before impregnation, and to act as a release layer after hardening.

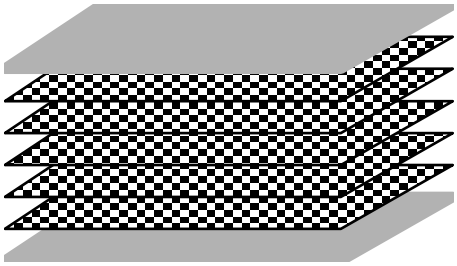


Figure 1. The carbon fibre/polycarbonate stack

The sample size used was 70 mm x 20 mm, with a total thickness of 6 mm. A conventional two component cold-curing epoxy laminating system from CIBA Polymers was used: Araldite LY 5052 with Hardener HY 5052[1]. This system is suitable for the resin transfer moulding used in these experiments. Gellation occurs between 8-16 hours at room temperature.

The stack of carbon fibre weave and polycarbonate was placed in a heat-shrink tube, and at one end a connector to a vacuum pump was fitted. The tube was heated to shrink onto the weave stack and vacuum connector. A vacuum pump was connected, giving a compaction pressure from the atmosphere. By dipping the open end of the tube into the premixed epoxy/hardener the stack was impregnated with the resin. The experimental arrangement is shown in figure 2 below.

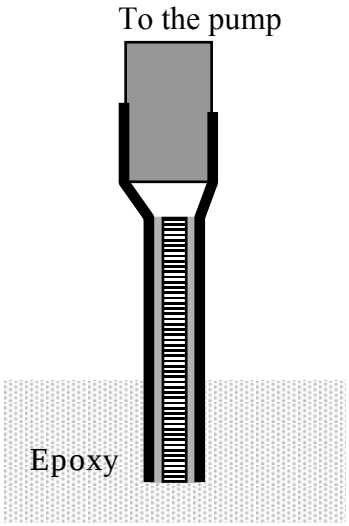


Figure 2. The impregnation process

When the impregnation process was complete, the part of the heat-shrink tube containing the connector was cut off and the remaining piece containing the impregnated weave was placed in another heat-shrink tube. Both ends of the tube were sealed using hot glue. A syringe was inserted through the glue seal and connected to the vacuum pump, as shown in figure 3 A vacuum was created in the tube, which was maintained by heating the glue at the same time as the syringe needle was removed (the vacuum pump was connected during this operation). As the needle was removed the softened glue sealed the hole. The result is a relatively pore-free composite in an evacuated elastic container, which was then placed in the isostatic press for hardening.

[1] CIBA Polymers matrix systems, publication nr 38285/1/e, February 1994

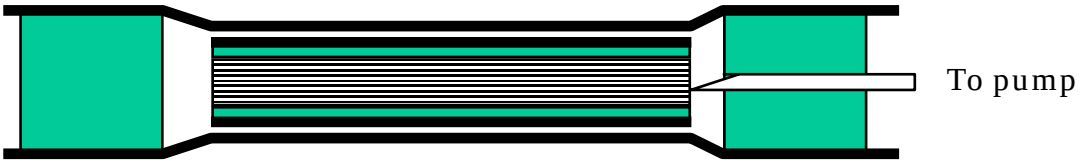


Figure 3. The impregnated weave placed in a heat-shrink tube, sealed with hot glue and evacuated.

The impregnation and sealing process took about one hour. The sample was then immediately placed in the isostatic press, and maximum pressure of 103 MPa (15000 psi) applied, for 24 hours. The pressure showed a tendency to drop slowly, presumable to slight leakage, so that at about 2 hour intervals the pressure was checked and if necessary increased again. At no time did the pressure drop below 101 MPa (14750 psi). After complete hardening the sample was removed from the press and the heat-shrink tube and polycarbonate removed.

As reference a sample was prepared under identical conditions, but allowed to harden under normal atmospheric pressure. Two samples were made, giving sufficient material for mechanical testing and microstructure characterisation.

The hardening time for the epoxy used was about 24 hours. After initial experiments showed that the infiltration and hardening under pressure was successful, the press was modified by wrapping a heating coil around the pressure cylinder, with an outer layer of glass-fibre insulation. The coil was 10 mm plastic tube, through which warm water from a heating bath was continuously pumped. After modification the pressure cylinder could be heated to a temperature of 60 °C and the hardening time reduced to less than 4 hours.

Mechanical property measurement

It was decided that measurement of the interlaminar shear strength (ILSS) would give a good indication of any mechanical property changes in the samples. ILSS is also a critical parameter in composite structures. ILSS test bars were cut from the samples prepared as above, and machined to dimensions 16 x 5,5 x 3,5 mm. These were loaded as shown in figure 4 using a hydraulic Instron testing frame in a three-point bending configuration. The lload to failure was registered, from which the interlaminar shear failure limit can be calculated from

$$S = \frac{0{,}75 \cdot F}{b \cdot t}$$

where b is the test bar width (14 mm) and t the thickness (3,5 mm). Four measurements were made on each material.

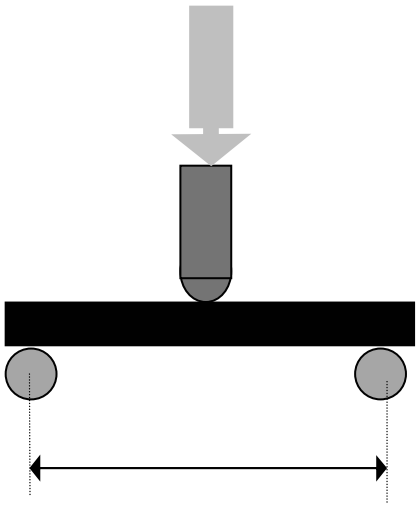


Figure 4. The three-point bend test for ILSS measurement

Microstructural characterisation

Pieces of the materials hardened under high pressure and under conventional conditions were prepared for microstructural characterisation. Of particular interest is any porosity, areas of poor impregnation, areas where the fibre tows are disturbed, etc.

Conventional sample preparation requires hot mounting in bakelite, but to avoid any changes in the sample caused by the high (approximately 150 °C) temperatures and pressures a cold resin: Epofix was used. After mounting in cylinders 25 mm diameter x 20 mm high the samples were successively ground on 180, 240, 320, and 1000 grade silicon carbide papers using water lubrication. The following polishing sequence was used:

1. 15 µm diamond paste on DP-PLAN cloth, 60-90 seconds at 250 rpm using blue lubricant and light pressure.
2. 6 µm diamond suspension on DP-DUR cloth, about 60 seconds at 250 rpm using blue lubricant and light pressure.
3. 3 µm diamond suspension on DP-DUR cloth, about 60 seconds at 250 rpm using blue lubricant and light pressure.
4. Final polish using 0,1 µm DP-S suspension on OP-NAP cloth at 125 rpm, 120 seconds and light pressure.

Following this procedure the samples were dried, examined, and photographed in an optical microscope.

Results and discussion

Two carbon fibre reinforced epoxy composite materials were produced under as close as possible to identical conditions with the exception that one was allowed to harden under high pressure (103 MPa) and the other (reference) under normal pressure (0,1 MPa). The hardening was performed at room temperature (ca 20 °C).

The figures below show the microstructure obtained by hardening under high pressure and the reference sample respectively.

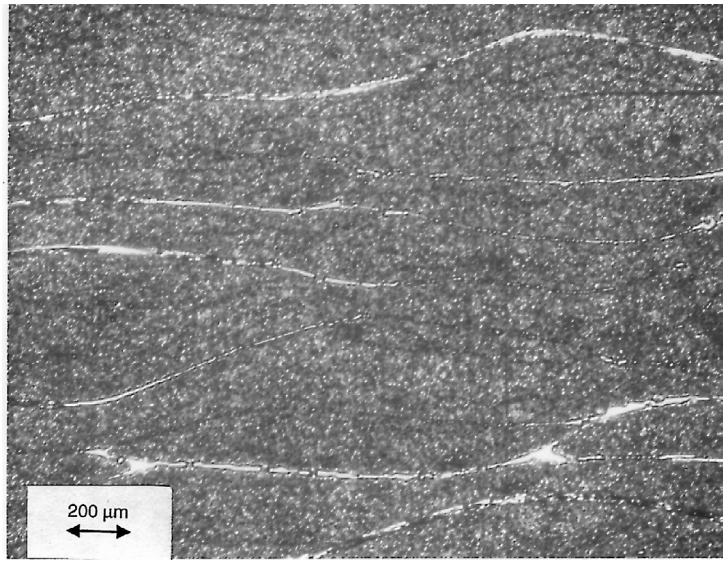


Figure 5. Microstructure from material hardened under high pressure

At this magnification the individual carbon fibres (size 3 µm dia) are not resolved. What can be seen is the outline of the fibre bundles (tows) and the (white) epoxy matrix between the tows In the reference material there is a greater amount of epoxy matrix visible, which in addition contains some residual porosity, indicated by the arrow.

Since the objective of this work is to reduce or eliminate porosity, it is important to quantify this parameter. Direct density measurement is made impossible by the difference in amount of epoxy, which would interfere with any density difference due to porosity. Density measurements have therefore not been made on the reference and high pressure hardened material. For meaningful measurements to be made the amount of epoxy in each sample needs to be measured. However, from the microstructures shown here it does appear that the level of porosity has been reduced significantly.

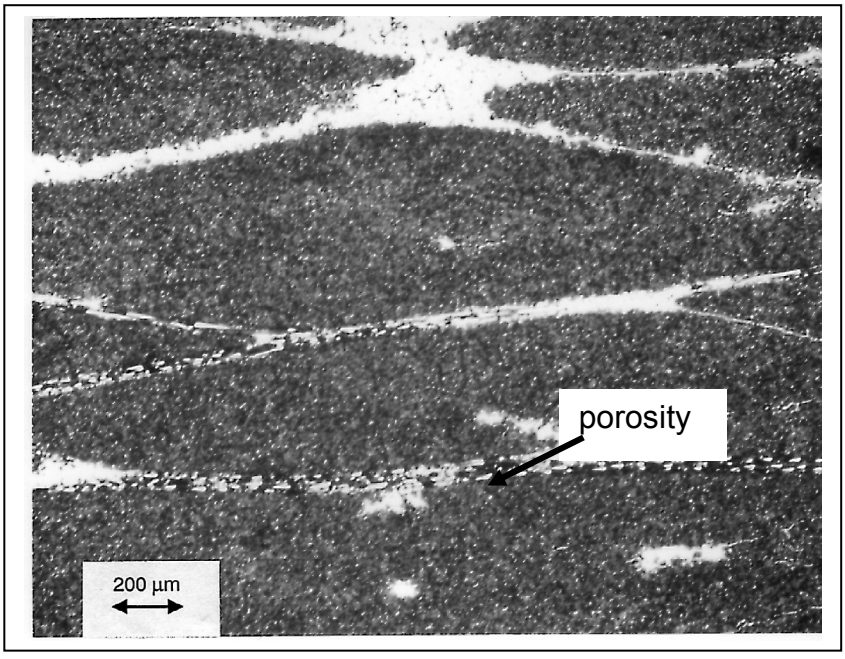


Figure 6. Microstructure from reference material hardened under normal pressure

Table 1 shows the results of interlaminar shear strength (ILSS) tests. This test was performed according to ASTM standard 2344, revision 1984[5]. For composite materials containing reinforcing fibres with Young's modulus greater than 100 GPa (which includes graphite fibres) the standard recommends a test bar length to thickness of at least 4. The test bars used were 3,5 mm x 5,5 mm x 14 mm (between the supports, see figure 4).

Table 1. The results of ILSS tests

Material	**Sample nr**	**S (MPa)**	**Average/ Median/ Spread**
Hardened under 103 MPa	1	56,9	56,8/ 57,2/ 3,8
	2	55,7	
	3	55,3	
	4	59,1	
Hardened under 0,1 MPa	1	51,4	56,0/ 55.3/ 7,7
	2	54,4	
	3	59,1	
	4	59,0	

From the table it is seen that the ILSS of both the "hardened under pressure" and the reference material are similar. The high pressure hardened material has a slightly higher average ILSS, but in view of the few measurements on only two materials this may well be within the experimental error. More interesting is the high median ILSS, and the lower scatter in the high pressure hardened material.

Summary and conclusions

A cold isostatic pressing method has been developed to harden a carbon-fibre epoxy composite under pressure much higher than conventional processing allows. Methods have been developed to impregnate the laminate, and encapsulate it before pressing. A procedure for preparing the materials for microstructural examination has been developed and tested.

A material produced by high pressure hardening has been examined and compared to an identical material produced by conventional processing at low pressure.

The microstructure of the high pressure hardened material is improved and shows a lower level of residual porosity and less interlaminar (un-reinforced) matrix. However, it has not been possible to quantify the porosity reduction due to the different epoxy contents.

The interlaminar shear strength of the high pressure hardened material is improved. The absolute strength is only slightly higher, but the median strength is improved by 4% and the scatter reduced by 50%. However, it should be noted that an insufficient number of different materials were tested.

The results obtained support the hypothesis that hardening under high pressure does lead to measurable improvements in strength of carbon-fibre composites.

Recommendations

These results should be confirmed by producing additional materials hardened at both high pressure and normal pressure. If the results are confirmed than the improvements in properties may be usable in some of the many military applicationsof carbon-fibre composites

References

1. *International conference on Hot Isostatic Pressing*. 1999: International Publishing House.
2. Iaconis, J.M. *Process variables evaluation of PEEK APC-2 thermoplastic matrix composite*. in *32 nd International SAMPE symposium*. 1987.
3. Campbell, F.C., A.R. Mallow, and C.E. Browning, *Porosity in carbon fibre composites: An overview of causes.* Journal of Advanced Materials, **26**(4) (1995) 18-33.
4. Månson, J.-A.E., in *Advanced Thermoplastic Composites: characterization and processing*, H.H. Kausch and R. Legras, Editors. 1993, Hanser: Munich. p. 297.
5. D-30.04, A.C., *Apparent interlaminar shear strength of parallel fibre composites by short-beam method*. 1984.