CARBON-CARBON COMPOSITE WITH COAL TAR PITCH BASED MATRIX AND SIMPLIFIED MANUFACTURING METHOD

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A novel method of carbon-carbon composite manufacture was designed and the possibility of its realization was proved. It is based on the continuous heat treatment at 450 - 500 °C of coal tar pitch which is soaked into carbon fibre bundle and on the subsequent hot press moulding at 400 - 600 °C. It can bring a significant shortening of the manufacturing cycle and cost reductions can thus be expected. The unidirectional composites prepared by this method reveal properties comparable to those manufactured by other routes utilizing the pitch-based matrix. They reach flexural strength up to 350 MPa (or up to 400 MPa when using filtered pitch), Young's modulus 130 - 150 GPa and density up to 1,75 g cm^{-3}. Furthermore, the described method promises an easy realization at the industrial level and advantageous incorporating into the carbon fibre production process.

INTRODUCTION

Carbon fibre reinforced carbon composites (CFRC) are - due to their outstanding properties namely in the high temperature region - doubtless the material of future. It is *e.g.* the only serious candidate for plasma limiters in nuclear fusion devices and for inert gas ducting and heat exchanges in gas-cooled fission reactors [1].

Unfortunately, to obtain dense CFRC materials with good mechanical properties, many impregnation-recarbonisation cycles are required in the conventional production. It is caused by a low carbon yield of the utilized matrix precursors - most commonly phenolic resins (the first step - formation of a porous rigid body) and coal tar pitch (next steps - impregnation of the mentioned porous body). These time- and energy-wasting procedures make CFRCs extremely expensive so that their use is very limited. To make CFRCs more competitive, changes in technology are necessary.

New methods enabling to avoid standard multiple impregnation-recarbonisation steps during manufacture of CFRC have begun to appear during last years [2-6]. Their common feature is *the enhanced carbon yield of the matrix precursor* which can be achieved by e.g. non-specified "self-sintering" carbon [2] or by blending of coal tar pitch with finely powdered pitch-coke [3], special oligomers [4] or thermally treated "mesophase" pitch [5] etc. To form the composite successfully, all types of matrix precursor mentioned require hot moulding to compensate for the high viscosity as only their slight softening occurs which is achieved solely within the temperature range of about 440 - 500 °C (in dependence on the heating rate). The coating of the carbon fibre bundle or the carbon fabric with such a precursor is not simple and it requires a very finely powdered consistency of the matrix precursor. The coating can be carried out through either electrophoresis [2] , dry electrostatic method or in the fluidised bed [5].

The starting point of our attempt to improve the process is the idea of performing all *the procedures of the thermal pre-treatment of pitch directly and continuously on the moving carbon fibre tow* (the procedure can be incorporated advantageously into the carbon fibre production process). Impregnation of the bundle by pitch is simple, because its viscosity is low (at the temperature of 200 °C). Thus the problems of costly powdering and coating technologies are avoided.

EXPERIMENTAL PART

Two sorts of coal tar pitch were employed in our experiments. The first one was used in the raw state. The second sort was filtered at 200 °C. Properties of both raw pitches and of filtered one are reported in the table 1.

Table 1. Properties of utilised coal tar pitchs.

parameter	sort 1	sort 2	sort 2 filtered
softening point (Mettler) (°C)	104.1	100.1	105.6
alcan coke yield (%)	56.4	55.0	58.3
ash (%)	0.19	0.21	0.08
viscosity (Pa s)	0.819	-	-
sulphur content (%)	0.46	0.46	0.31
TI (%)	31.6	25.3	-
QI (%)	11.95	7.2	1.2

The amount of pitch soaked into a Torayca T800H bundle of 6 000 filaments at 200 °C was controlled so as to reach the required matrix content in the final composite. Under conditions of a simple laboratory equipment the control was not fully satisfactory and so the fiber volume fraction did not exceed 50 % while recommended values are about 60 %. The heat treatment of the pitch-impregnated carbon bundle was achieved by pulling it through a tube furnace heated to a required temperature (450 - 500 °C) in a stream of nitrogen. This temperature (named heat treatment temperature - *HTT* - in the present paper) is a key parameter of the process and its optimum band is narrow. The velocity of pulling was 1 m min^{-1} and the length of the furnace was 2 m.

The heat treated bundle (tow-preg) is a not very stiff rod and it is possible to make it flexible through "breaking" it by passing over the pulley with a diameter of less than about 20 mm without significant matrix precursor loss, hence a plain weave fabric can be manufactured. Nevertheless, the present stage focuses on the unidirectional composite.

The tow-preg was wound on a drum of diameter of 300 mm. Then it was cut to 500 mm pieces whose linear density was checked by weighing. After further cutting to 68 mm rods their required number was stacked into a steel mould of the cross-section of 36 × 72 mm (2 mm gaps were left at each end of the longer dimension of the mould). This set-up enabled one directly to determine a weight loss of the matrix precursor during the hot moulding and the subsequent secondary carbonisation operations. The mould was then heated at a rate of 2.5 °C min^{-1} and the pressure of 100 MPa was applied from 400 °C onward. It was proved in the preliminary experiments that a lower pressure is not sufficient to form a dense "green" composite while a higher one could not be reached without problems. After reaching 600 °C the temperature was kept constant for 30 min. The pressure was released after cooling the mould down to 500 °C. Some additional experiments with variation of heating rate during hot moulding were carried out for tow-pregs of HTT 470 °C. The secondary carbonisation of the "green" composite was carried out to 1000 °C at a heating rate of 5 °C min^{-1} in nitrogen environment at an atmospheric pressure.

1.3 - 1.8 mm thick CFRC plates were manufactured under various heat treatment conditions using non-filtered Sort1 pitch (specimens A) and filtered Sort2 pitch (specimens B). Four 60 × 6 - 8 mm specimens were cut from each plate. The specimens were subjected to evaluation of density and of flexural properties. The density was calculated from weights and dimensions of specimens. A testing apparatus MINIMAT (Polymer Laboratories Ltd.) was used for the flexural strength test in a centre-loading three-point arrangement (support span 35 mm, cross-head velocity 0.5 mm min^{-1}, load cell 1000 N). The static Young's modulus was determined from the linear part of the load vs. displacement curve.

RESULTS

The total weight loss of the matrix precursor achieved during the hot moulding and secondary carbonisation steps is very low and decreases from 4.2 % for *HTT* = 450 °C to 2.7 % for *HTT* = 500 °C as shown in figure 1. (Note: this total weight loss is not equal to the "volatile matter content" used in fuel analysis. The latter value is higher because of the significantly higher heating rate of the assay).

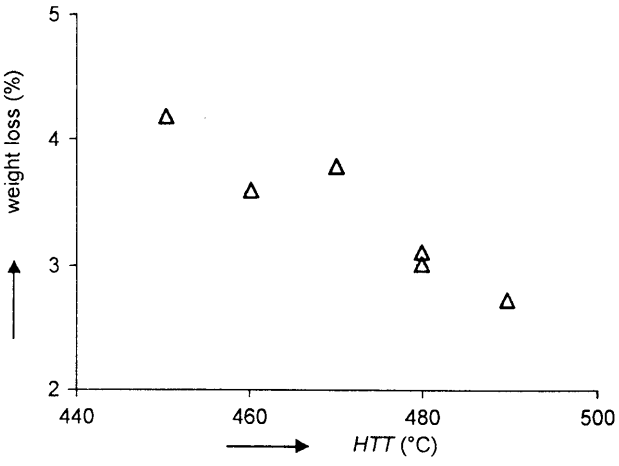

Figure 1. Weight loss during the hot moulding and secondary carbonisation steps vs. heat treatment temperature of tow-preg.

The plot of the dependence of flexural strength *vs.* HTT of the A type specimens (figure 2*a*) reaches maximum values 270 - 350 MPa at 470 - 480 °C but the data for individual specimens are considerably scattered. The latter is true also for the B type specimens but their flexural strength values reach up to 400 MPa (figure 2*b*). The modulus values range from 30 to 130 GPa and from 35 to 150 GPa for the A and B type specimens, respecti-

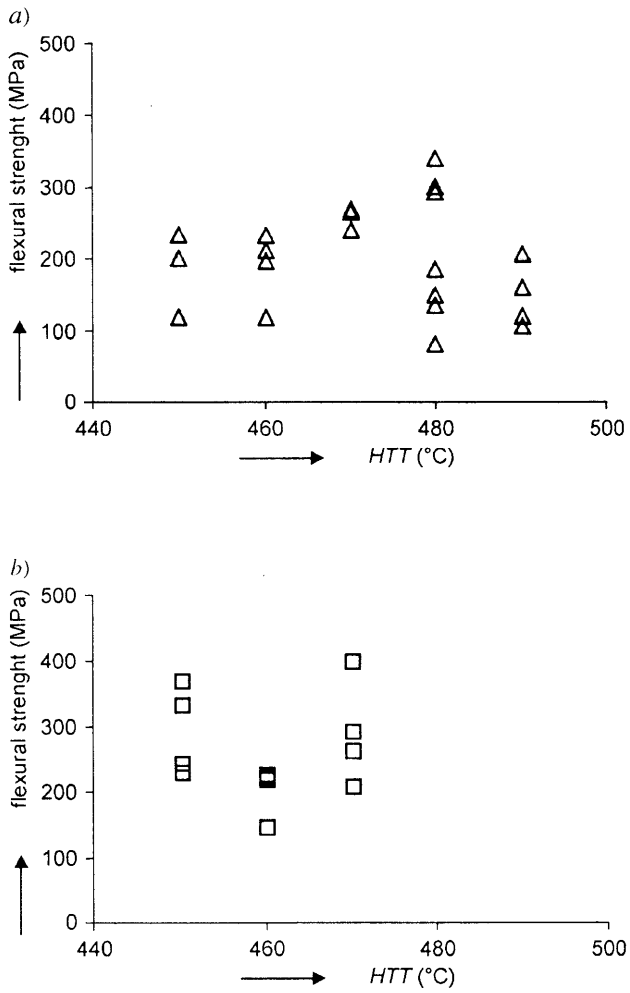

Figure 2. Flexural strength of the composite vs. heat treatment temperature of tow-preg.
a) Series A, *b*) Series B

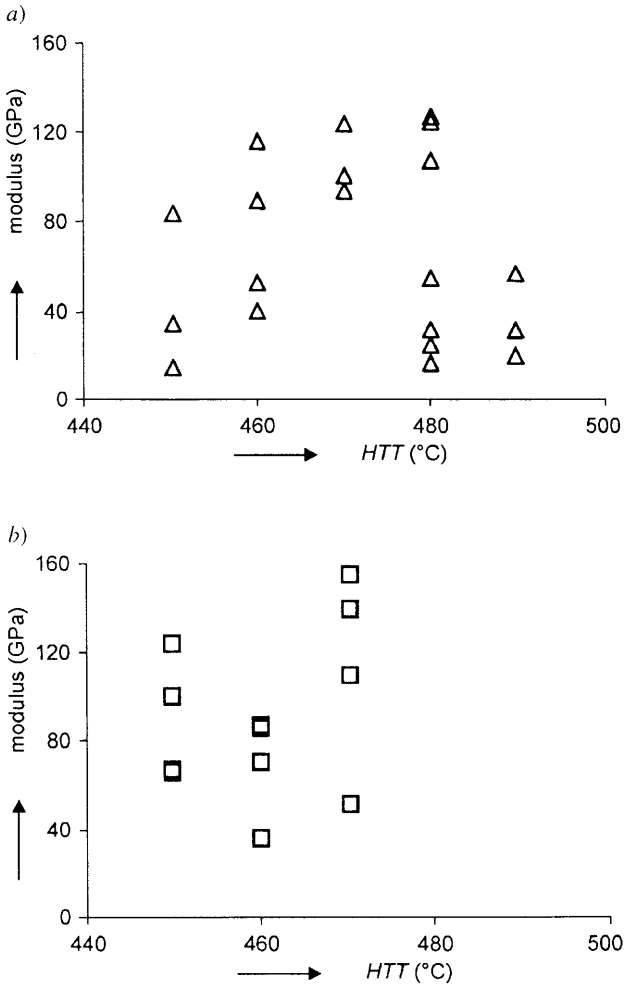

Figure 3. Elastic modulus of the composite vs. heat treatment temperature of tow-preg.
a) Series A , *b*) Series B

vely (figures 3*a* and 3*b*). (It must be born in mind that the manufacture process is still far from perfection and reproducibility. The best achieved values indicate the present upper limits which are not always reached due probably to occurrence of voids or other structural defects).

In spite of a large spread of individual values, a substantial degree of correlation between flexural strength and modulus values was observed for both A and B type specimens: the specimens with higher modulus revealed systematically higher strength values. Such a tendency can be tentatively explained as being due to a layered structure of the composite. It can be shown that (in an oversimplified example) a beam-shaped specimen consisting of i adjacent layers (each characterised by flexural strength σ and modulus E) reveals effective strength $\sigma^* = \sigma/i$ and effective modulus $E^* = E/i^2$. A relation $\sigma^* \propto (E^*)^{0.5}$ follows from the mentioned equations. By fitting the experimental data to a power function curve $\sigma^* = k\,(E^*)^n$ very close exponent values $n = 0.47$ and 0.55 were obtained for A and B type specimens, respectively (figures 4*a* and 4*b*). Though the real specimen structure is by no means that simple as in the mentioned model example, the evidence for pronounced cracks/voids parallel to the stacked lamina can be seen in figures 5*a*, *b*.

The plot of dependence of density of CFRC on *HTT* of tow-preg is similar to that of flexural strength. The maximum is slightly wider (between 460 and 480 °C) as shown in figure 6.

The decreasing heating rate in the hot moulding step has a positive influence on both density and flexural strength of CFRC as reported in figure 7 and figure 8, respectively. This can be explained by the lower volume of evolved gaseous products at lower heating rates and, therefore, less deterioration of the formed material. On the other hand, too low heating rates (under 1 °C min^{-1}) impact unfavourably softening of the matrix precursor.

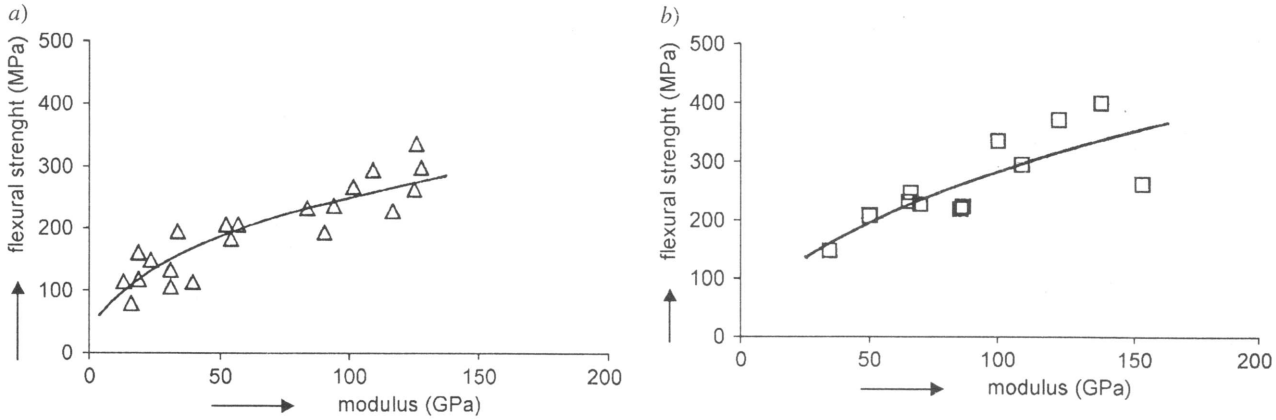

Figure 4. Correlation between flexural strength and elastic modulus of the composites.
a) Series A: $y = 28.303\ x^{0.474}$, $r^2 = 0.783$, *b*) Series B: $y = 21.734\ x^{0.555}$, $r^2 = 0.708$

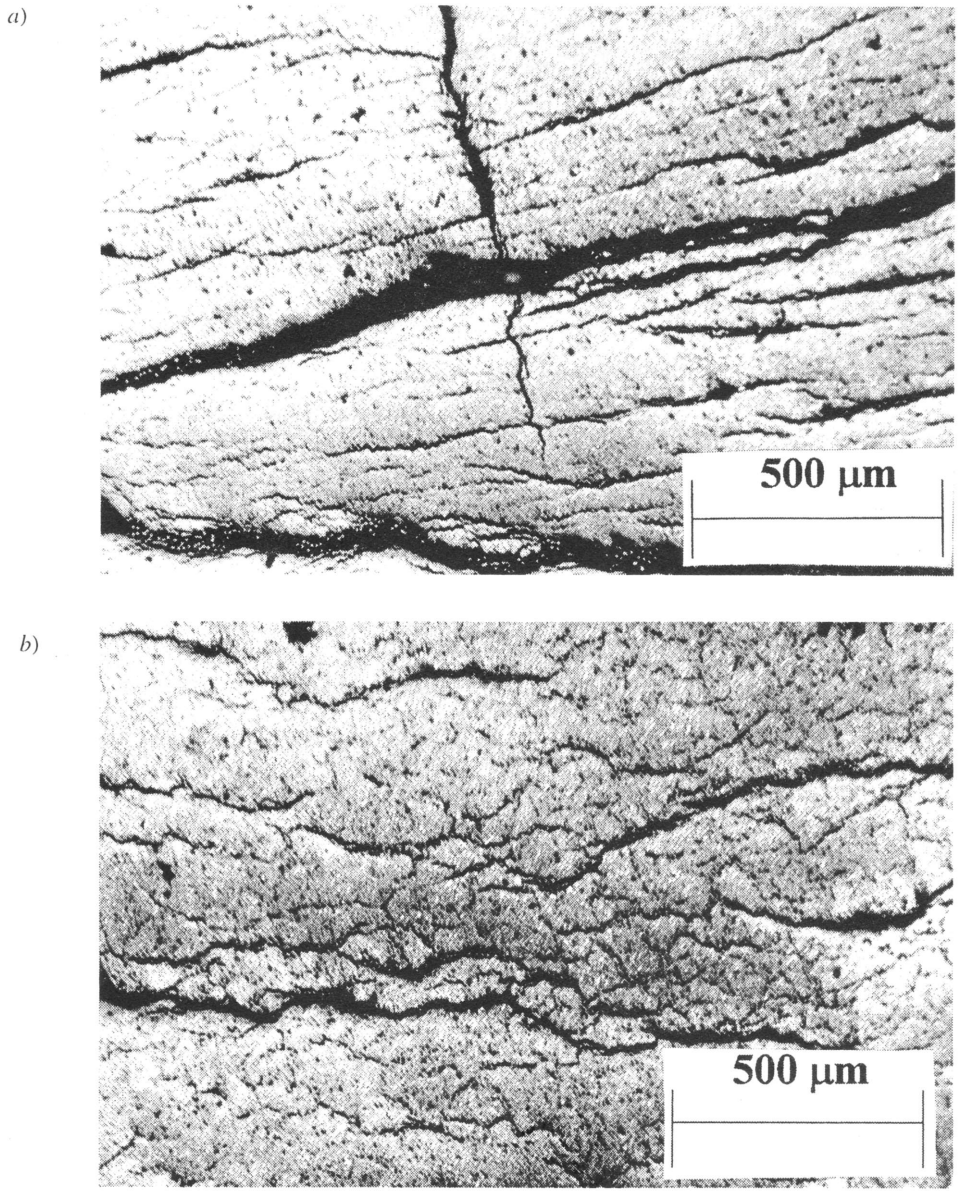

Figure 5. Microphotographs of polished cross-sections of composites with *HTT* = 460 °C. *a*) Series A, *b*) Series B (polarised light)

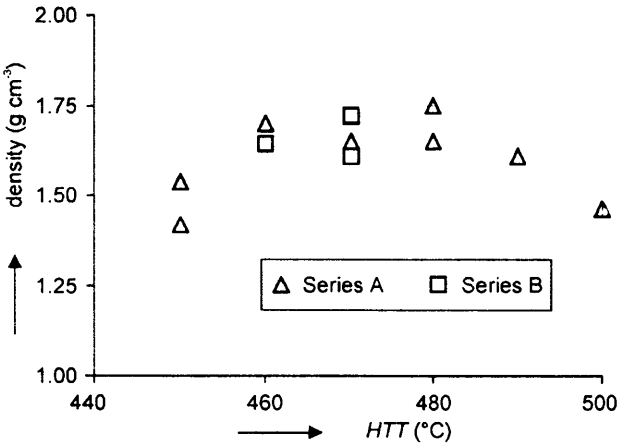

Figure 6. Dependence of density of CFRC on heat treatment temperature of tow-preg.

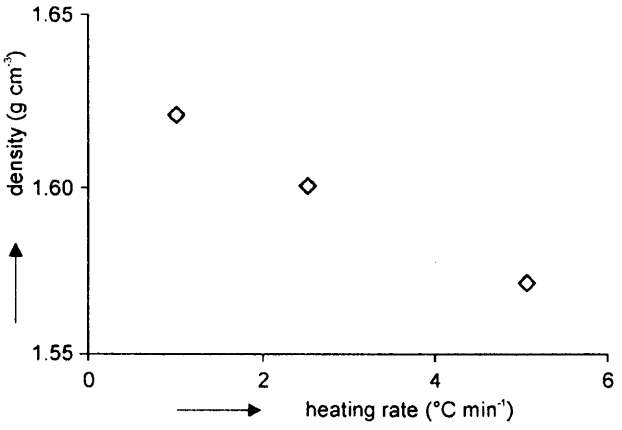

Figure 7. Density vs heating rate during the hot moulding of Series A composites.

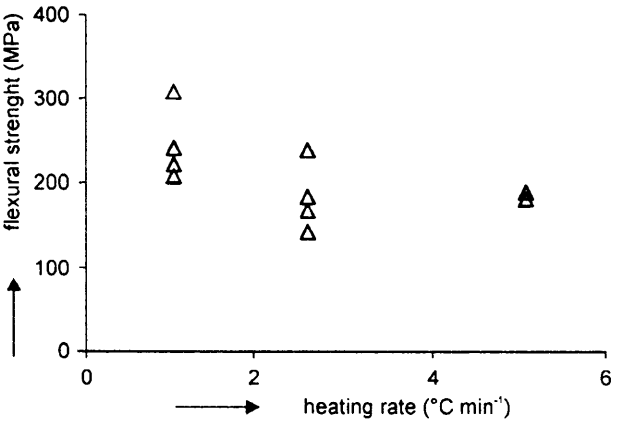

Figure 8. Flexural strength of the Series A composite vs. heating rate during the hot moulding.

CONCLUSIONS

Despite texture imperfections where many cavities or cracks occurs, mechanical properties of CFRC prepared by our method are comparable with those referred in [4] and [5].

The considerable improvement of CFRC properties was achieved by utilisation of filtered coal tar pitch.

The method is simple and utilises cheap coal tar pitch as a raw material for carbon matrix. Furthermore, this method is easily realisable at the industrial level and could be incorporated advantageously into the carbon fibre production process.

Further optimisation of the tow-preg manufacture, hot-press and secondary carbonisation conditions together with an optimal choice of the fibre/matrix ratio and fibre and/or pitch quality are expected to bring more uniformity to the texture and the considerable improvement of the CFRC properties. The efficient tools for such improvement were demonstrated.

Acknowledgement

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KOMPOZITNÍ MATERIÁL UHLÍK-UHLÍK S MATRICÍ NA BÁZI ČERNOUHELNÉ SMOLY A ZJEDNODUŠENÝM POSTUPEM PŘÍPRAVY

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Přes vynikající vlastnosti kompozitů typu uhlík-uhlík je jejich použití omezeno, většinou na vojenskou techniku. Důvodem jsou jejich vysoké ceny, způsobené do značné míry

vysokými náklady konvenční technologie jejich výroby, pro níž je typické několikanásobné opakování cyklu impregnace - rekarbonizace. Zařazením tohoto mnohonásobně opakovaného cyklu do technologického procesu je kompenzována vysoká pórovitost materiálu po první karbonizaci, způsobená nízkým výtěžkem uhlíku používaných prekurzorů matrice (pro první stupeň obvykle fenolformaldehydová pryskyřice, pro další stupně většinou černouhelná impregnační smola).

Zde popsaný způsob přípravy C-C kompozitů obchází nejen tento problém, ale i nejzávažnější problém nekonvenčních technologií - nanesení tepelně předupraveného prekurzoru matrice na pramenec uhlíkových vláken, vyžadující ultrajemné mletí prekurzoru. Je založen na tom, že tepelné předúpravě podrobuje přímo pramenec, nasycený černouhelnou smolou. Předúprava probíhá kontinuálně, ve dvojici trubkových pecí v proudu dusíku. Při těchto experimentech se vycházelo ze dvou druhů černouhelné smoly - první byla v původním stavu a z druhé byla nejprve filtrací odstraněna velká většina partikulí.

Tímto způsobem se získá tzv. tow-preg, z něhož se kompozit připraví lisováním ve vyhřívané formě (do 600 °C) po uspořádání do žádaného tvaru. V našem případě byla orientace tyčinek, vzniklých nařezáním tow-pregu, vzájemně rovnoběžná. Lisovací tlak činil 100 MPa a byl aplikován od dosažení teploty 400 °C. Rychlost ohřevu byla variantně 5, 2.5 a 1°C/min. Po dosažení 600 °C a 30 minutové prodlevě na této teplotě bylo vypnuto topení a po ochlazení na 500 °C byl uvolněn tlak. Získané destičky "zeleného" kompozitu byly podrobeny beztlakové sekundární karbonizaci v atmosféře dusíku do 1000 °C.

Z destiček zkarbonizovaného kompozitu byly připraveny vzorky a u nich byla stanovena hustota a provedeny ohybové zkoušky. Experimentální uspořádání umožnilo rovněž stanovení úbytku hmotnosti během formování za horka a sekundární karbonizace.

Výsledky potvrzují výchozí předpoklad celého projektu, úbytek hmotnosti během formování za horka a sekundární karbonizace je malý a klesá od 4,2 % (pro teplotu zpracování impregnovaného uhlíkového pramence *HTT* = 450°C) k 2,7% (pro *HTT* = 500 °C). To vede k vysokým hustotám připravených vzorků (1.60 - 1.75 g cm^{-3} pro *HTT* = 460 - 480 °C). Mechanické vlastnosti připravených vzorků jsou i přes četné texturní poruchy srovnatelné s publikovanými vlastnostmi kompozitů, připravených rovněž s použitím tepelné předúpravy smoly. Mez pevnosti za ohybu pro vzorky z nefiltrované smoly dosahuje nejvyšších hodnot 270 - 350 MPa, ale výsledky pro jednotlivé vzorky vykazují značný rozptyl. Totéž platí i pro vzorky z filtrované smoly, ale jejich mez pevnosti dosahuje až 400 MPa. Hodnoty modulu pružnosti se pohybují od 30 do 130 GPa pro vzorky z nefiltrované smoly a od 35 do 150 GPa pro vzorky z filtrované smoly. Vzorky s vyšším modulem systematicky vykazují vyšší pevnost. Tato tendence může být způsobena vrstevnatou strukturou kompozitů.

Navržený postup je jednoduchý a využívá jako surovinu pro přípravu uhlíkové matrice levnou černouhelnou smolu. Je snadno realizovatelný na průmyslové úrovni a mohl by být zařazen do procesu výroby uhlíkového vlákna. Další zlepšení homogenity a vlastností připravovaných CFRC kompozitních materiálů lze očekávat po optimalizaci procesů impregnace pramence, lisování za horka a sekundární karbonizace, jakož i po dosažení příznivějšího poměru množství vláken a matrice a volbě vhodného druhu vlákna a černouhelné smoly.