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CENTRE OF PHARMACEUTICAL, ENVIRONMENTAL- AND SAFETY MATERIALS

FLAME RETARDANCY OF EPOXY RESIN COMPOSITES REINFORCED WITH CNT-LOADED CARBON NANOFIBRE

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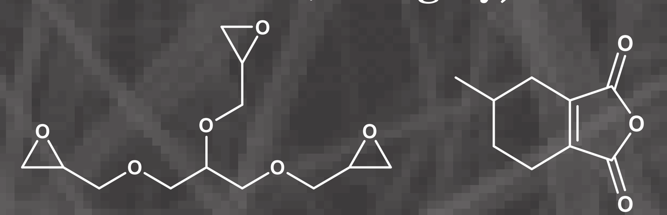
Introduction

The use of the parts made of composites of high mechanical loading capability, being suitable for replacing metallic structures, is rapidly increasing in the aircraft industry [1]. In the newest large airliners the fuselage, the wings and the empennage are also made of carbon fibre reinforced composites. For enhancing the thermal and electrical conductivity of these composites, CNTs can be incorporated into the matrix [2], or into the reinforcing fibres. The electrospinning method provides a simple and cost-effective method to produce ultra fine fibres even with the deposition of carbon nanotubes (CNTs) inside the nanofibres [3]. Considering the flammability of the composites, the incorporation of the carbon fibres has a reducing effect. By the addition of CNT to epoxy resins, improved thermal stability can be reached.

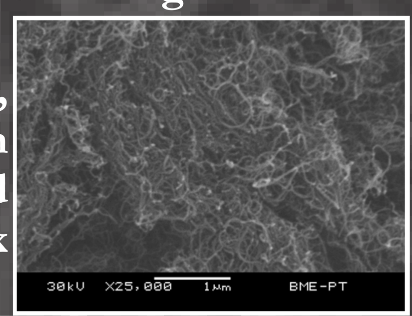
Materials

As matrix material, CL-12 glycerol-based epoxy resin was used, cured with T-111 anhydrid-type hardener (IPOX Chemicals, Hungary) .

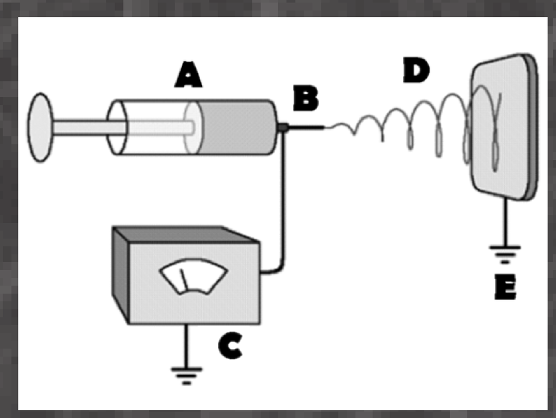


As conventional carbon fibre reinforcement, Zoltek PX35FBUD0300 type unidirectional fabric was used. The fabric consisted of Panex 35 50k rovings and had a surface weight of 333 g/m².

Baytubes C 150 HP (Bayer, Germany), multiwalled carbon nanotubes were used as nanosized reinforcement both in the matrix and in the nanofibers.



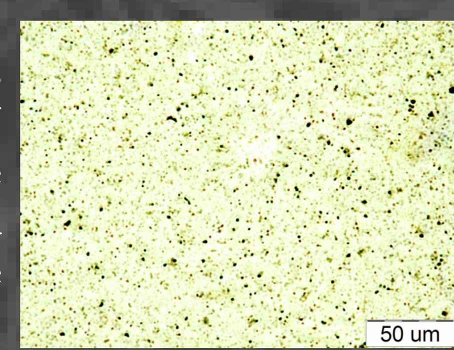
Electrospinning

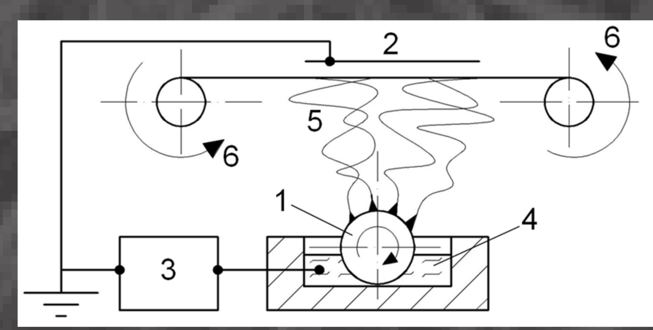


A: Polymer solution feed
B: Spinneret electrode
C: High voltage power supply
D: Space of fiber formation
E: Collector electrode

The method uses electrostatic forces to draw the fibres from the polymer solution. The electrostatic field between the two electrodes is provided by a high voltage power supply. Because of the applied field strength, a cone-shape, called Taylor cone is formed from the polymer droplet and a thin jet emerges from the tip of this cone. This jet elongates and solidifies as it travels to the collector. In case of a basic set up, a nanofibrous mat structure is formed on the collector electrode.

The electrospinning was carried out from a 12 wt% PAN solution in DMF solvent. The amount of the dispersed nanotubes was 2 wt% of the mass of the polymer precursor. CNTs were dispersed in the solution by ultrasonic mixing.





1: rotary electrode, 2: grounded plate electrode, 3: high voltage power supply, 4: solution, 5: fiber formation space, 6: rollers

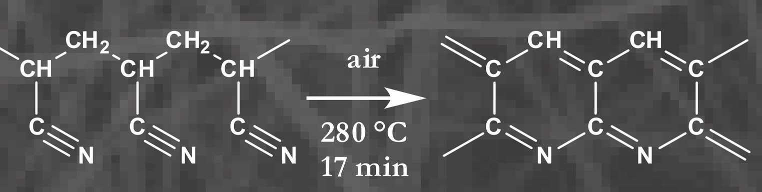
Sample preparation

For the flame retardancy measurements 12 samples were prepared by vacuum-bag method. The fabrics were impregnated with the resin and then cured at 80 °C for 8 hours. The CNTs were dispersed in the matrix using masterbatch mixing technology.

sample name	conventional carbon fabric (cC)	CNT in the matrix (T)	carbon nanofibre (nF)
E	no	no	no
ET	no	yes	no
EnF_TB	no	no	top-bottom (TB)
ETnF_TB	no	yes	top-bottom (TB)
EcC	yes	no	no
EcCT	yes	yes	no
EcCnF_I	yes	no	interlayer (I)
EcCTnF_I	yes	yes	interlayer (I)
EcCnF_TB	yes	no	top-bottom (TB)
EcCTnF_TB	yes	yes	top-bottom (TB)
EcCnF_All	yes	no	everywhere (TB+I)
EcCTnF_All	yes	yes	everywhere (TB+I)

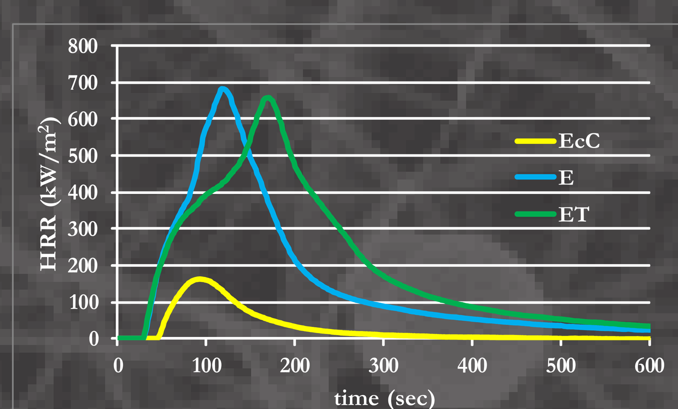
Stabilization, carbonization

In order to prepare carbon nanofibres from the electrospun PAN mat, stabilization followed by carbonization must be carried out. During the stabilization, the cyclization of the polymer takes place.

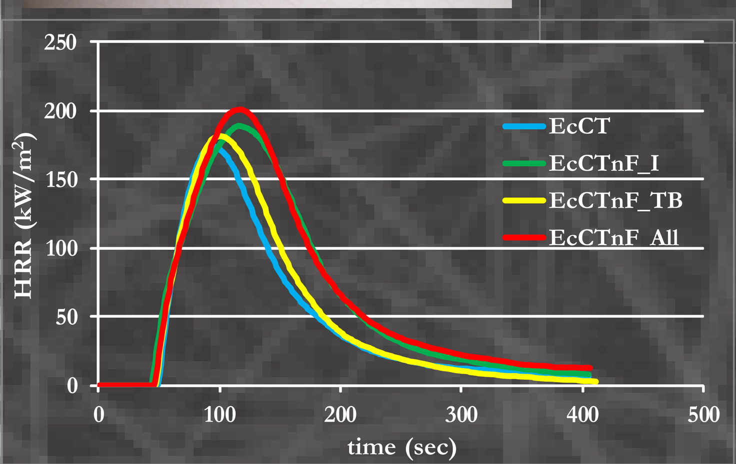


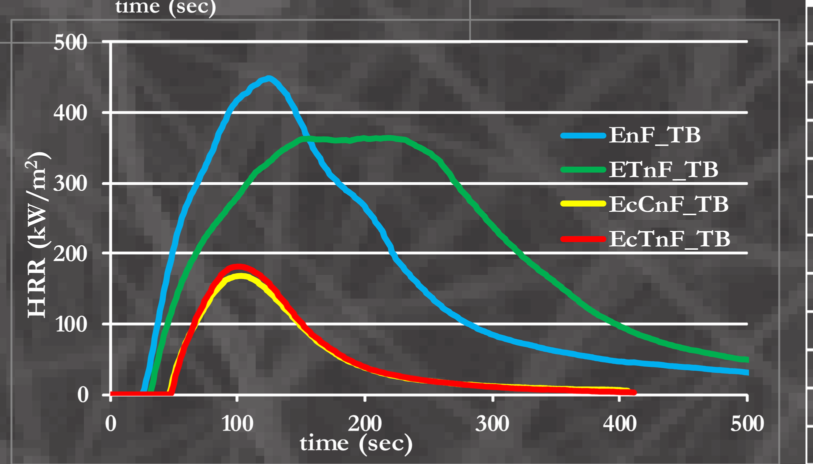
Aftet that, the carbonization requires high temperature (up to 830 °C) to provide fully graphitized structure for the electrospun nanofibrous mat.

Cone calorimeter tests



The CTN-loading in the matrix lowers somewhat the pHRR in neat resins, but when applied together with carbon fibres, the effect is inverse. The CNT-containing nanofibres have no significant effect in the cone calorimeter tests.

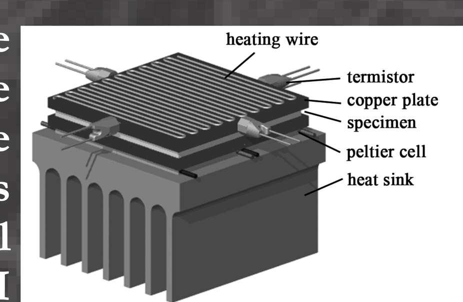


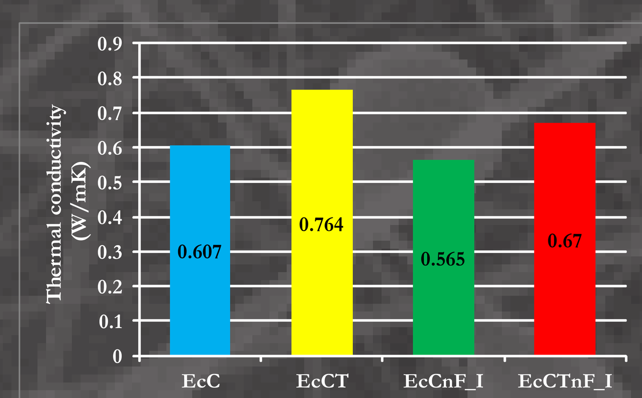


sample name	TTI (sec)	pHRR (kW/m²)	THR (MJ/m²g)	residue (%)
E	22	682.3	2.100	0
ET	24	658.6	1.982	0
EnF_TB	22	448.7	1.938	0
ETnF_TB	27	363.9	1.747	0
EcC	44	162.3	0.469	60.26
EcCT	44	174.2	0.486	61.60
EcCnF_I	51	164.2	0.546	56.96
EcCTnF_I	40	189.0	0.591	56.50
EcCnF_TB	40	168.1	0.493	58.41
EcCTnF_TB	45	181.5	0.516	58.75
EcCnF_All	51	162.8	0.485	61.31
EcCTnF_All	43	200.9	0.633	54.31

Thermal conductivity

As the flammability of the materials depends also on the heat conductive properties, the thermal conductivity [4] was also determined for several samples (EcC, EcCT, EcCnF_I and EcCTnF_I). The CNT loading in the matrix increases the thermal conductivity of the samples, however, the presence of the CNT-loaded nano-fibres (nF) has no significant effect, moreover, the values measured for these samples are some-what lower.





LOI and UL-94

When no conventional carbon fabric reinforcement (cC) is used, the samples can be ignited easily. When CNTs are present in the matrix, the flame spreading rate is 70% higher. When cC is used, the LOI value increases by about 7 V/V%, and no flame spreading can be detected in the UL-94 test. Considering the LOI values, no significant difference can be detected in the case of the cC reinforced samples, in spite of the CNT or nF content.

sample name	LOI	UL-94
E	23	HB (13.9±6.5 mm/min)
ET	22	HB (23.6±3.0 mm/min)
EcC	33	HB (vertical test)
EcCT	30	HB (vertical test)
EcCnF_I	31	HB (vertical test)
EcCTnF_I	30	HB (vertical test)
EcCnF_TB	30	HB (vertical test)
EcCTnF_TB	30	HB (vertical test)
EcCnF_All	29	HB (vertical test)
EcCTnF_All	30	HB (vertical test)

Conclusions

In this work CNT-loaded carbon nanofibre-carbon fibre reinforced hybrid epoxy resin composites were prepared and tested. The CNT-loaded nanofibres were produced via elecrospinning, followed by stabilization and carbonization in order to prepare hybrid nano reinforcing carbon fibres. The epoxy resin matrix also contained CNT. The application of the nanomaterial increases the thermal conductivity of the composites, however the effect of the nanofibres is negligible. In the cone calorimeter, when no carbon fibre reinforcement is applied, the CNT decreases the pHRR of the samples. In the hybrid composites, due to the increased heat conductivty, the samples burn easier, however no significant difference can be found. The LOI values increase with the incorporation of carbon fabrics, and also in UL-94 test only vertical burning can be observed.

Acknowledgement

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