ADHESION BONDING TECHNIQUES FOR HIGHLY LOADED PARTS OF CONTINUOUS CARBON-FIBER REINFORCED POLYETHERETHERKETONE (CF-PEEK / APC 2)

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Abstract

In this paper it will be shown that the adhesion technology is applicable also to the bonding of continuous fibre reinforced thermoplastics. The conditions and influences under which an improvement of the bonding strength can be achieved will be pointed out.

Introduction

The Institute for Structures and Design, at the DLR in Stuttgart, has been investigating since 1983 the processing of a series of high-temperature resistant thermoplastics. Besides the optimisation of material performance during processing, forming and winding of continuous fibre reinforced thermoplastics, the investigation of suitable and cost saving joining techniques represents a further main activity at the institute.

The main point of this investigation has been the applicability of the adhesion technique to continuous fibre reinforced Polyetheretherketone, having in mind that PEEK is very resistant to chemicals and, therefore, a bad candidate for the method.

Joining of carbon fibre reinforced PEEK with adhesives

On the basis of preliminary tests with various adhesives the following two were selected for a more detailed investigation:

Adhesive Foil:	FM 300
Manufacturer:	Cyanamid
Adhesive Paste:	EA 929 Na
Manufacturer:	Hysol

Adhesive foils are easy to handle and therefore suitable for industrial use. Adhesive pastes enable the smoothing out of surface irregularities in the interface.

The advantages of the adhesion technique are, that a greater joint area can be chosen compared to that required for the welding of the parts and that the temperature influences during the hardening process are weaker than in the case of welding.

Disadvantages of the adhesion technique are the different chemical structures of adhesive and matrix, which is equivalent to introducing foreign material into the workpiece, as well as the different physical behaviour of the two materials on either side of the interface.

The bond strength can be greatly affected by the surface preparation. Other important factors influencing the strength are the test temperature and the ageing of the adhesive. Therefore, a number of bonded specimens has been tested, in order to investigate the dependence of the adhesion strength on the following conditions:

- different specimen preparations without surface activation
- surface activation and varying activation parameters
- activation and varying adhesive thickness
- activation and varying time interval between activation and bonding
- test temperature
- ageing conditions

The results of these investigations will show the effects of each one of the above factors on the bonding of CF/PEEK and will provide information about applying the adhesive. These results are, however, not to be taken as design data.

Selection of specimen geometry

Two different types of specimens were used for the investigations:

- notched lap-shear specimens corresponding approximately to the DIN 65 148 standard (fig. 1). The bonded specimen is notched, in the manner shown, with the notches going through the layer of adhesive. If a tensile load is applied

this will result in a shear stress in the bond interface between the notches. The fabrication of these specimens is complicated. It allows, however, a minimization of effects which are caused by specimen bending.

- 3-point bending specimens corresponding approximately to the DIN 29 971 standard (short bending, fig. 1). The fabrication of these specimens is very simple.

A comparison between the results obtained from the two specimen types shows, despite a considerable difference in the absolute values, a good qualitative agreement (fig.7).

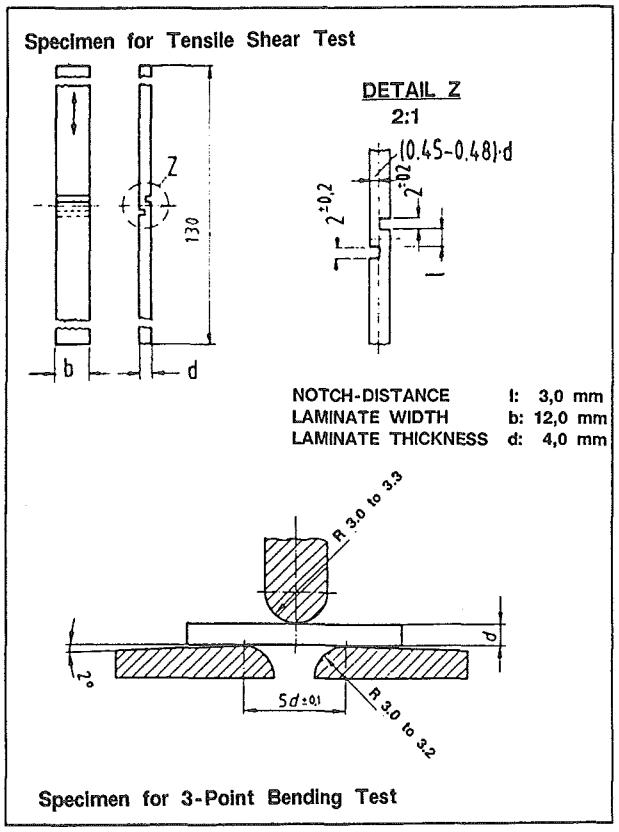

FIG. 1 Specimen geometry

Mechanical performance of the adhesives (without activation)

The specimens were prepared as follows:

- degreasing with a suitable solvent (see below)
- slight roughening of joint surface (400 abrasive paper)
- cleaning with a suitable medium (see below)
- applying adhesive

The adhesives were cured under low pressure, as recommended by the respective manufacturers.

adhesive	FM 300	EA 929 NA
curing temperature	170 °C	200 °C
curing time	30 minutes heating up at constant rate, additionally 60 minutes at curing temperature	30 minutes at curing temperature

TABLE 1 Curing parameters recommended by ahesive manufacturers

The curing cycles for both adhesive were reproduced in a thermal analysis equipment using the differential scanning calorimetry method (DSC). The hardening of the FM 300 adhesive begins already during heating up as clearly shown in fig. 2. The adhesive is fully hardened after 30 min at 170 C. The EA 929 NA adhesive is fully hardened already after 3 min. Even if one considers the time needed to heat a continuous fibre reinforced plate, up to the required temperature, that is, for a 2 mm thickness approx. 7 min., it can nevertheless be expected that after a heat-treatment duration of 90 and 30 min. respectively all bonded specimens are fully hardened.

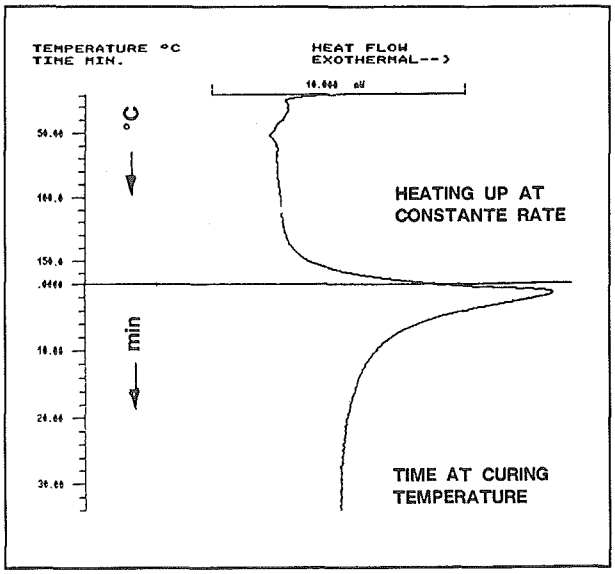

FIG. 2 DSC-Analysis chart showing curing cycle of FM 300

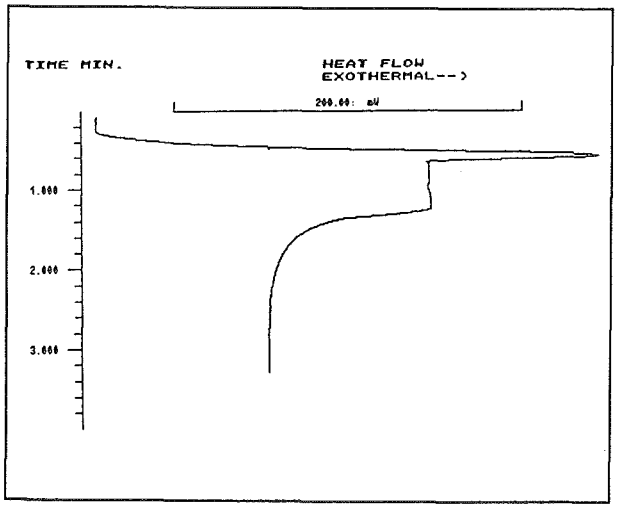

FIG. 3 DSC-Analysis chart showing curing cycle of EA 929 NA

Three solvents were investigated prior to the bonding experiments, in order to decide which one is the most suitable for the removel of dirt and release agent from the joint surface. The suitability of the solvents was tested by means of 3-point-bending specimens. The results are summarized in the following table.

without surface roughening:	shear strength MPa (3-point bending)	
	adhesive	
cleaning agent	FM 300	EA 929 NA
Acetone	14,45 ± 4,0	-----
Frigen	16,24 ± 7,8	-----
Ethylacetate	17,05 ± 3,6	-----
surface roughening:	shear strength MPa (3-point bending)	
	adhesive	
cleaning agent	FM 300	EA 929 NA
Acetone	26,99 ± 2,5	36,85 ± 8,2
Frigen	25,24 ± 4,6	48,57 ± 3,5
Ethylacetate	30,06 ± 5,4	46,46 ± 7,7

TABLE 2 Influence of cleaning agent

The best results were obtained with Ethylacetate, which has the additional advantage of not being harmful to the environment. This solvent was, therefore, used in all subsequent tests.

The next step was to determine what values of bond strength can be reached without an activated CF/PEEK specimen surface. Tests were performed with both adhesives in order to determine the mechanical constants of the bonded

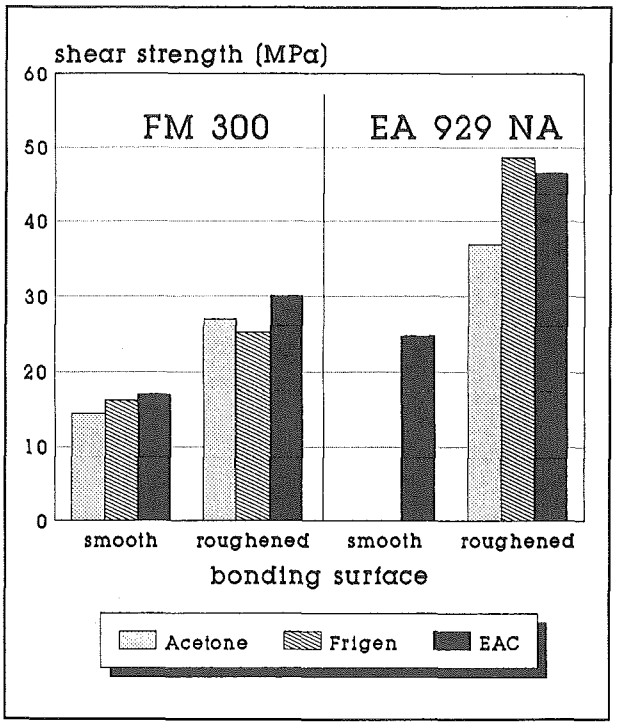

FIG. 4 Influence of solvent

specimens. Specimen preparation and results are summarized in table 3.

lap-shear:	shear strength MPa	
	adhesive	
primary treatment	FM 300	EA 929 NA
only cleaning	failed during handling	failed during handling
cleaning and roughening	50% failed during handling rest 11,0	failed during handling
cleaning, roughening parallel to loading direction	----	37,9 v 26,8%
cleaning, roughening transverse to loading direction	----	45,4 v 6,4%
roughening by detaching a peel-ply	----	failed during handling

TABLE 3 Evaluation of lap-shear tests. No activation

From the results can be clearly seen that in specimens which had not been surface treated prior to adhering. i.e. without surface rounghening, no bonding strength was recorded. This means that bonding was so poor that failure took place already during specimen handling (cutting and milling) as well as on clamping in the test equipment. Surface roughening has produced useful values, it represents, however, an additional work stage. Besides, it must be carried out in such a manner, that it results in a uniform roughness over the whole joint surface.

Another possibility of inducing surface roughness is by detaching a peel-ply, which has been previously pressed onto the surface of the laminate. The ply used in this test (7035, manufacturer: Flontex) led, however to unsatisfactory results.

In order to avoid the problems associated with interface damage caused during specimen preparation, e.g. failure due to mechanical loading during milling of the notches, additional tests were carried out with 3-point bending specimens. In this case no failure occured during the preparation. The results of the tests show the same trend as in the case of the lap-shear specimens (see table 4 and fig. 5).

A comparison of the results shown in tables 3 and 4 indicate that specimens with a bond strength of less than 20 MPa, measured in 3-point bending, are not suitable for lap-shear tests. They will most probably fail during preparation.

3-point bending: shear strength MPa		
primary treatment	adhesive	
	FM 300	EA 929 NA
cleaning	17,05 v 21,3%	24,70 v 26,0%
cleaning and roughening	30,06 v 17,0%	46,46 v 16,7%
cleaning, roughening parallel to loading direction	-----	43,50 v 8,3%
cleaning, roughening transverse to loading direction	-----	60,90 v 4,5%
roughening by detaching a peel-ply	-----	11,80 v 32,0%

TABLE 4 Evaluation of 3-point bending tests. No activation

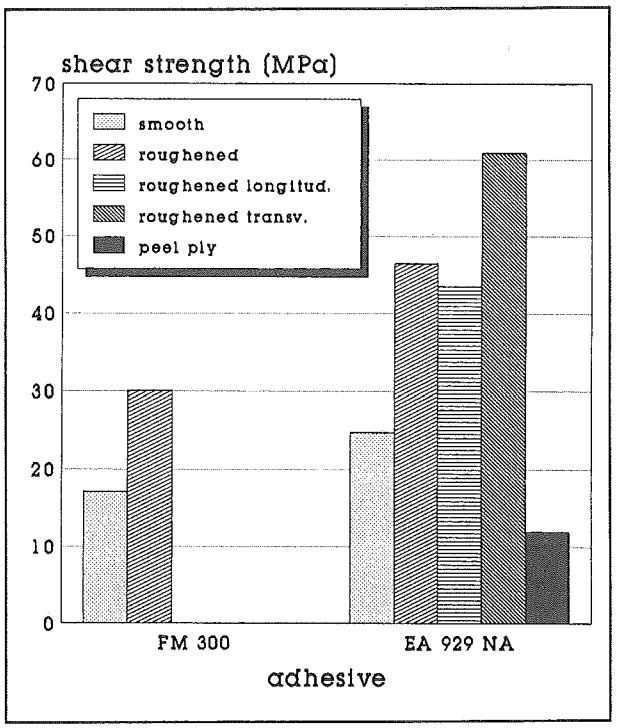

FIG. 5 Influence of surface roughness

Surface activation by means of a low pressure plasma (LPP)

In order to achieve optimal clean and activated joint surfaces, parts made by the DLR were, by courtesy of Plasma Elektronik GmbH, Filderstadt, subjected prior to bonding to a plasma treatment, which took place at the firm's premises. The parts were subsequently bonded and cut in order to produce lap-shear and 3-point bending specimens. No specimen failure occurred during the preparation. Furthermore, a considerable improvement in the bond strength was observed.

The plasma treatment involves a low pressure plasma gas (oxygen or argon), which is electrically conductive and consists of:
- positively charged carriers (positive ions)
- negatively charged carriers (free ions)
- electrically neutral molecules and
- photons

interacting constantly with each other /1/,/2/.

The plasma particles react not only with each other but also with the surfaces which are exposed to the gas, giving rise to the following effects:
- surface cleaning
- degradation of the polymer chains
- removal of material from the surface
- formation of radicals on the surface
- change of tacticity of the polymer chains

The combined effect of these processes results in an improvement of the adhesion properties of the surface.

A simple description of a plasma treatment reads as follows: The parts to be treated are placed in a plasma chamber, which is then closed and evacuated. When the pressure reaches its minimum value the working gas is let into the chamber, while the vacuum pump is continuously operating. The gas flow is regulated so that the desired working pressure is reached. Switching on the high frequency alternating electric field results in plasma formation due to ionization by impact. When the desired treatment time expires, the high frequency will be switched off, the plasma chamber ventilated, and the specimens can be removed. Fig. 6 shows a LPP equipment.

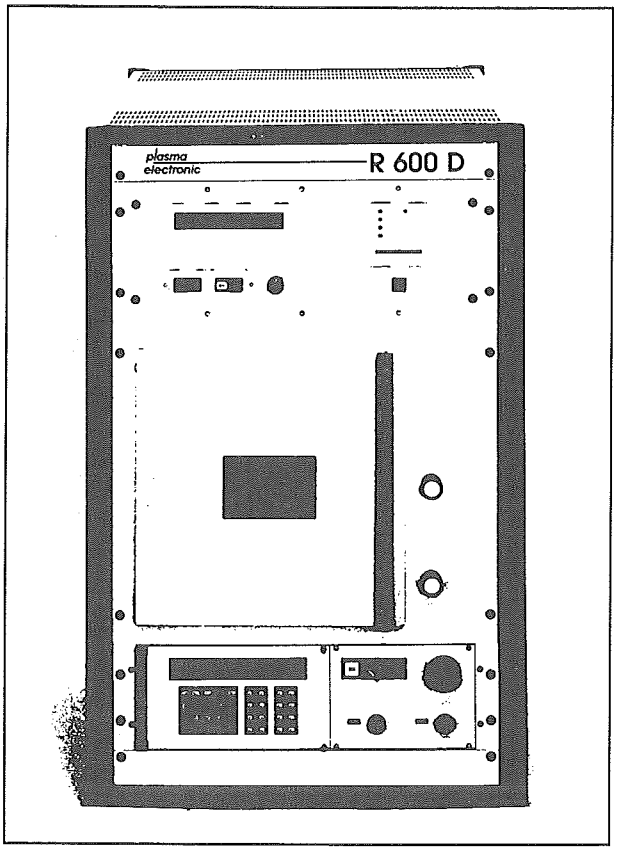

FIG. 6 Low pressure plasma equipment

Mechanical performance of the adhesives (applied on activated surfaces)

Parts were prepared for bonding, whereby the surfaces were cleaned and activated with a low pressure plasma (oxygen). After bonding and curing of the adhesive, lap-shear specimens were prepared and tested. The results show a considerable improvement of the bond strength (see table 5) compared to other preparation methods.

lap-shear:	shear strength MPa	
primary treadment	adhesive FM 300	EA 929 NA
cleaning	failed during handling	failed during handling
cleaning and roughening	50% 11,0 50% failed	failed during handling
cleaning, activation, quick bonding	33,4 v 22,4%	58,8 v 8,4%
roughening by detaching peel-ply	-----	failed during handling
roughening by detaching peel-ply, activation	-----	44,95 v 11,4%
reference sample welded in a mold	68,5	

TABLE 5 Comparison of different specimen preparation methods.

The tests revealed a number of factors, which influence the strength values:
- activation parameters
- time delay between activation and adhering
- thickness of adhesive layer

Dependence of the mechanical performance on the activation parameters

The change of the bond strength has been investigated with respect to the following activation parameters:
- plasma gas
- activation time
- electrical power of the equipment
- chamber pressure

No difference in the mechanical characteristics of the adhesives has been found between specimens activated in argon and the ones activated in oxygen. Therefore, all subsequent treatments were performed in oxygen.

In order to reduce the number of tests, power and pressure were set to 300 W and 1 mbar respectively and were kept constant thereafter.

These tests were performed only with the EA 929 NA adhesive. The results of the lap-shear and the 3-point bending tests indicate that the optimal activation duration lies between 3 and 5 minutes (Table 6, fig. 7).

activation time	shear strength MPa lap-shear test	3-point bending test
1 min	44,6 v 26,7%	61,2 v 12,1%
2 min	--	66,4 v 3,1%
3 min	58,8 v 8,4%	76,2 v 8,5%
5 min	58,6 v 14,5%	77,4 v 4,5%
6 min	56,9 v 22,0%	74,9 v 3,6%
7 min	49,7 v 6,1%	71,1 v 5,4%

TABLE 6 Influence of the activation duration, EA 929 NA

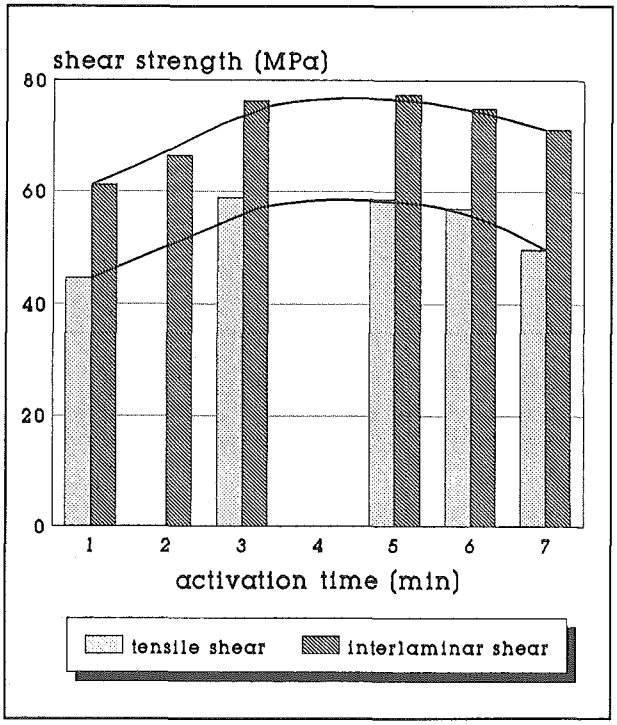

FIG. 7 Influence of the activation duration

Influence of the time interval between activation and bonding on the bond strength

The time dependence of the effectivity of activation with respect to the bond strength was investigated in more detail by means of specimens, which were bonded at 24 hour intervals following the activation treatment. The results are summarized in table 7 and fig. 8.

It is obvious that with increasing time between activation and bonding the strength decreases too. This applies to both adhesives, although they differ clearly in their mechanical behaviour. It can, therefore, be concluded that the time interval between activation and bonding should not exceed 2 hours.

lap-shear	shear strength MPa	
primary treatment	adhesive FM 300	EA 929 NA
cleaning, activation, immediate bonding	33,4 (= 100%) v 22,4%	58,8 (=100%) v 8,4%
cleaning, activation, bonding after 24h	24,9 (= 74,6%) v 9,0%	55,7 (= 94,7%) v 7,1%
cleaning, activation, bonding after 48h	24,0 (= 71,9%) v 40,4%	44,8 (= 76,2%) v 22,6%
cleaning, activation, bonding after 72h	21,0 (= 62,9%) v 21,6%	45,4 (= 77,2%) v 6,3%

TABLE 7 Influence of time interval between activation and bonding

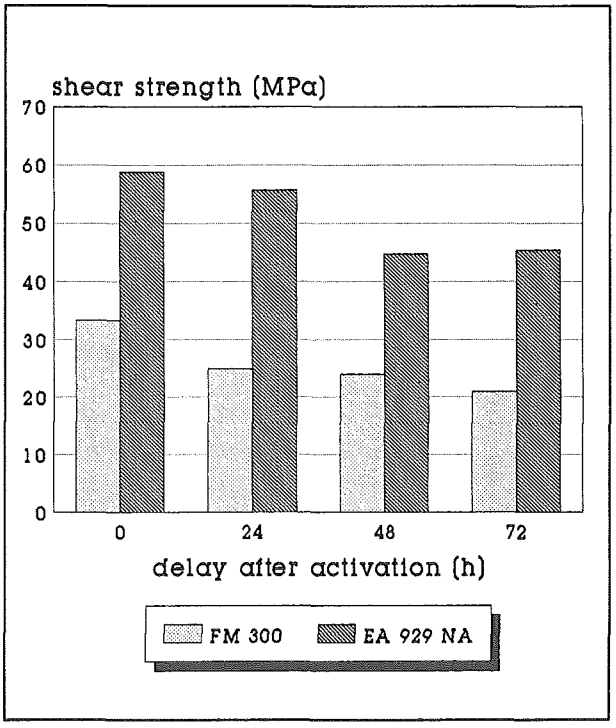

FIG. 8 Influence of time interval between activation and bonding

Dependence of the mechanical performance of the adhesives on the thickness of the adhesive layer

Differences in the dimensional tolerances of the parts and in the applied pressure during the curing process may cause fluctuations in the thickness of the adhesive layer. In order to investigate this influence in more datail, the thickness of the adhesive layer was varied in parts with activated surfaces. The thickness of an adhesive layer was normally about 0.2 mm. The influence of

the adhesive thickness was investigated in the range 0.1 to 0.6 mm by means of lap-shear and 3-point bending tests. Lap-shear specimens with an adhesive film of less than 0.2 mm failed during the preparation or on clamping onto the testing apparatus and could not, therefore, be tested. A comparison of the results shows similar behaviours for both types of tests. Below a film thickness of about 0.2 mm the bond strength decreases considerably, whereas between 0.2 and 0.6 mm the strength remains constant.

adhesive EA 929 NA: shear strength MPa		
thickness of the adhesive layer mm	lap-shear test	3-point bending test
0,09	failed during handling	49,0 single test
0,11	failed during handling	58,0 single test
0,15	failed during handling	65,5 single test
0,20	44,95 v 11,4%	66,4 v 3,1%
0,40	45,97 v 21,8%	65,6 v 9,0%
0,60	46,04 v 7,8%	66,0 v 7,0%

TABLE 8 Influence of the adhesive layer thickness

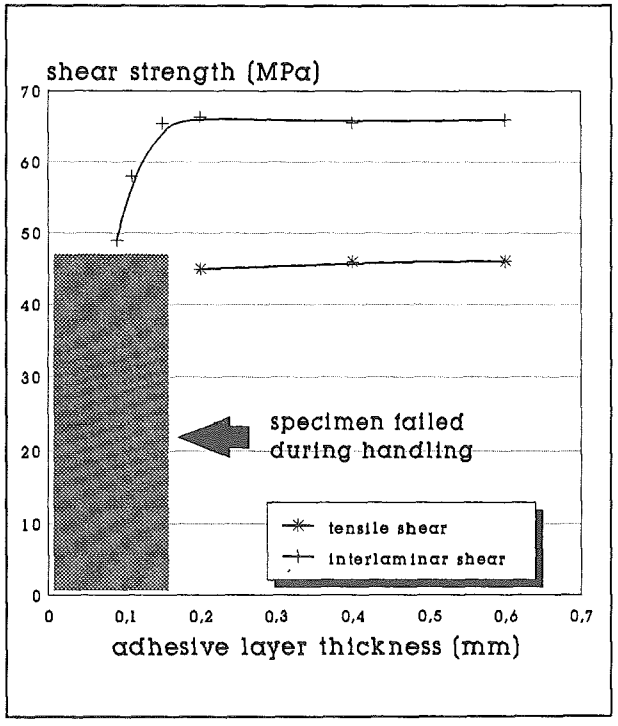

FIG 9 Influence of the adhesive layer thickness

Influence of the test temperature on the bond strength

All results until now (for activated and non activated surfaces) were obtained from tests performed at room temperature(23°C). In order to investigate the influence of temperature on the adhesive performance, 3-point bending tests were carried out in the temperature range -40°C to 140°C. The results are summarized in table 9.

A comparison of these results with the values obtained from earlier investigations on one-piece PEEK specimens /3/ show a similar behaviour at temperatures above 40°C, although the bonded specimens reach lower strengths. However, at decreasing temperature, below -40°C, no increase in the interlaminar strength of

adhesive EA 929 NA: shear strength MPa	
test temperature °C	3-point bending
40	66,81 v 8,28
23	69,00 v 12,0
40	69,30 v 2,31
80	61,42 v 7,8
120	49,15 v 9,3
140	45,45 v 1,4

TABLE 9 Influence of the test temperature

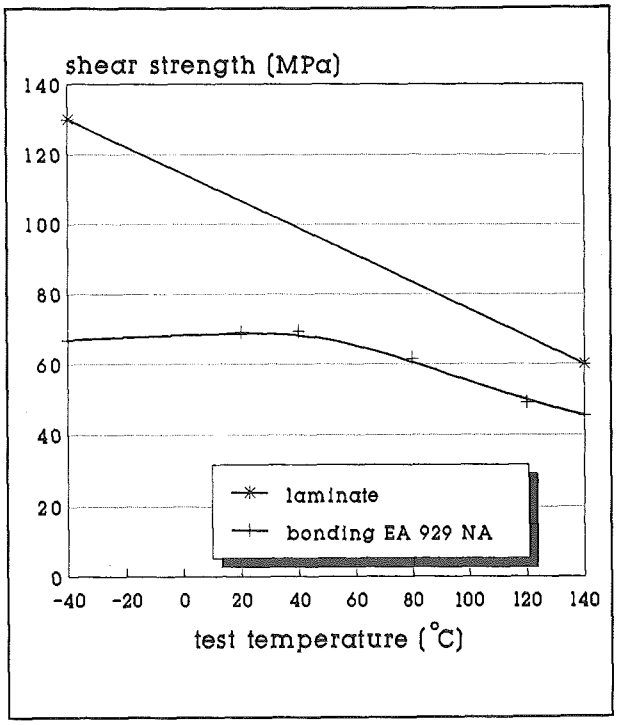

FIG. 10 Influence of the test temperature. Comparison between bonded specimens and laminates

bonded specimens was observed. This can be attributed to high residual stresses in the bond interface.

According to the manufacturer of the EA 929 NA adhesive, the material shows no loss of strength in the range -40°C to 200°C (Fig. 11). This could mean that the low bond strengths of the specimens in the range -40°C to +40°C are due to the residual stresses induced by the curing process. The curves of the failure stress are, for both bonded specimens and laminates, above 40°C (up to 140°C) approximately parallel, however, the bonded specimens reach lower absolute values.

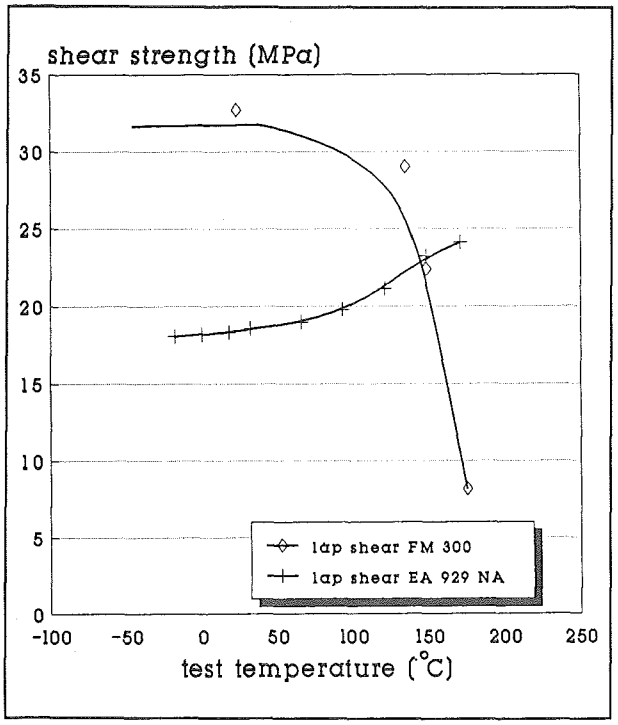

FIG. 11 Temperature dependence of strength for FM 300 and EA 929 NA, bonded with epoxy, according to the manufacturer.

Fig. 11 shows also the manufacturer's data for FM 300 and EA 929 NA. The values are obtained from single lap-shear tests on a fiber reinforced thermoset without surface activation. FM 300 show a decrease in the bond strength at much lower temperatures than in the case of EA 929 NA, although, at very low temperatures FM 300 possesses the highest strength.

Influence of ageing on the performance of the adhesion

The extent to which ageing can reduce the strength and, therfore restrict the applicability of the adhesion process, has been investigated on a limited number of specimens, thus allowing only a qualitative evaluation.

The influence of ageing has been investigated on specimens:
- aged at 70°C in water
- aged at 70°C in air with 85 % relative humidity and
- aged for 3 years in air with normal humidity (60 %) at room temperature

The results of the tests showed a decrease in strength of about 10 %, which is considered to be low. For a conclusive statement further investigations are required.

3-point bending:	shear strength %	
ageing	adhesive	
	FM 300	EA 929 NA
70°C, water (test temp. 80°C)	93	100
70°C, air (test temp. 23°C)	--	90
3 years stored (test temp. 23°C)	100	90

TABLE 10 Bond strength after ageing (not aged: 100%)

Comparison of the adhesion technique with other bonding methods

If one compares the performance of the adhesion method to results from welded specimens /4/,/5/, obtained in recent years at the institute (fig. 12), one sees that for the two adhesives, FM 300 and

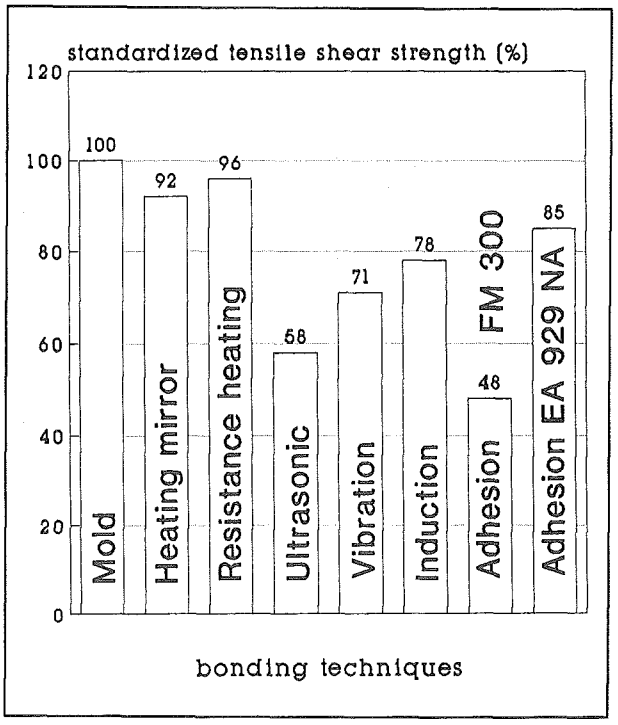

FIG. 12 Comparison of bonding techniques

EA 929 NA, the corresponding adhesion strength reaches 48% and 85% of the strength obtained in parts welded in the mould. This represents, in the case of FM 300, the worst result, however, considering the straightforwardness of the technique, it is an acceptable value. The strength reached with the EA 929 NA represents a good result, showing a better performance than in the case of those welding processes, which are based on the principle of friction. The possibility of working with larger joint areas makes the adhesion technique a process, which, in combination with surface activation and an adequate adhesive thickness, can yield results comparable to those of welding.

Summary

The bonding of CF/PEEK by adhesion, without prior activation of the joint surface, is problematical. The results obtained, provided that the specimens did not fail during preparation, were very poor. With specimen surfaces treated with a low pressure plasma gas it was shown that it is possible to achieve high strengths. However, more experience with the ageing behaviour of adhesives must be gained. Investigations with a number of new adhesives should also be undertaken. The main advantages of adhesion are the relatively simple handling, despite the need to activate the surfaces, and the bonding of larger areas of surface without causing damage to matrix or fibres.

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