PROCESSING AND MECHANICAL PROPERTIES
OF FIBER-REINFORCED POLYETHERETHERKETONE (PEEK)

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Abstract

Fiber reinforced Polyetheretherketone (PEEK) composite laminates were manufactured in house, and tested. Bending, impact, moisture absorption, flammability, smoke and toxicity, and formability tests were performed on specimens manufactured in a heated press. Results are presented comparing carbon fiber reinforced PEEK with several carbon fiber reinforced epoxies. Manufacturing problems are identified and discussed and a rolling mill is developed for processing and forming laminates.

I.   Introduction

In the past thermosetting plastics have been the primary resins for high performance composites. Thermoplastics were not used in primary structures because of their low temperature range.

Thermoplastics tend to creep which can result in shape change at high continuous loading. However, this provides the possibility of reducing internal stresses by plastic deformation.

FIGURE 1.   Rolling Mill

Further development of thermoplastics such as Polysulfone and Polyethersulfone raised their temperature range but still left problems with chemical resistance. Most recently, however, Polyetheretherketone (PEEK) has been introduced[1,2]. Having none of the problems mentioned above, PEEK promises to open many possibilities for the application of thermoplastics to high performance composites.

The most important manufacturing advantages are:
- repeatably formable
- formable with conventional metal techniques (heated presses and rollers)
- short forming time
- unlimited storage time
- storage at room temperature
- recycling is possible

Some of the problems are:
- difficult fiber impregnation of continuous fibers
- poorer thermal conductivity than metals requires longer heating and cooling times.

The aim of this work was to develop the methodology and the hardware for the manufacturing of continuous laminates and profiles of fiber reinforced PEEK. The welding of prepregs and the forming of laminates require heat and pressure. For this purpose, a heated rolling mill, Fig. 1, was designed and installed.

II.   Prepreg Production

In the early stages of our work, PEEK, produced by Imperial Chemical Industries, Incorporated (ICI), was available in granule or powder form only.

So we attempted to produce our own PEEK prepreg[2]. The first step was to verify the processing temperature of PEEK. This was done using a thermoanalysis-system Mettler TA 3ooo. The melting temperature of PEEK as well as the temperature at which the thermal decomposition begins, must be defined so that processing temperatures can be maintained within this range. To determine the melting temperature, the Differential Scanning Calorimetry (DSC) method was used: a test specimen is heated at constant rate of temperature increase. Heat flow from or to the specimen is recorded and plotted as a function of temperature. The beginning of thermal decomposition is identified using the Thermogravimetry (TG) method; the test specimen is heated with constant temperature increase, the weight of the specimen is measured continuously using a microscale and plotted as a function of time and temperature respectively. The beginning of thermal decomposition is easily noticeable in the weight/temperature diagram as the weight begins to decrease.
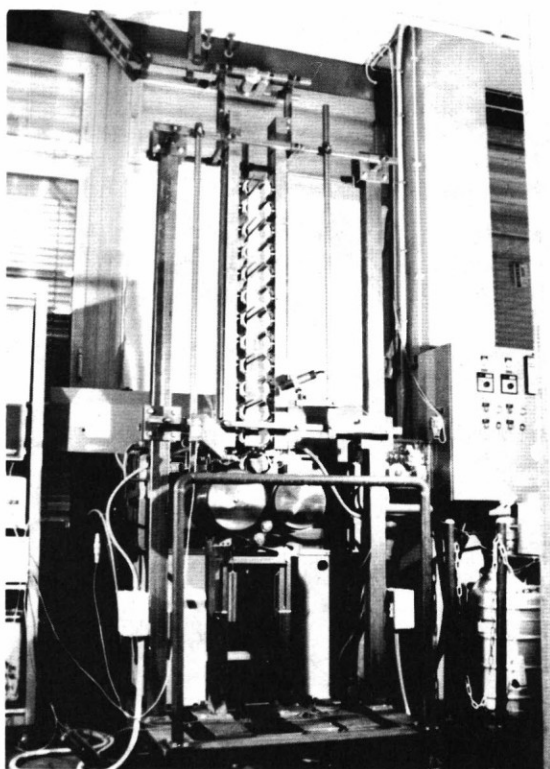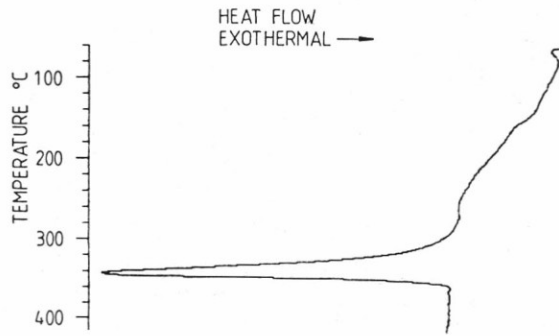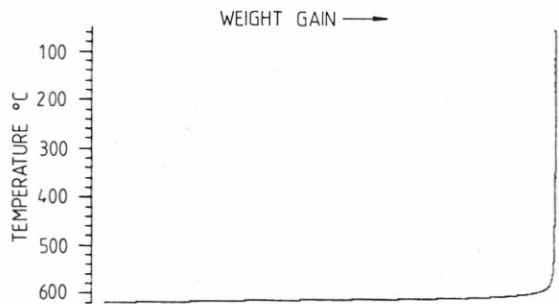
FIGURE 2. DSC-Diagram PEEK Unreinforced

FIGURE 3. TG-Diagram PEEK Unreinforced

The melting point temperature was 342°C, Fig.2, the melting process was completed at 360°C. Weight loss was not noticeable up to 400°C, Fig. 3. Therefore, the processing temperature must be between 360°C and 400°C. These results correspond to later ICI data.
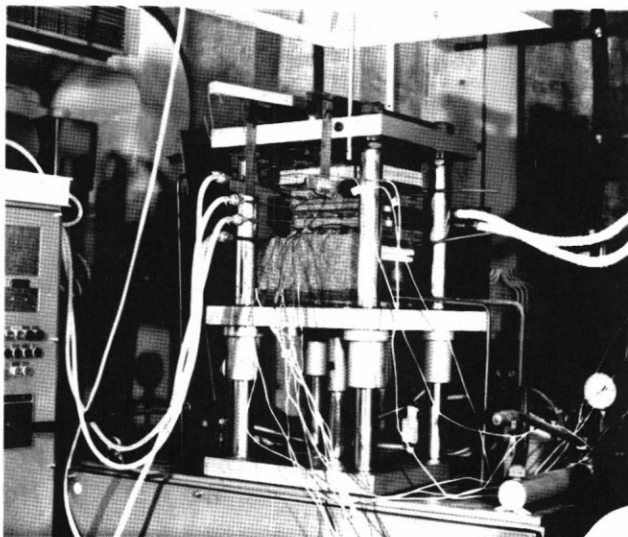

FIGURE 4. Heated Press

The first prepreg manufacturing approach was performed in the heated press, Fig. 4. After first calculating the amount required to produce a specific matrix content, the measured granules are even-

ly distributed on a heatable plate, and then covered with a fiber fabric and a second heatable plate. Both plates are heated up to the processing temperature of the PEEK and then slowly pressed together, forcing the PEEK into the fabric. To improve impregnation and to prevent voids, vacuum was applied.

To reduce production time, the mold shown in Fig. 5 was used. It was possible to produce 3 prepregs at the same time, sufficient to make a 1o layer laminate, 2,1 mm thick and 6o mm x 1oo mm large. Fiber content of 5o to 55% by weight was obtained.
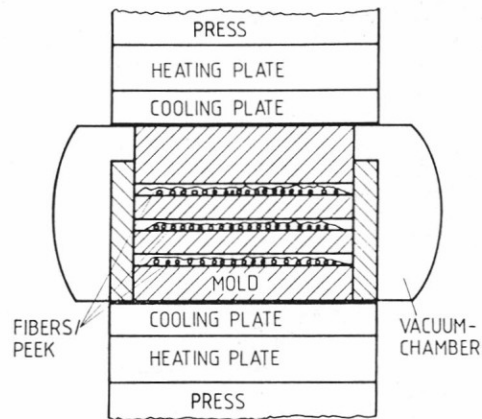

FIGURE 5. Method for Manufacturing of PEEK Prepreg in a Heated Press

The use of fabric (glass and also carbon) instead of unidirectional tapes prevented fiber floating during pressing. Both the glass and the carbon fabrics were delivered with a finish designed for epoxy resins. Because of the high processing temperature it was decided to remove this finish. This was accomplished by heat in a muffle furnace.

To produce a continuous PEEK prepreg, a rolling mill as shown in Fig. 6 was used.
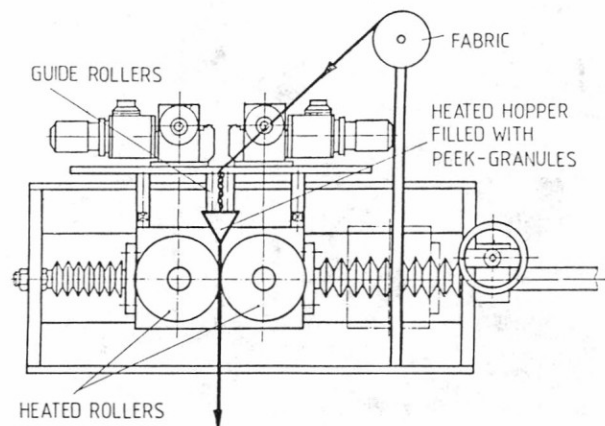

FIGURE 6. Rolling Mill for Manufacturing of PEEK Prepreg

The same equipment -without hopper- had been successfully used for the production of reinforced Polysulfone laminates up to 2,5 mm thickness. PEEK needs higher processing temperature, therefore a preheat area had to be installed. To manufacture laminates in the meantime, PEEK granules were melted and applied to the fabric as it passed through the hopper and then continued on between heated rollers to improve impregnation and produce a constant thickness. Hopper temperature was maintained at 360°C using electric cartridge heating. At higher feed rates the glass fabric used tended to fold and to contract transversely in the hopper because of the high viscositiy of PEEK, indicating the need to have guide vanes in the hopper to control the flow of the PEEK. These tests also showed the necessity to apply tension to the outcoming prepreg to prevent it from sticking to the rollers and to avoid waviness. Therefore, an extraction equipment was installed.

Further efforts to improve the process were not made as PEEK prepregs became commercially available by the end of 1983.

However, by these tests we gained valuable data to adapt our rolling mill to a standard test suited for PEEK processing.

III. Rolling Mill

The mill consists of three basic elements: the preheat area; the actual press rollers; and the extraction rollers, Fig. 7
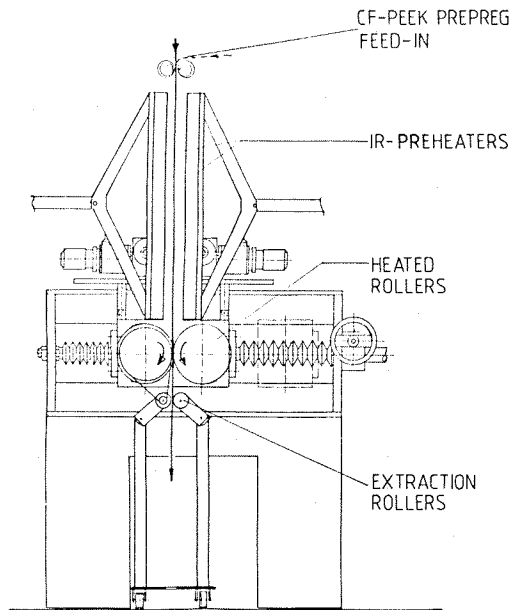

FIGURE 7. Rolling Mill

Preheat Area
It is not possible to heat PEEK up to the required 360°C - 400°C processing temperature only by use of heated rollers without destroying the thermoplastic material at the contact point because of the higher roller temperature required to transfer enough heat to the material. It is therefore necessary that the material is preheated to the required temperature. In this preheat area the prepreg is drawn between a series of 6 stages of infrared heaters. For the first 5 stages, temperature is maintained within a given range by on-off control of the infrared heaters. The last stage, directly before the rollers, is controlled by measuring the prepreg's surface temperature with a built-in pyrometer.

Press Rollers
The rollers have the following technical data:

width:	4oo mm
distance between rollers:	0 - 19o mm
max. pressure:	2oo N/(cm width)
heating element:	21,6 kW electric cartridge heater with 2-step controller
max. temperature:	37o$^\circ$C

Extraction Rollers
The extraction rollers are mechanically driven by a chain from a press roller. Roller sprockets were designed so that the extraction rollers have a feed rate 8,5% faster than the press rollers in order to keep the pressed material in tension. The extraction roller pressure is adjustable.

The extraction rollers are necessary to improve the material's surface quality and to increase the cooling rate.

IV. Manufacturing of Test Specimens

To obtain the most effective operation parameters for the rolling mill, laminates were fabricated in our press with varying contact time, pressure, and cooling rate. Starting points were a press time of 5 min, a pressure of 1o bar, and a cooling rate of >4o K/min. These values had been recommended by ICI for the ply number involved. During parameter variation, it was taken into account that rolling mills need shorter contact times and allow higher pressures.

The heated press is shown in Fig. 4. The technical data is:

press area (heated):		13o mm x 23o mm
pressure	:	0 - 5o bar
heating	:	electric cartridge heating, 6 stages-thyristor-control
max. temperature	:	7oo$^\circ$C
pressure control	:	hydraulic

Till Nov '83 we used our DFVLR prepreg containing carbon fabric (Interglas o2924), fiber weight content 5o-55% (Chapter II). From Nov '83 to May '84 we used ICI prepreg, type APC 1, (Aromatic Polymer Composite), reinforcement fiber Grafil XAS, fiber weight content 62%. This was followed by APC 2, reinforcement fiber Hercules XAS, fiber weight content 68%. The recommended press conditions for APC 2 were the same as for APC 1, but the cooling rate was 5 K/min.

V. Test Results

The following tests were considered to deliver the most interesting material properties: bending tests according to DIN standard 29971, in-house developed drop tests[3], Charpy tests, moisture absorption, flammability according to FAR 25-858, smoke density and toxicity[5,6].

Bending Tests at Room Temperature
The bending test results at room temperature are listed in Table 1.

The variation of press time (between 1 and 3o min) and pressure (between 5 and 2o bar) has no influence on strength and Young's modulus. There is only a small difference between APC 1 and APC 2 in spite of the different fiber content. The bending strength of reinforced PEEK corresponds to the bending strength of comparable reinforced thermosetting plastics, i.e. epoxies[7].

Transverse Bending Tests at Room Temperature
The transverse bending tests also show no strength decrease with shorter press time. The strengths of APC 1 and APC 2 is at the same level; the Young's modulus of APC 2 is higher due to the higher fiber content.

All strength values are significantly better than the transverse bending strength of reinforced thermosetting plastics[7] due to the good interface of carbon fiber/PEEK.

Short Beam Tests at Room Temperature
The short beam test results are similar to those of the other bending tests. There is no influence of the different press times and pressures on strength and no difference between APC 1 and APC 2.

The measured strength values are in the upper range of comparable reinforced thermosetting plastics[7].

Short Beam Tests, Variation of Test Temperature
The results are shown in Fig. 8. The lower band shows the results for the PEEK prepreg (fabric) manufactured in house, the upper band shows the test results for the unidirectional APC 1 including the curve for the unidirectional APC 2. There is no difference between APC 1 and APC 2. For comparison, the results for unidirectional T3oo/914 are plotted. As can be seen, between -2o° and 12o°C, the APC 1/APC 2 results are better.

In contrast to reinforced thermosetting resins with shear failure, reinforced PEEK exhibits the following failure modes:

specimens made of DFVLR-prepreg: tension/compression failure between -4o°C and 14o°C; only plastic deformation without visible damage at 16o°C;

Plate No.	Material	Number of Layers	Press Temperature °C	Pressure bar	Press Time min	Cooling Rate K/min	Bending σ_{f2} N/mm²	E kN/mm²	Transverse Bending σ_{f2} N/mm²	E kN/mm²	Short Beam τ_{f2} N/mm²
16	APC 1	14 UD	383	10	5	40	2 182,3	118,0	115,8	8,57	107,6
							1 684,1	106,4	133,8	8,80	99,2
							1 901,4	107,2	98,9	8,56	107,7
									87,3	8,43	
17	APC 1	14 UD	383	10	1	40	1 661,2	115,0	112,7	8,70	100,0
							1 772,4	112,1	123,9	8,74	102,6
							1 613,9	110,0	130,8	9,38	103,7
									114,3	8,4o	
18	APC 1	14 UD	383	10	30	40	1 787,0	110,7	138,0	8,93	102,8
							1 509,5	110,2	139,0	8,83	105,8
							1 847,3	110,1	112,9	8,80	107,0
									157,9	8,56	
									131,9	8,56	
19	APC 1	14 UD	383	5	5	40	1 865,7	118,5	115,6	9,12	104,9
							1 985,0	106,8	132,7	9,30	109,3
							1 858,3	99,8	145,8	9,55	110,5
									141,5	9,48	
20	APC 1	14 UD	383	5	5	40	1 841,5	120,5			112,7
							2 089,4	119,6			112,0
							1 925,9	109,9			111,3
21	APC 1	14 UD	383	5	5	40	2 048,2	133,8			112,0
							1 845,3	123,6			111,3
							1 602,1	115,6			110,8
22	APC 1	14 UD	383	20	5	40	2 133,4	118,5			109,8
							2 089,6	130,5			107,3
							2 156,1	112,9			105,4
29	APC 2	16 UD	383	5	5	5÷10	2 035,1	127,8	134,2	10,48	109,2
							1 998,8	131,3	126,0	10,35	110,1
							2 097,4	131,5	118,8	10,24	106,0
							1 749,1	127,4	124,8	9,96	
							1 655,4	131,2	113,3	10,25	
31	APC 2	16 UD	383	5	5	5÷10	2 052,6	131,6	131,0	10,36	110,8
							1 973,3	125,8	120,1	10,25	106,7
							1 763,3	126,5	120,0	10,24	105,0
							1 822,9	129,6	120,5	10,72	
							2 075,4	128,9	116,3	10,51	

TABLE 1. Manufacturing Conditions of CF-PEEK Laminates and Results of Bending Tests at Room Temperature

specimens made of APC 1:
shear/tension failure at -4o°C, plastic deformati-
on with cracks at the central load introduction
line due to high deformation between room tempera-
ture and 160°C.

specimens made of APC 2:
plastic deformation with cracks at the central load
introduction line due to high deformation between
-4o°C and 14o°C, plastic deformation without visi-
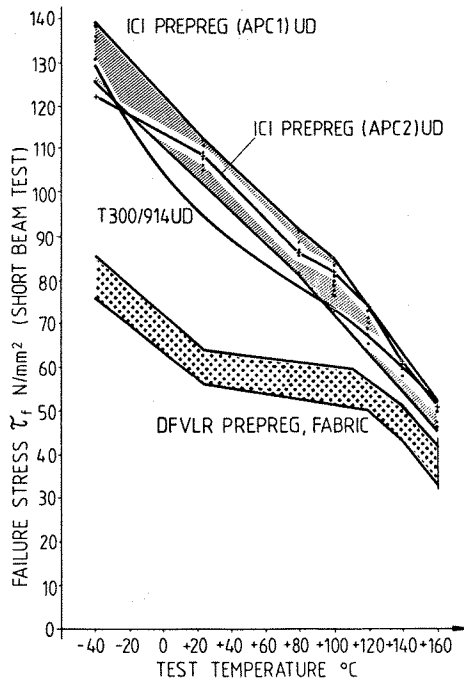ble damage at 160°C.

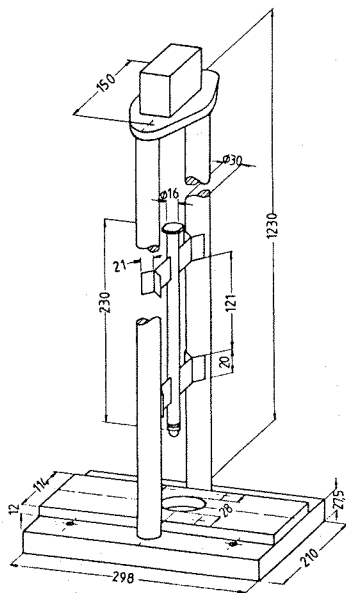FIGURE 8.   Short Beam Tests,
            Variation of Test Temperature

FIGURE 9.   Test Equipment
            for Repeated Drop-Weight Tests
            with Increasing Energy[3]

Drop Tests

Drop weight impact tests were conducted to de-
termine the difference in energy absorption charac-
teristics between thermosetting resins and thermo-
plastics. In this test a weight is dropped repeated-
ly onto the same spot of a clamped specimen, each
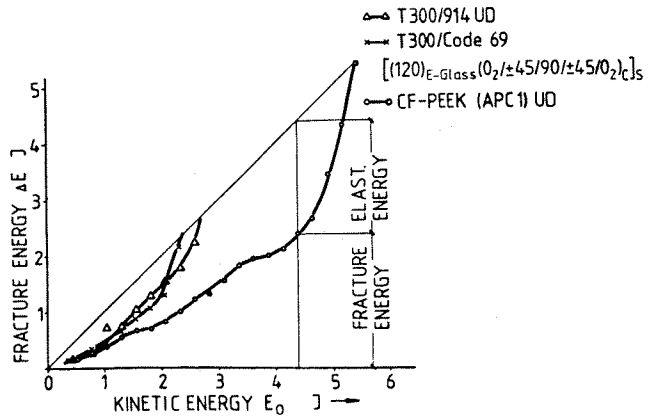time with increasing energy. The test equipment is
shown in Fig. 9.

FIGURE 1o. Repeated Drop-Weight Tests
            with Increasing Energy,
            Energy Balance[4]

The results with specimens sized 13o mm x 13o mm
and 2,o mm thick, Fig. 1o, point out that APC 1 is
markedly better than the thermosetting plastics.
Energy dissipated by fracture - as compared to
elastic rebound - is plotted vs. the total kinetic
energy at impact. APC 1 can absorb more energy -
both elastic and irreversible - as the comparable
carbon epoxies. This is also evident from Fig. 11,
where APC 1 requires more than twice the kinetic
energy to produce the same bending deformation as
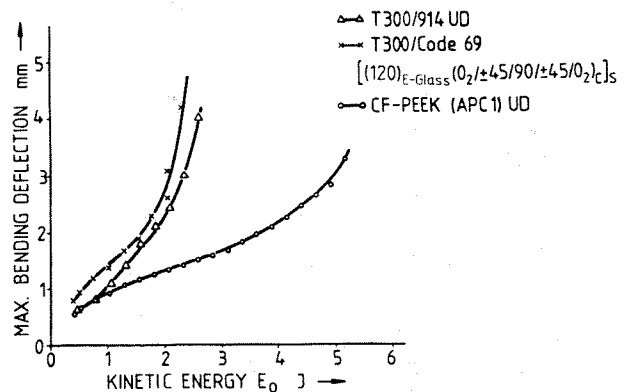comparable thermosetting plastics.

FIGURE 11. Repeated Drop-Weight Tests
            with Increasing Energy,
            Max. Bending Deflection[4]

The drop tests were continued with smaller specimens, 75 mm x 65 mm, 2,1 mm thick. The results in Figs. 12 and 13 show the influence of the manufacturing process on the impact behaviour of PEEK laminates. Specimens A, B, C, and D were produced from APC 1 and specimen E from APC 2. Specimen D, fabricated by ICI, and specimen E absorbed more impact energy than other specimens.
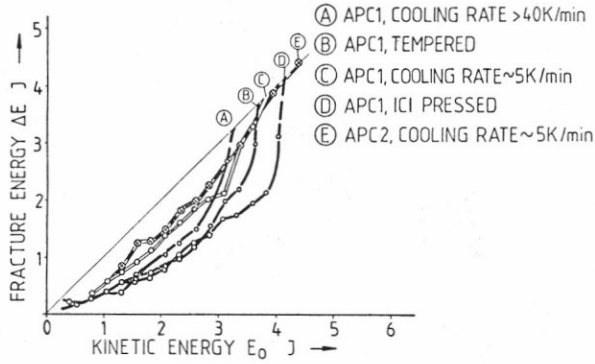

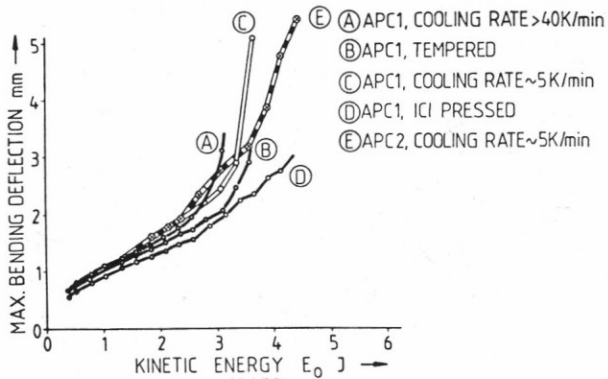FIGURE 12. Repeated Drop-Weight Tests with Increasing Energy, Energy Balance(4)

FIGURE 13. Repeated Drop-Weight Tests with Increasing Energy, Max. Bending Deflection(4)

Specimen A with the lowest impact energy absorption was cooled down from pressing temperature with the fast cooling rate>4o K/min, as specified by ICI. Specimen B, tempered at 3oo°C after rapid cooling, as well as specimen C, slowly cooled with 5 K/min, show a better impact behavior . However, none of these specimens absorbed as much impact energy as the ICI-fabricated specimen D. To find the reason for this difference, DSC measurements with laminates manufactured under identical conditions were done, Fig. 14. In contrast to laminate 1, manufactured by ICI, laminate 2 has a clear glass transition point. Laminate 1 shows an inflection point at the beginning of the melting process, not visible with laminate 2. Generally, APC 1 laminates cooled with a high cooling rate without tempering showed a pronounced glass transition temperature at 14o°C and a crystallization peak at
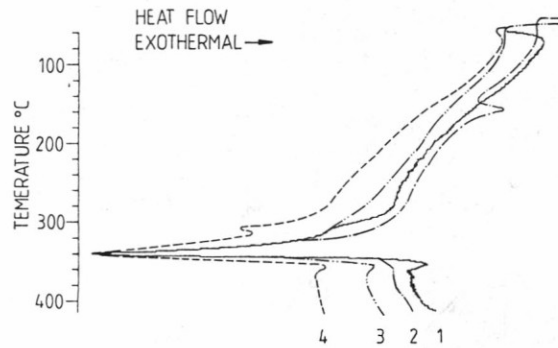

FIGURE 14. DSC-Diagrams/APC 1
    1: ICI-pressed
    2: Cooling rate>1oo K/min
    3: Tempered at 3oo°C
    4: Cooling rate 5 K/min

17o°C. If rapidly cooled APC 1, laminate 3, is tempered, the cristallization peak temperature is higher than the temper temperature. Slowly cooled (5 K/min) APC 1 laminates 4 show comparable DSC curves to the laminate manufactured by ICI 1, i.e. neither visible glass transition points nor cristallization peaks.

Although the DSC curves of laminates 1, 3 and 4 are similar, their impact behavior, as mentioned before, is different.

Micrographs show that the ICI-manufactured APC 1 laminates, Fig. 15, have a more regular matrix distribution respectively fiber distribution than the laminates manufactured in house, Fig. 16. This difference can be attributed mainly to the irregular distribution of matrix material in the APC 1 prepregs as delivered by ICI. APC 2 prepreg material manufactured by ICI with new equipment presented a regular matrix distribution just as the in house pressed APC 2 laminates, Fig. 17.

The uniformity of the matrix distribution in the delivered prepreg and the fiber content of the resulting laminates seem to influence primarily the impact energy absorption behavior.
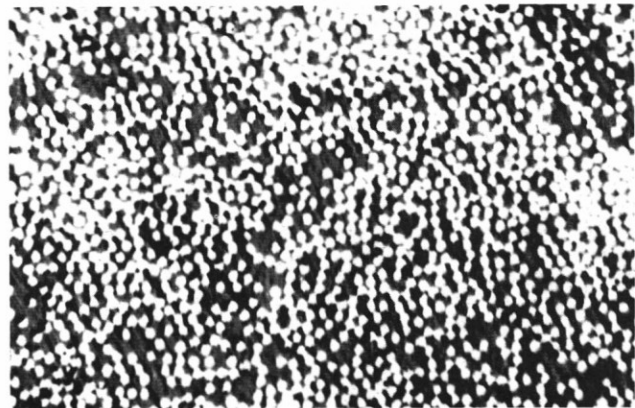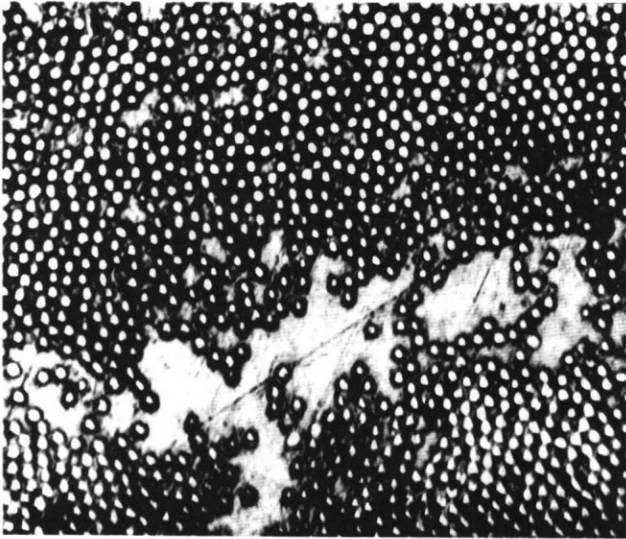

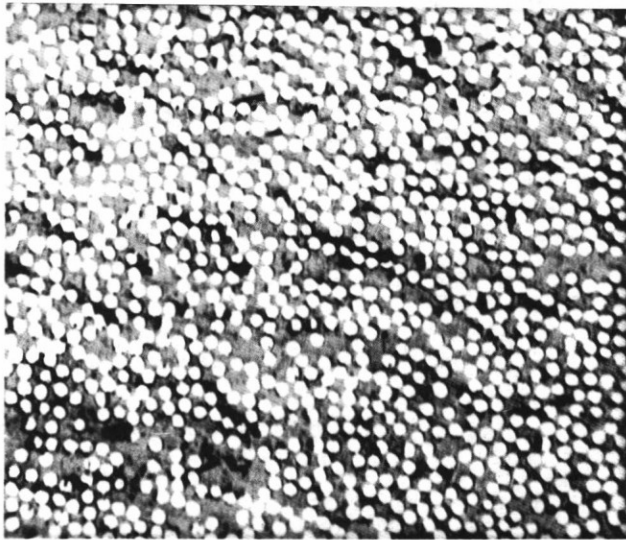FIGURE 15. Micrograph APC 1, ICI-Pressed

FIGURE 16. Micrograph APC 1
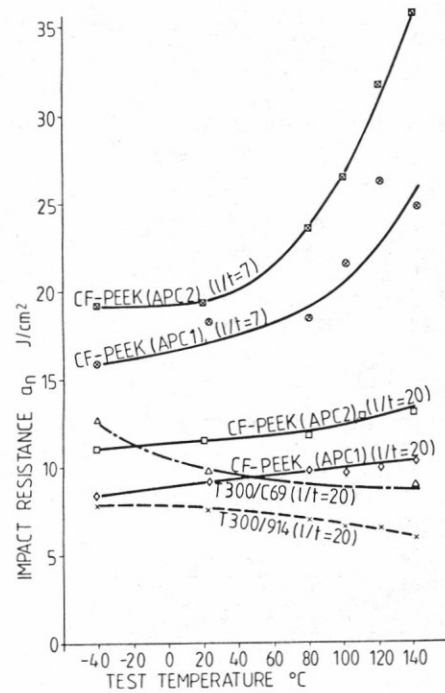

FIGURE 17. Micrograph APC 2

FIGURE 18. Impact Resistance (Charpy Test) as a Function of Test Temperature and Length to Thickness Ratio
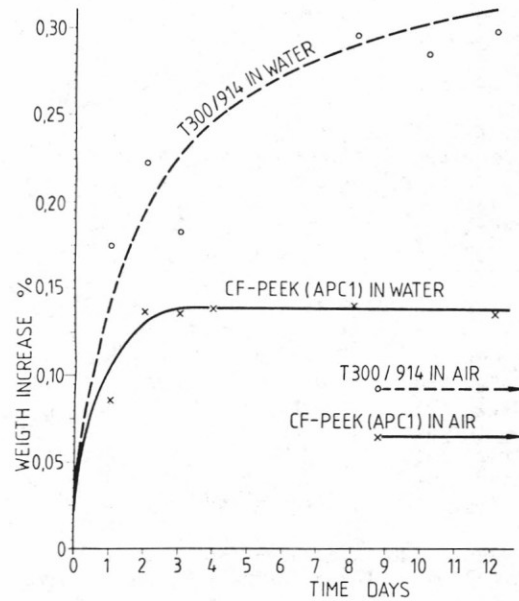
FIGURE 19. Moisture Absorption, Specimens in Water at Room Temperature

Charpy Tests

The Charpy tests were performed on a pendulum impact test machine. The results of these tests, Fig. 14, show that the impact resistance of APC 1 is better than that of T 3oo/914 and T3oo/C 69 and improves with increasing test temperature. If the length/thickness ratio is reduced from $l/t = 2o$ to $l/t = 7$, this difference becomes even clearer. The impact resistance of APC 2 is significantly better than that of APC 1.

Moisture Absorption

Short beam specimens were dried at $12o^oC$ for 2 hours and then placed in water at room temperature. After the second day APC 1 showed no further weight increase, Fig. 19. The T3oo/914 specimens on the other hand still had a slight weight increase after 12 days. At ambient room conditions APC 1 also absorbed less moisture than T3oo/914.

Flammability Testing

Fiber reinforced plastics used inside the pressurized part of aircraft fuselages must fulfill specifications concerning flammability, smoke density and toxicity of smoke gases.

The flammability testing was made according to specification FAR 25-853, Appendix F.

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The test results show[8]:
at 2,5 W/cm^2: no burning (required specification)
at 2,8 W/cm^2: burning only under flame
at 5,o W/cm^2: self-burning

The flammability testing of CF-PEEK rendered excellent results; for comparison: CF-epoxy burns at 2,5 W/cm^2.

Smoke Density and Toxicity Testing of Smoke Gases
These tests were made according to the specification ATS looo.ool[6]. At 2,5 W/cm^2, no measurable smoke and toxicity values were obtained[8]. The CF-PEEK is comparable to CF-phenolics.

VI. Formability

First steps concerning formability were done in a V-shaped mold, Fig. 2o, into which the UD test specimens (75 mm long, 25 mm wide, 2,o mm thick) were placed lengthwise and formed at 45° and 9o° angles.
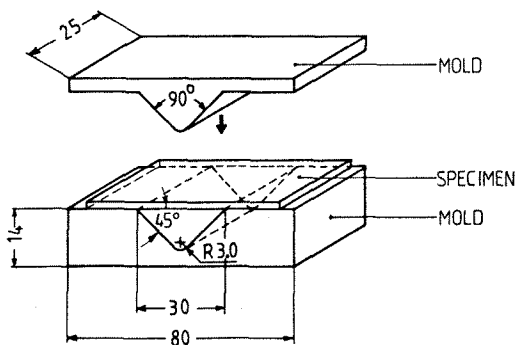

FIGURE 2o. Mold for Formability Tests

The initial results are:
- the required heating time of 14 minutes (1 minute per layer) for unpreheated test specimens is relatively long.

- good formability occurs at 34o°C. However, the specimen must be cooled to 26o°C before it can be removed, otherwise the shape stability during removal is not assured.

- the required forming time is relatively long. After 15 sec forming time, matrix cracking on the outer side and fiber misalignment on the inner side of the 9o° bend occured. After 18o sec forming time, there was still fiber misalignment, but matrix cracks disappeared.

The requirements deduced from these experiments can be easily realized in the rolling mill (see Chapter III) to form profiles in a continuous process:

the laminates are heated in the preheat area to a temperature of 34o°C. The press rollers are kept at a temperature below 26o°C, firstly, to realize a fast cooling rate between 34o°C and 26o°C, secondly, to guarantee formability, and thirdly, to avoid problems with release agents. After completion of the rolling mill the next work to be done is to realize in a continuous process the good results gained with specimens manufactured in a heated press. The influence of the cooling rate on the properties of PEEK will be investigated in depth.

VII. Conclusions

Processing and mechanical properties of fiber reinforced Polyetheretherketone were investigated during the last two years. In house manufactured prepregs and ICI delivered APC 1 and APC 2 prepregs were used for the fabrication of test specimens. The following test results were obtained.

Compared to carbon fiber reinforced thermosetting resins (epoxies), carbon fiber reinforced PEEK exhibits:

- equivalent strength and Young's-modulus, obtained from 3-point bending tests.
- better strength in transverse bending tests
- similar strength, but deformation instead of shear failure in short beam tests
- superior energy absorption in impact tests
- lower moisture absorption

APC 2 in comparison to APC 1 has lower deviation in test results and better energy absorption in impact-tests. This can be attributed to the better prepregs quality.

Concerning smoke and toxicity behavior , reinforced PEEK is comparable to reinforced phenolic resins.

The processing of endless laminates and profiles from fiber reinforced PEEK-prepregs is possible in a rolling mill by applying a preheat area and an extraction equipment.

VIII. References

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