

# STRUCTURAL POWER COMPOSITES AS ENERGY STORAGE DEVICES

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## Abstract

*A novel concept of structural supercapacitors based on CF reinforced composites has been introduced that can simultaneously act as a structural component and an electrical energy storing device. Supercapacitors consisting of woven carbon fibre mat based electrodes; filter paper insulator and PEGDGE/DGEBA based polymer electrolyte were fabricated. BET surface area analysis and tensile tests were conducted on the as-received and activated carbon fibre reinforcements. Compression tests and ionic conductivity measurements were conducted on the polymer electrolyte whilst charge/discharge electrochemical tests were done on the structural supercapacitors. This was to investigate the implications of increased DGEBA loading in PEGDGE polymer electrolyte and carbon fibre activation on the multifunctionality of structural supercapacitors. The addition of DGEBA increased the compressive stiffness, although the ionic conductivity was compromised. Specific capacitance of the structural supercapacitor was increased with the chemical activation of CF based electrodes. Carbon fibre activation led to improved specific capacitance of the structural supercapacitors and the addition of DGEBA increased the compressive stiffness, although the ionic conductivity was compromised.*

## 1 Introduction

Carbon fibre (CF) reinforced epoxy based composites are playing an important role in a wide variety of civil and military applications because of their outstanding properties, ease of fabrication, low shrinkage after curing and good thermal resistance[1]. Conventional composites are fabricated from two or more distinctive materials that are disparate in nature with widely differing property values (fibre and matrix usually) but when combined possess better engineering performance than the individual components[2]. Currently, focus is on the development of smaller, smarter and efficient materials and one promising route is to fabricate composite materials that have multifunctionality. Multifunctional composite systems are used for material development and thus, act as a structural material and also exhibit at least one additional performance-linked function such as mechanical, electrical, thermal, optical, chemical and

electromagnetic properties. Composite systems are ideally suited for multifunctional performance as the best features of different materials can be integrated to form a new material that behaves as a homogeneous entity and possess a broad spectrum of desired features.

Over the years, multifunctional composites have been designed for various applications such as self-healing composite materials[3] in which microencapsulated epoxy is embedded into the structural composite matrix containing a catalyst. The catalyst in the structural composite matrix polymerises the healing agent upon contact resulting in polymerisation in the damaged region. In addition, structural batteries[4], for the skin of micro air vehicle, were developed to increase flight time while maintaining the total aircraft weight. Another area of interest in multifunctional composites is a structural supercapacitor that carries, by nature of its application, mechanical loads (i.e. resists imposed mechanical stresses in service) as well as stores electrochemical energy

and thus replacing the traditional static load bearing components for volume and mass savings of the overall system. Previous studies have utilized different approaches for optimising the electrical and mechanical properties in composite system, including structural battery [5–9], structural capacitor [10–12] and structural fuel cell [13, 14]. Each of these devices has different power-energy capabilities and ranked using the “Ragone plot” [15, 16]. Such plot reveals the discharge rate of specific power versus the delivery capacity of specific energy being available for a load. Ideally, a storage device should have high energy density as well as high power density, but in reality compromises have to be made between energy density and power density.

This study demonstrates a multifunctional carbon fibre reinforced polymer composite which can store electrical energy as well as bear mechanical loads. Carbon fibre activation was conducted with the aim of increasing the accessible surface area of electrode to the ions of the solid electrolyte without deteriorating the tensile properties of carbon fibres. Polymer matrix has also been modified by introducing ions within the crosslinked resin in order to develop an optimised polymer electrolyte that is suitable for multifunctional roles within a structural supercapacitor. The effect of electrolyte concentration in polymer matrix was also examined. Polymer electrolyte was prepared by making a blend of poly (ethylene glycol) diglycidylether and diglycidylether of bisphenol-A (DGEBA) in different weight ratios. In this study, multifunctional structural supercapacitors are also fabricated. The electrochemical performance of structural supercapacitors was studied using charge-discharge measurements.

## 2 Materials and Synthesis

PAN-based woven (HTA, five harness satin weave) carbon fibre matt (30×21 cm, 200 g/m<sup>2</sup>) with an average fibre diameter of around 7 μm and woven mat thickness of 0.21 mm was purchased from Tissa Glasweberei AG (Oberkulm, Switzerland) and was used as electrodes in structural supercapacitor. Filter paper (1001-917, Whatman Grade 1, Fisher Scientific, UK) and the glass fibre (GF) matt (Tissa Glasweberei AG, Oberkulm, Switzerland) were used as separators. Potassium hydroxide (KOH) pellets were used for the chemical activation of carbon fibres. Nitrogen gas (BOC, UK) was used as an inert gas during chemical

activation of carbon fibre mats. For matrix formulation, lithium bis(trifluoromethyl sulfonyl) imide (LiTFSI, purity ≥ 99.0 wt%, Sigma Aldrich, UK) and propylene carbonate (PC, HPLC grade, 99.7%, Sigma Aldrich, UK), was used as electrolyte. Tri-ethylene-tetramine (TETA ≥ 97 wt%, Sigma, UK) and methylene bis(cyclo-hexyl-amine) (MCHA, Sigma, UK) were used as hardener for epoxies i.e. poly (ethylene glycol) diglycidylether (PEGDGE, Mn~526, Sigma Aldrich, UK) and diglycidylether of bisphenol-A (DGEBA, Sigma Aldrich, UK) respectively. All chemicals were used as received.

### 2.1 Chemical activation of carbon fibre mats

Chemical activation of carbon fibre involved impregnation of carbon fibres with thick potassium hydroxide (KOH) slurry followed by heat treatment. A 30×21 cm sized carbon fibre mat was placed in Pyrex® tray while slurry of 1.85 M KOH in water (typical KOH loading was approximately 6.5 wt% after drying) was transferred onto the fibre mat. The sample was left inside a fume cupboard for 3 hours before the excess KOH was dispensed away and the cloth was placed on a PETF (Polyethylene terephthalate film) to dry overnight. Subsequently, the dried carbon fibre fabric was transferred onto a perforated stainless steel frame and positioned into the retort (Lenton ECF 12/30) where it was heated at 5°C/min to 800°C under nitrogen (flow rate of 0.5 L/min) and held at temperature for 30 min. After which the system was allowed to cool to room temperature while in inert nitrogen atmosphere over approximately 14 h. The resultant activated carbon fibres mat was then washed excessively with deionised water to eliminate any residual alkali until pH7, and was finally dried in a vacuum oven at 80 °C.

### 2.2 Surface properties of the carbon fibre mat

For the determination of specific surface area ( $A_s$ ) of as received and activated carbon fibre mats from nitrogen adsorption isotherm at 77.35K through BET (Brunauer-Emmett-Teller) method, a Micromeritics ASAP 2010 analyser (Micromeritics Ltd. UK) was used that determined the specific surface area  $A_s$  according to the industrial standard ISO 9277 [17]. For the examination of surface morphology of activated carbon fibre mats, LEO Gemini FEG Scanning Electron Microscope (Oberkochen, Germany) was used.

For the measurement of tensile properties of single carbon fibre filaments from as-received and activated carbon fibre mats, a 20 N load cell (TST

350 Tensile stress testing system, Linkam Scientific Instruments, Surrey, UK) was used. The tensile test was performed according to ISO British Standard 11566. For each measurement a single carbon fibre was glued onto a paper frame using cyanoacrylate adhesive. The gauge length, i.e. free fibre length, was set to 25 mm. The single fibre was loaded at a rate of  $0.01 \text{ mm s}^{-1}$  until the fibre failed while the loading force versus displacement was logged using a computer. System compliance  $C$  was estimated to be  $0.7 \text{ mm/N}$  under relevant systematic conditions. For each fibre, the tensile strength and Young's modulus were calculated using equations 1 and 2:

$$\sigma_f = \frac{F}{A_f} \quad (1)$$

where  $\sigma_f$  is the tensile strength (MPa),  $F$  is the tensile force (N) at break and  $A_f$  is the fibre cross-sectional area ( $\text{mm}^2$ ). All measurements were repeated on at least twenty different samples of each type to obtain a statistical average. The errors are presented as standard errors.

### 2.3 Preparation of polymer electrolytes

#### PEGDGE polymer electrolyte

The synthesis of PEGDGE based polymer electrolyte involved PC as a solvent, PEGDGE, LiTFSI as conducting electrolyte and TETA as a hardener (crosslinker). LiTFSI (0.18 wt%) was dissolved in PC (0.60 wt%) and while still stirring, PEGDGE (92.6 wt%) was added and stirring continued until a homogeneous solution was obtained (approx. 5 min). TETA (6.62 wt%) was then added to the solution and the mixture was further stirred for 10 min.

#### DGEBA/PEGDGE polymer electrolyte

The synthesis of PEGDGE/DGEBA blend based polymer electrolyte involved PEGDGE and DGEBA as polymer matrix, PC as a solvent, LiTFSI as a conducting electrolyte, TETA and MCHA as a hardener (crosslinker). LiTFSI (0.18 wt%) was dissolved in PC (0.60 wt%) and the mixture was stirred for 15 min and then DGEBA (15.6 wt%) and PEGDGE (72.7 wt%) was added and the mixture was further stirred in magnetic stirrer (300 rpm) in open air at room temperature for 1 h. MCHA (4.26 wt%) and TETA (6.66 wt%) was added in mixture and was further stirred for 2-3 minutes.

### 2.4 Fabrication of structural supercapacitors

Supercapacitor specimens (six specimens for each configuration) were fabricated via a brushing method. The carbon fibre and filter paper,

impregnated with polymer electrolyte, were assembled in such a way that filter paper was sandwiched between two layers of carbon fibre mat and the composite was laid up by hand ensuring that the lay-up was balanced (i.e. the crimp lines of the CF plies were mirrored about the midplane). The samples were then kept at  $80^\circ\text{C}$  for 24 h whilst under a small applied pressure. Laminates were fabricated from either as-received or activated carbon fibre cloths with filter paper (Grade 1 Whatman) as the insulator.

### 2.5 Electrochemical characterisation

For the electrochemical characterisation, impedance spectroscopy of the PEGDGE and DGEBA based polymer electrolyte matrices and the charge/discharge experiments of the fabricated structural supercapacitors were carried out using an Ivium-n-Stat Multichannel Potentiostat (Ivium Technologies, The Netherlands). The impedance spectroscopy measurements were conducted in frequency window of  $10^{-1} \text{ Hz}$  to  $10^5 \text{ Hz}$  and the amplitude of the sinusoidal voltage was  $0.5 \text{ V}$ . Ionic conductivity of polymer electrolyte samples were measured using the equation,

$$\sigma = \frac{l}{R_B \cdot A} \quad (2)$$

where  $R_B$  is the bulk resistance ( $\Omega$ ) calculated from the intercept of high frequency curve in impedance plot,  $l$  is the height of specimen (cm) and  $A$  is the surface area of specimen ( $\text{cm}^2$ ). All measurements were repeated on at least five nominally identical samples to obtain a statistical average. The values presented were averaged and errors are presented as standard deviations. The charge-discharge measurements of fabricated structural supercapacitors were conducted at room temperature using a  $0.1 \text{ V}$  step voltage applied for 10 s, and the inherent capacitance was determined using the following equation:

$$C = \frac{I \cdot \Delta t}{V} \quad (3)$$

where  $I$  is the discharge current (A) and  $\Delta t$  is the time period for the voltage change ( $\Delta V$ ). The specific capacitance was calculated as capacitance per unit volume ( $\text{F/cm}^3$ ).

### 2.6 Mechanical characterisation

PEGDGE-based electrolyte matrix (see section 2.4) was transferred into a 10 ml syringes (13 mm inner diameter, BD Plastipak) and allowed to cure at  $80^\circ\text{C}$  for 24 h inside an oven. The resultant crosslinked electrolyte resin was then removed from the syringe and cut into 26 mm long cylindrical specimens using a scalpel for

compression testing in accordance to the ASTM D695 standard [18]. Each specimen was aligned between the plattens and a compressive force was applied in an axial direction to the faces of the specimen at a stroke of 0.1 mm/min. Following the standard, the compressive properties were determined at applied strains of between 0.02%-0.25%. All measurements were repeated on at least five nominally identical samples to obtain a statistical average. The values presented were averaged and errors are presented as standard deviations.

### 3 Results and discussion

#### 3.1 Surface area and tensile strength of chemical activated carbon fibres

The surface area of chemically activated carbon fibre (ACF) mat was increased significantly from 0.33 m<sup>2</sup>/g (as-received CF) to 32.8 m<sup>2</sup>/g (ACF) as shown in Table 1. The increase in surface area of ACF can be attributed to the removal of disordered and perfect basal plane regions of the carbon fibres during KOH based chemical activation. It is thought that the increase in surface area of CF mats may improve the bonding with polymer electrolyte in CF reinforced composites resulting in improved structural performance. Also, the increase in surface area of CF based electrodes may provide increased number of sites to the ions of polymer electrolyte to be adsorbed during the charging of structural supercapacitor resulting in improved electrochemical performance. Also the tensile strength of carbon fibres (Table 1) suggests that the chemical activation had a minor effect on the structural performance of the carbon fibre mats. The tensile strength of as-received CF (Table 1) was comparable to literature values [19] of this fibre type. This is important as a decrease in tensile properties of the CFs could eliminate these reinforcements for use in composites.

Carbon fibre sample	Surface area [m <sup>2</sup> /g]	Tensile strength [GPa]
As-received CF	0.33	3.27 ± 0.15
ACF	32.8	3.46 ± 0.22

Table 1 Surface area and tensile strength of as received and activated carbon fibres

SEM micrographs of the as-received CF and ACF are shown in Fig. 1. The SEM micrographs confirmed the typical surface appearance of PAN based CFs with crenulations along the fibre axis after activation. The unaffected surface morphology of the ACF (Fig. 1) suggests that the

fibres have not been subjected to microscale surface damages as a result of fibre activation. It is assumed that the increase in surface area is attributed to nanoscale pores.

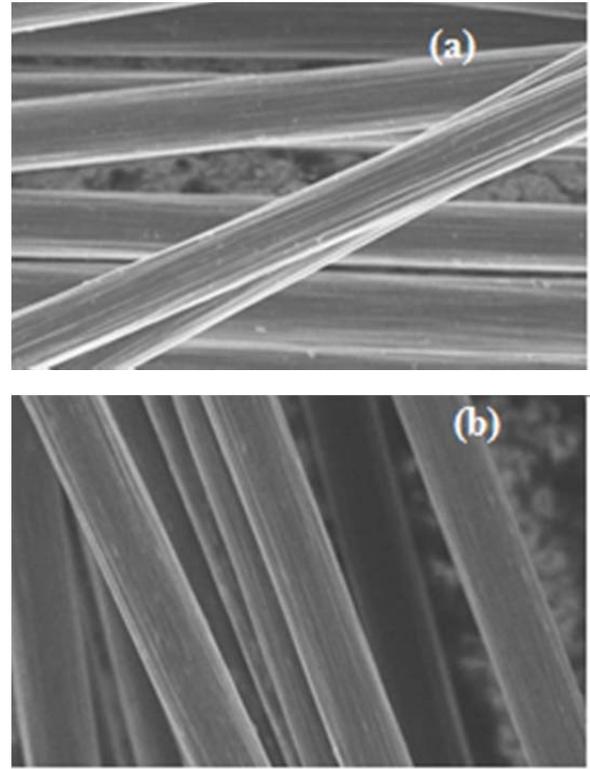


Fig. 1 Representative SEM images ( $\times 2000$ ) of as received (a) and activated carbon fibres (b)

#### 3.2 Ionic conductivity and compressive properties of polymer electrolyte

PEGDGE and DGEBA systems were studied for their possible use in the structural supercapacitors as polymer electrolyte. Ionic conductivity and compressive stiffness were measured for the PEGDGE polymer electrolyte by increasing the DGEBA loading as shown in Fig. 2. These properties were considered to be important for the performance of the subsequent structural supercapacitors. The addition of DGEBA to PEGDGE led to an increase in the stiffness of the PEGDGE based polymer electrolytes but a fall in ionic conductivity. An optimum balance appears to occur for the 95:5 PEGDGE: DGEBA composition. DGEBA is good structural matrix but the high crosslinked density resulted in the hindering of ionic transportation within the polymer matrix and therefore compromising the energy storage capability of structural supercapacitors.

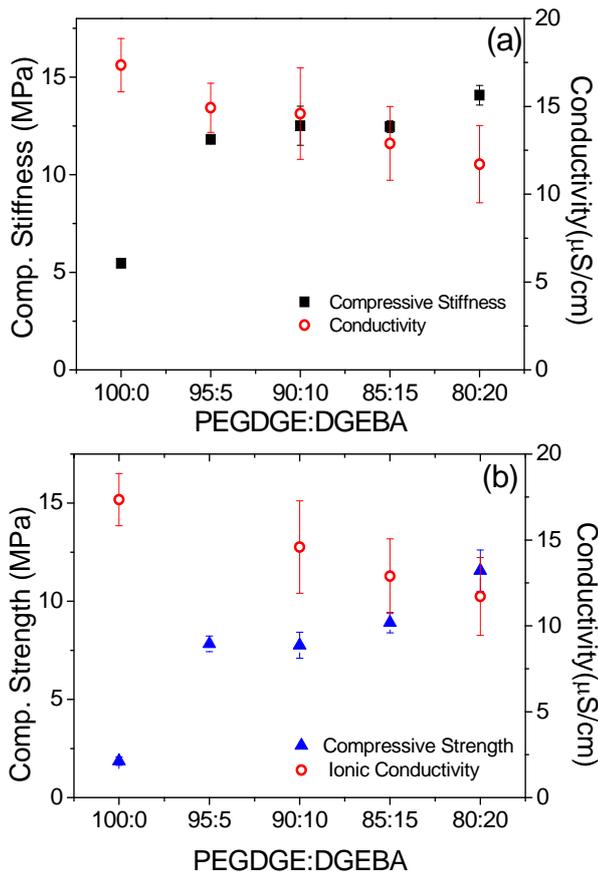


Fig. 2 Multifunctionality of PEGDGE polymer electrolyte with increased DGEBA loading, (a) PEGDGE:DGEBA vs. compressive stiffness and ionic conductivity, (b) PEGDGE:DGEBA vs. compressive strength and ionic conductivity

### 3.3 Influence of resin formulation on electrical behaviour of supercapacitors

PEGDGE ( $E \sim 6\text{MPa}$ ) is a very soft and rubbery material and therefore, does not offer good structural properties. Therefore, different blends of PEGDGE:DGEBA polymer electrolytes were formulated (as discussed in Section 3.2) with the aim of enhancing the structural performance of the supercapacitors. Measurements of the specific capacitance of these systems are given in Table 2. It can be seen from this Table, the ratio between PEGDGE:DGEBA resin strongly influenced the specific capacitance of the supercapacitors. That is, as the DGEBA loading increased, the specific capacitance fell.

PEGDGE:DGEBA	$C_g$ ( $\mu\text{F}/\text{cm}^3$ )
100:0	$212 \pm 8.8$
95:5	$98.8 \pm 3.7$
90:10	$45.6 \pm 6.0$
85:15	$18.4 \pm 2.7$
80:20	$6.68 \pm 0.4$

Table 2 Electrochemical performance of structural supercapacitors with as received carbon fibre

fabric and PEGDGE polymer electrolyte with increased DGEBA loading

### 3.4 Influence of carbon fibre activation on the electrical properties of structural supercapacitors

ACF and filter paper reinforced PEGDGE polymer electrolyte composites were fabricated and were tested electrochemically. The results of the charge-discharge experiment are shown in Fig. 3. The composites fabricated with activated carbon fibres exhibited a 90% higher specific capacitance as compared to the supercapacitors with as-received carbon fibres. This result correlates to some extent with the BET surface area data reported in Section 3.1.

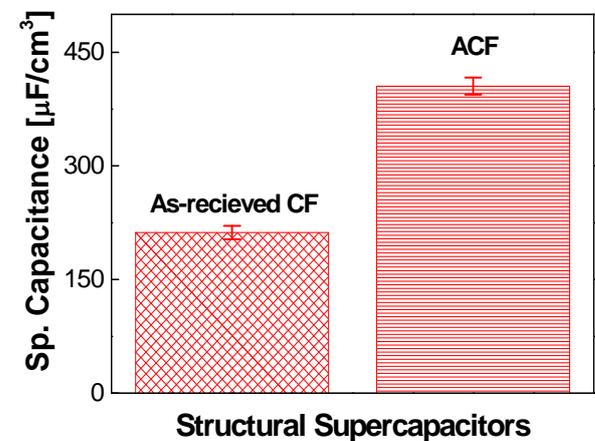


Fig. 3 Effect of chemical activation on specific capacitance of fabricated structural supercapacitors

## 4 Conclusion

As part an on-going research program at Imperial College London to develop structural supercapacitors, it was demonstrated that CF-reinforced composites are capable of simultaneously acting as structural components as well as energy-storing supercapacitors. The design was based on using woven CF mats as both electrodes and mechanical reinforcement. Such electrodes were separated using filter paper insulators and bound together with a PEGDGE/DGEBA based polymer electrolyte. Activation of carbon fibre mats had a positive influence on the electrical properties of the structural supercapacitors. It was also found that although addition of DGEBA into the PEGDGE matrix blend could enhance the mechanical properties of the polymer electrolyte, the ion transportation activity within the electrolyte was suppressed. Nevertheless, this development of the novel concept potentially could have significant mass and/or volume efficiencies for applications

that utilise both structural components and energy storage devices.

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## References

- [1] S.M. Lee, International Encyclopedia of Composites, VCH Publishers, 1990.
- [2] Klaus Friedrich, Stoyko Fakirov, and Zhong Zhang, Polymer Composites; From Nano- to Macro-Scale, Springer Science & Business Media, Inc., 2005.
- [3] S.R. White, N.R. Sottos, P.H. Geubelle, J.S. Moore, M.R. Kessler, S.R. Sriram, E.N. Brown, and S. Viswanathan, Autonomic healing of polymer composites, *Nature*, 409 (2001) 794-797.
- [4] L. Christodoulou and J. Venables, Multifunctional material systems: The first generation, *JOM Journal of the Minerals, Metals and Materials Society*, 55 (2003) 39-45.
- [5] G.H. Kim, A. Pesaran, and R. Spotnitz, A three-dimensional thermal abuse model for lithium-ion cells, *Journal of Power Sources*, 170 (2007) 476-489.
- [6] X.L. Wang, Q. Cai, L.Z. Fan, T. Hua, Y.H. Lin, and C.W. Nan, Gel-based composite polymer electrolytes with novel hierarchical mesoporous silica network for lithium batteries, *Electrochimica. Acta*, 53 (2008) 8001-8007.
- [7] M.C. Borghini, M. Mastragostino, and A. Zanelli, Investigation on lithium/polymer electrolyte interface for high performance lithium rechargeable batteries, *Journal of Power Sources*, 68 (1997) 52-58.
- [8] J.F. Snyder, E.D. Wetzel, E.H. Hgo, P.A. Nguyen, E.I. Wong, K. Xu, and R.H. Carter, Multifunctional Structural Composite batteries for US Army Applications, Proceedings of the 2006 Army Science Conference, (2007).
- [9] F. Croce, G.B. Appetecchi, L. Persi, and B. Scrosati, Nanocomposite polymer electrolytes for lithium batteries, *Nature*, 394 (1998) 456-458.
- [10] W.J. Sarjeant and F.W. MacDougall, Capacitors for high power electronics, *Pulsed Power Conference, 1997. Digest of Technical Papers. 1997 11th IEEE International*, 1997, pp. 603-609.
- [11] X. Luo and D.D.L. Chung, Carbon-fiber/polymer-matrix composites as capacitors, *Composites Science and Technology*, 61 (2001) 885-888.
- [12] D.J.O'Brien, D.M.Baechle, and E.D.Wetzel, Multifunctional Structural Composite Capacitors For U.S. Army Applications, *38th ISTC*, Army Research Laboratory, Dallas, Texas, 2009, p. -11.
- [13] Daniel Peairs, Corydon Hilton, Scott Case, John (Jack) Lesko, Dave Sitton, and Ronald Moffitt, Development of Prototype Pultruded Structural Fuel Cell, *COMPOSITES & POLYCON 2007*, (2007).
- [14] R.K. Gupta and C.M. Whang, Structural study of a sol-gel derived novel solid oxide fuel cell perovskite, *Journal of Physics: Condensed Matter*, 19 (2007) 196209.
- [15] T. Christen and M.W. Carlen, Theory of Ragone plots, *Journal of Power Sources*, 91 (2000) 210-216.
- [16] T. Christen and C. Ohler, Optimizing energy storage devices using Ragone plots, *Journal of Power Sources*, 110 (2002) 107-116.
- [17] BS ISO 13320. Particle size analysis - laser diffraction methods. 1-12-2009.
- [18] ASTM D 695. Standard test method for compressive properties of rigid plastics. 2002.
- [19] J.B. Donnet, Carbon fibers, Marcel Dekker, 1998.