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A Critical Review on Multifunctional Composites as Structural Capacitors for Energy Storage

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Abstract

Due to the increasing greenhouse gas emissions and gradual run out of fossil fuels, there is a growing concern on the environmental protections and global energy demands in the world. Therefore, new energy storage technologies have been continuously developed to be integrated with renewable energy systems in recent years. Nowadays, advanced composites are popular in automotive and aerospace industries because of their significant advantages such as high specific strength to weight ratio and non-corrosion properties. Therefore, research interests in developing multifunctional composite materials in order to reduce the fuel and energy consumption have increased significantly. Therefore, this paper is focused on the development of multifunctional energy storage systems. The introduction of structural dielectric capacitors and structural electric double layer capacitors (EDLC) are presented. Then, experimental findings, in terms of improvements on the mechanical and electrical properties of structural dielectric capacitors, and factors on the overall performance of structural EDLC conducted by other researchers are given. In addition, it has been proven that the structural dielectric capacitors could maintain their capacitive function under a mechanical loading. Lastly, challenges that would be faced in the realization of structural dielectric capacitors and structural EDLC are discussed.

Keywords: Advanced composites; Multifunctional; Energy storage; Carbon fibres

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1. Introduction

Fuel consumptions and CO₂ emissions are major concerns in entire aerospace and automotive industries. To reduce the fuel consumption for flying and on-road vehicles, lightweight designs such as the use of advanced composites for structural parts have been adopted in recent years. The significances of being lightweight, mechanically strong and resistant to corrosion make the advanced composites very popular for structural applications. Usually, they are made by strong fibres cushioned with matrix, in which its strength is relatively weak as compared with the fibre, to form a new material with a high stiffness-to-weight ratio. Matrices such as polyester, vinyl-ester and epoxy, and fibre reinforcements such as natural fibre, glass fibre and carbon fibre are used commonly to make the advanced composites. Apart from the transportation sector, the advanced composites are also employed for supporting components for energy storage systems, such as fly-wheel systems, to improve the overall efficiency of systems through the reduction of their mass and ultimately enhancing their mechanical performance.

On the other hand, the environmental issues mentioned above also motivate the rapid development of renewable energy technologies in a conjunction with energy storage systems. In general, traditional energy storage systems are heavy, corrosive and easily damaged, resulting in a relatively short lifetime. For instance, lead acid batteries are commonly used in the industry because they are the most economical for large power applications, in where weight is less concerned. However, they are not environmentally friendly due to the corrosive electrolytes and lead used as their constituents. In addition, the applications of lead acid batteries are restricted in the automotive industry because they are large in size and heavy. Therefore, more research works have appeared along the line of innovating new advanced energy storage technologies.

Recently, the creation of multifunctional materials opens a new research area in the advanced energy storage systems [1]. The multifunctional material is defined as a material with an integration of structural and non-structural functions. The combination of functions and properties into an individual structure offers significant advantages of weight and energy saving. The non-structural functions can be optical, electrical, magnetic, thermal etc. As a result, the multifunctional materials have a great potential to be applied in many areas, for examples healthcare, security, energy, and packaging and military. These kinds of materials would bring engineered systems to a higher level with a better functionality and adaptability in the future. Therefore, the realization of multifunctional materials raises the greatest attention in different research and engineering fields.

From the multifunctional perspective, carbon fibre reinforced composite (CFRP) plays a critical role in developing a load-carrying structure with the capacitive function. The attraction of using carbon materials to replace conventional conductive materials as electrodes is arisen from their unique combination of high electrical conductivity and surface area range, as well as their comparably stability in different chemical solutions, which are acidic or basic, and various thermal conditions [2,

3]. Embedded battery composites (EBC) and structural dielectric capacitors are typical examples of electrical energy storage technologies by using CFRP [4-6].

The purpose of this paper is to summarize the state of knowledge on the multifunctional materials for structural dielectric capacitors and structural electric double layer capacitors (EDLC). Experimental results shown in literatures and common methodologies to optimize the overall performance of multifunctional materials are also presented. Moreover, existing technical challenges for the development of multifunctional energy storage systems are discussed separately in this paper.

2. Multifunctional energy storage systems

Conventional dielectric capacitors have lower energy density as compared to batteries and supercapacitors. However, they have higher power density than those of batteries because there is no redox reaction but only electron transmissions involved in their charging and discharging process. As a result, the supercapacitors have been developed to give an intermediate energy and power densities between the batteries and dielectric capacitors. Apart from the electrical performance, lifetime is another important criteria for energy storage systems. Since there are chemical depletions at conductive electrodes in the charging and discharging process of batteries, their lifetimes are limited as compared to structural dielectric capacitors and structural supercapacitors. In addition, most of the batteries are restricted to work in various thermal conditions, resulting in a narrow range of applications. Although the energy densities of structural dielectric capacitors and structural supercapacitors are not as high as that of batteries, electronics are allowed to be integrated into their structures by using CFRP for electrodes, leading to a significant space saving [7]. Hence, multiple carbon fibre layers used in structural dielectric capacitors and supercapacitors could provide more extensive capacitances than conventional energy storage methods due to the increase in the surface area of electrodes. Therefore, this paper is focused on multifunctional composite materials for structural dielectric capacitors and structural supercapacitors only.

The energy and power densities of energy storage systems are important parameters in the electrical characterization. Most of the research works have been focused on achieving the high capacity-to-volume ratio of conventional energy storage systems, rather than investigating their mechanical performances. Since the multifunctional composite materials are proposed for structural applications, their mechanical performance is becoming as important as their electrical performance. Therefore, both mechanical and electrical properties of multifunctional composite materials should be investigated simultaneously.

Multifunctional efficiency (η_{mf}) provides the definition of a mass-saving multifunctional design, as shown in Equation (1), and fair comparisons on the multifunctional performance, which is the evaluation of mechanical and electrical performance at the same time, between different structural

power composites [5]. In the analysis, the electrical efficiency (η_e) of multifunctional material is the ratio of its specific energy density to that of conventional capacitor while the mechanical efficiency (η_s) of multifunctional composite material is the ratio of its specific mechanical performance to that of conventional structure. If the multifunctional efficiency of material exceeds unity, there would be a weight reduction achieved by the new advanced energy storage system as compared to the conventional system, which consists of both capacitive and structural components. In the following sections, the introduction of structural dielectric capacitors and structural supercapacitors, and overviews on modifying their mechanical and electrical properties are given.

$$\eta_{mf} = \eta_e + \eta_s \quad (1)$$

Where $\eta_{mf} > 1$ for mass-saving multifunctional design.

3. Structural dielectric capacitors

3.1 Introduction

In the dielectric capacitor, electrostatic energy is stored in the form of electric charges at two or more electrically conductive plates, which are separated by a dielectric material, as presented in Fig. 1. The capacitance of dielectric capacitors is highly depended on the overlapping area between two conductive plates and separation between them [8]. The purposes of dielectric separator are to avoid any contact between two conductive plates and to obtain a high capacitance from the dielectric polarization. As mentioned above, since only electron transmission takes place in the charging and discharging process of dielectric capacitors, their cycle life and recharge function are longer and faster as compared to the batteries [9]. Furthermore, the electrical energy can be stored in the dielectric capacitors over long charging time and discharged within a short period of time [8]. However, the energy density of dielectric capacitor is relatively low. As a result, it is usually used for flattening short-term variations in a flow of the electrical energy rather than a bulk energy storage [10]. With the development of multifunctional composites, more energy can be stored in the structural dielectric capacitors and their multifunctional characters could expand their applications to the automotive industry and unmanned aerial vehicles (UAV).

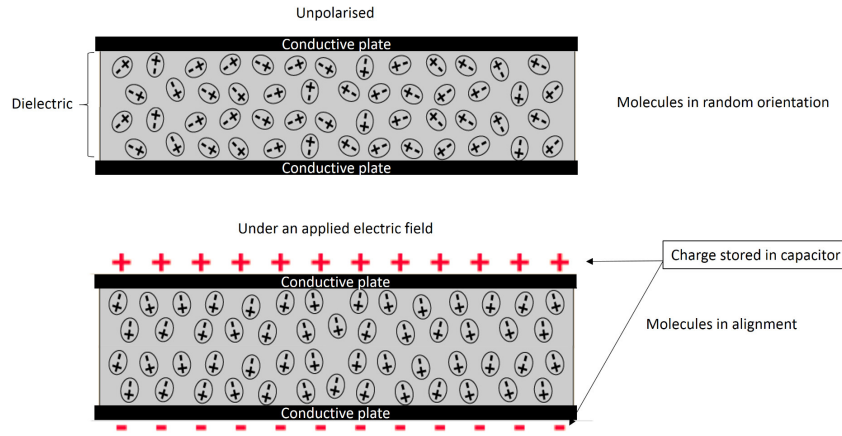


Fig. 1 – A schematic configuration of a dielectric capacitor

In previous studies, two different configurations of existing structural dielectric capacitors were investigated, as shown in Fig. 2. For a glass fibre reinforced prepreg (GFRP) dielectric capacitor, GFRP is used for the dielectric material and supporting structure while metallized polymer films (MPF) are used for conductive electrodes. The dielectric permittivity of GFRP can be measured experimentally or calculated by using the rule of mixture with the assumed values of the permittivity of epoxy and glass fibres. For a polymer film dielectric capacitor, different polymer thin films can be used for the dielectric materials while CFRP is employed for conductive electrodes as well as structural support. This kind of lightweight design incredibly reduces the energy consumption in operations. Although the energy density of structural dielectric capacitors is relatively low as compared to other structural energy storage systems such as embedded battery composites [4, 11] and structural supercapacitors [12], the high consistency of constituents in entire structure and the use of solid-state dielectrics could achieve high mechanical performance. Therefore, it could aim to be a load-carry composite for energy storage applications such as advanced structures for automobiles and UAV [7, 13].

The potential of structural dielectric capacitors for load-carrying composites have been demonstrated since 1999 [14]. However, dielectric materials such as polyethylene terephthalate (PET) and epoxy used for structural dielectric capacitors in the literature usually have relatively low dielectric permittivity, resulting in the low energy density and multifunctional efficiency. In addition, the interfacial bonding between dielectrics and electrodes restricts the mechanical performance of structural dielectric capacitors. To optimize the overall performance of structural dielectric capacitors, the dielectric permittivity of dielectric separator and the interfacial bonding between electrodes and dielectrics have to be modified. In the following section, experimental findings, in terms of factors which would affect the mechanical and electrical properties of structural dielectric capacitors, conducted by other researchers are given.

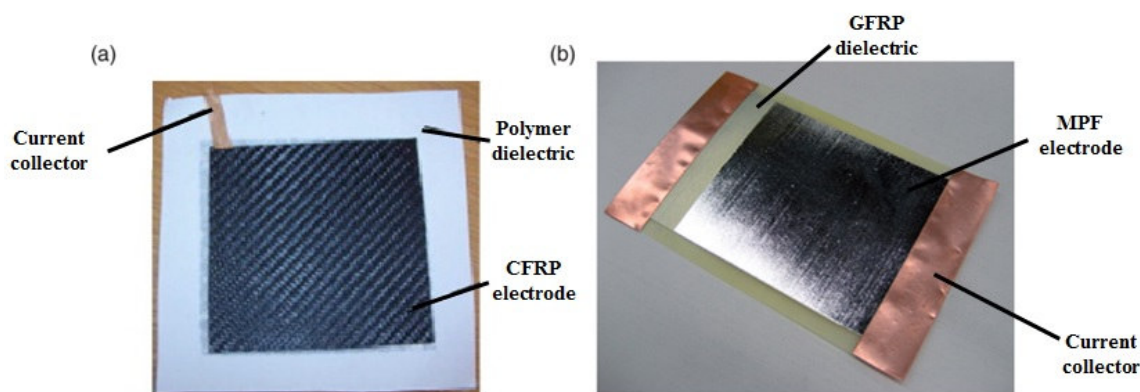


Fig. 2 - Common configurations of current structural dielectric capacitors: (a) polymer film dielectric capacitor[15]; (b) GFRP dielectric capacitor [1]

3.2 Effect of electrode materials on the electrical performance of dielectric capacitors

In the dielectric capacitors, factors such as the type of metals used for electrodes and surface resistivity, could affect their electrical properties, especially electric breakdown strength (EBD) [16-18]. The relationship between EBD of dielectric capacitors and work function of electrodes have been studied by other researchers [16, 17, 19]. It is concluded that EBD of dielectric capacitors is directly proportional to the work function of metal, which is used for electrodes.

To study the effects of electrode characteristics, O'Brien et al. [20] carried out a comprehensive evaluation on the electrical properties of structural dielectric capacitors by using metallized paper and biaxially oriented polypropylene (BOPP) for structural electrodes, and GFRP for the dielectric material, as shown in Fig. 3. The metallization of either Aluminum (Al), Zinc (Zn) or a Zn-Al alloy in various thicknesses from 4.3 to 12 nm was applied on the electrode films. The summary of the electrical properties of GFRP based structural dielectric capacitors is presented in Table 1. It shows that the electrical performance of Zn-Al metallized specimens is better than those of Al and Zn metallized specimens. Moreover, it is observed that the energy density of GFRP dielectric capacitors increases with increasing the surface resistivity of metallized films. Compatibly, Chen [21] also indicated that EBD of dielectric capacitors could be enhanced with an appropriate surface resistivity for balancing the capability of self-healing and electrical conductivity of metallized electrodes.

Therefore, it is proven that thickness and surface resistivity of metals used for conductive electrodes are key parameters on the electrical performance of structural dielectric capacitors. As a result, it is expected that the fibre volume fraction of CFRP electrodes used in the structural dielectric capacitors could also be one of the factors on their electrical performance.

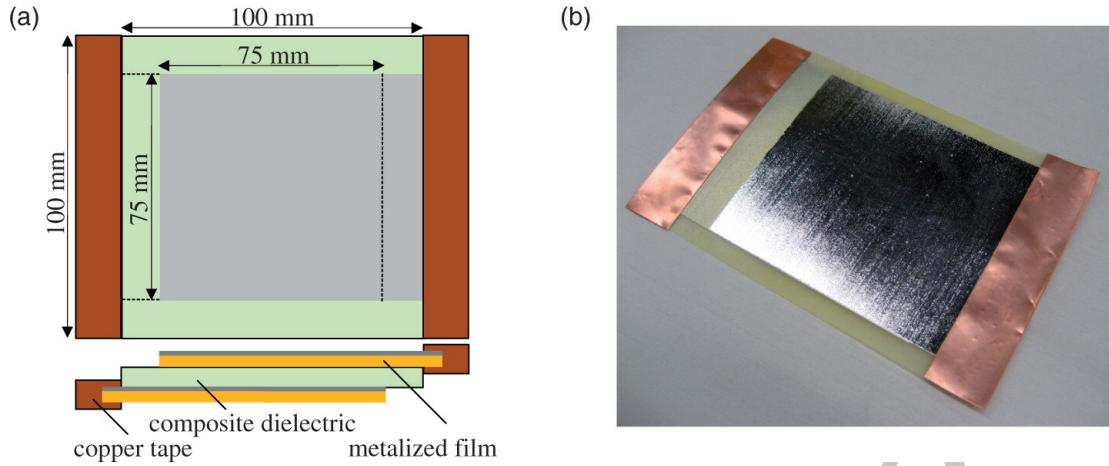


Fig. 3 – (a) a schematic configuration; (b) a fabricated GFRP dielectric capacitor [5]

Table 1 - Electrical properties of GFRP based structural dielectric capacitors [20]

Electrode material	Metal thickness (nm)	Resistivity ($\Omega/\text{sq.}$)	Capacitance (nF)	Energy density (J/g)
Zn metallized BOPP	6-12	5-10	1.09 ± 0.358	0.113 ± 0.030
Zn-Al metallized BOPP	4.3-8.7	5-10	1.47 ± 0.047	0.252 ± 0.052
Al metallized BOPP	3.4-6.8	4-8	1.44 ± 0.055	0.177 ± 0.045
Al metallized Paper	27-54	0.5-1	1.94 ± 0.131	0.091 ± 0.061
Al metallized Paper	7-14	2-4	1.80 ± 0.082	0.274 ± 0.111

3.3 Effect of separator materials on the overall performance of dielectric capacitors

Parameters of dielectric separators, such as dielectric permittivity and thickness, are considered as important factors on the mechanical and electrical properties of structural dielectric capacitors. At the beginning of the development of structural dielectric capacitors, Luo and Chung [7] demonstrated the preliminary test for energy storage ability of structural dielectric capacitors by using CFRP for conductive electrodes and different papers for dielectric separators. Later, Carlson et al. [15] and O'Brien et al. [5] developed other structural dielectric capacitors by using various polymer thin films and GFRP for dielectric materials respectively.

For the electrical properties of structural dielectric capacitors, as presented in Table 2, it is observed that the average energy density of polymer film dielectric capacitors is almost 80 times more

than those of using impregnated papers for the dielectric. This is because of the superior EBD of polymer films as compared to the impregnated papers. In addition, the energy density of all GFRP specimens are higher as compared with PET film specimens although they have relatively low capacitances and moderate breakdown voltages. This may be attributed to the extremely thin metallized electrodes used in the GFRP structural dielectric capacitors, leading to a significant mass reduction.

Furthermore, Carlson et al. [22] studied the electrical properties of PET-film dielectric capacitors in various dielectric thicknesses (50, 75 and 125 μm). Table 2 shows that the capacitance of specimens decreases with increasing the thickness of dielectric separators. In addition, the 125 μm PET-film specimen has the highest breakdown voltage but lowest EBD as compared to 50 μm and 75 μm PET-film specimens. It may be because the volume of 125 μm PET-film specimen is larger than those of 50 μm and 75 μm PET-film specimens, there is a high possibility of having flaws, which initiate an earlier dielectric breakdown, in the 125 μm PET-film specimen. Consistently, Palomo et al. [23] also determined that the EBD of epoxy based dielectrics decreases with increasing their thickness, as presented in Fig. 4. Besides, the capacitance of 125 μm PET-film sample is the lowest but its specific energy density is still the highest as compared to 50 μm and 75 μm PET-film specimens due to the compensation from the relatively high breakdown voltage.

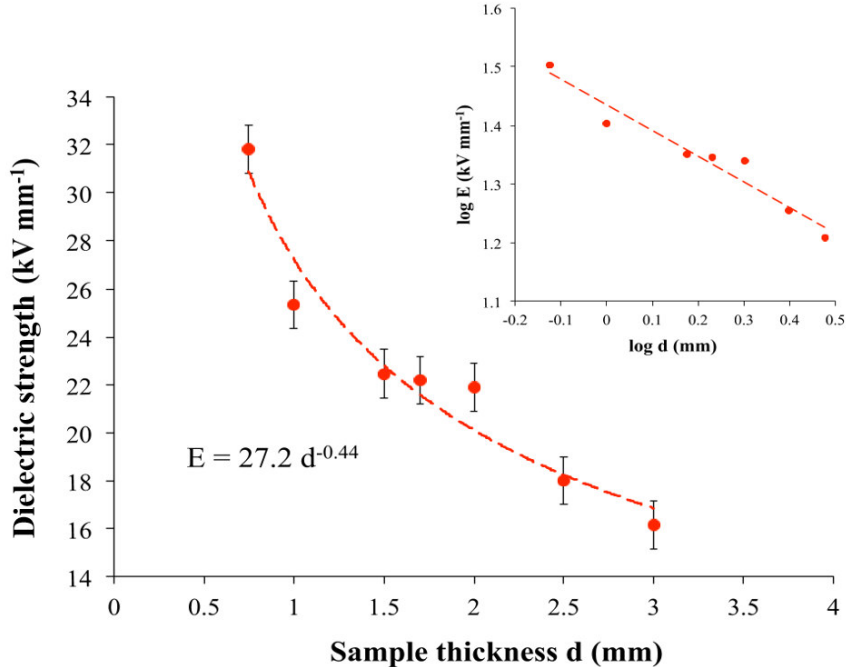


Fig. 4 - Relationship between thickness and dielectric strength of the epoxy sample [23]

Table 2 - Electrical properties of structural dielectric capacitors [5, 15]

Dielectric material	Dielectric thickness (mm)	Capacitance ($\mu\text{F}/\text{m}^2$)	EBD (kV/mm)	\bar{E} (J/g)
Electrode material: CFRP				
Paper (40 g/m ²)	0.071	0.712	7.75	0.00013
Paper (80 g/m ²)	0.089	2.466	8.76	0.00088
Paper (150 g/m ²)	0.173	0.766	9.77	0.00120
PA film	0.050	0.868	156	0.03400
PET film	0.019	1.860	337	0.05200
PC film	0.155	0.206	183 [#]	0.08900 [#]
PET film	0.050	0.447	292	0.06
PET film	0.075	0.300	299	0.08
PET film	0.125	0.193	235	0.09
Electrode material: MPF				
GFRP ($V_f = 20.6\%$)	0.140	0.286	164	0.34
GFRP ($V_f = 27.9\%$)	0.160	0.256	152	0.28
GFRP ($V_f = 33.4\%$)	0.150	0.293	165	0.34
GFRP ($V_f = 49.5\%$)	0.110	0.444	63	0.05
GFRP ($V_f = 61.6\%$)	0.220	0.231	107	0.17

[#] The samples had not failed at maximum voltage in the breakdown tests

For the mechanical properties of structural dielectric capacitors, interlaminar shear strength (ILSS) and tensile properties are the most important factors in their structural characterization. Since structural dielectric capacitors are made of laminates, delamination is the major failure mode and restricts their mechanical properties, especially tensile properties. Therefore, a good interfacial adhesion is the key to provide excellent stress distributions between constituents and achieve the high mechanical performance. Experimental findings on the mechanical properties of structural dielectric capacitors conducted by Carlson et al. [15] and O'Brien et al. [5] are presented in Table 3. It is observed that the tensile modulus and strength of GFRP dielectric capacitors increase with increasing

the fibre volume fraction of GFRP dielectric, which is consistent with the rule of mixture of composite materials. On the other hand, Carlson et al. observed that there was a great knockdown in the tensile stiffness and ultimate tensile strength (UTS) of PET-film dielectric capacitors as compared to the reference value of CFRP. Meanwhile, the tensile stiffness of PET- film dielectric capacitors decreases with increasing the dielectric thickness. It may be due to the presence of a relatively weak PET film between two CFRP electrodes. Delamination behavior between CFRP electrodes and dielectric separators, as shown in Fig. 5, was also found in the tensile test. The result is compatible with the study conducted by Kim and Lee [24] on investigating the influence of interleaving films on the mechanical properties of CFRP. They suggested that the reduction in the tensile strengths could be caused by decreasing the fibre volume fraction of interleaved specimens, leading to the low mechanical performance.

Table 3 - Mechanical properties of the structural dielectric capacitors [5, 15]

Dielectric material	Dielectric thickness (mm)	Young's modulus (GPa)	UTS (MPa)	ILSS (MPa)
Electrode material: CFRP				
PET film	0.050	42.7	354	29.5
PET film	0.075	44.6	377	30.6
PET film	0.155	36.5	317	32.5
CFRP reference	-	56.1	631	54.4
Electrode material: MPF				
GFRP ($V_f = 20.6\%$)	0.140	6.0	118	-
GFRP ($V_f = 27.9\%$)	0.160	9.7	188	-
GFRP ($V_f = 33.4\%$)	0.150	13.4	156	-
GFRP ($V_f = 49.5\%$)	0.110	19.1	293	-
GFRP ($V_f = 61.6\%$)	0.220	23.8	388	-

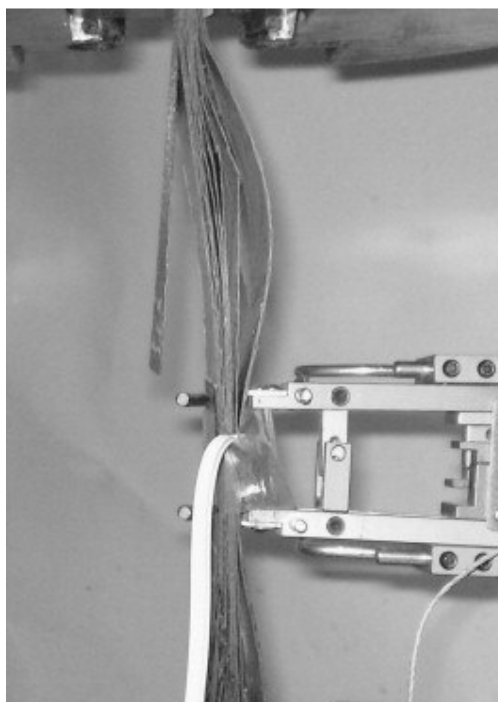


Fig. 5 - Failure modes of a tensile specimen [22]

3.4 Effect of cure cycles on the electrical performance of structural dielectrics

Apart from the characteristics of electrodes, parameters in the fabrication of structural dielectric capacitors also play the critical roles in the overall performance. For the mechanical performance, effects of cure cycles and void content of structural composites have been studied comprehensively [25-28]. Generally, the mechanical properties of structural composites could be enhanced by using the high cure pressure due to the reduction of void fractions. Besides, it is shown that the void fraction of polymer has significant influences on their electrical properties [29-31]. Palomo et al. [23] observed that EBD of epoxy based dielectric capacitors is directly proportional to their degree of crosslinking, reflected by their glass transition temperature (T_g), as presented in Table 4. It could be explained by the reduction of chain movements of epoxy at the high crosslinking degree, resulting in a relatively weak ability of polarization but high EBD of epoxy dielectrics [23, 32].

Table 4 - Cure conditions and corresponding properties of epoxy based dielectric [23]

Curing condition	EBD (kV mm⁻¹)	T_g (°C)
1 st step: 80°C for 3 hours; 2 nd step: 140°C for 8 hours	29 ± 1	97
1 st step: 80°C for 3 hours; 2 nd step: 140°C for 9 hours	22 ± 1	88
1 st step: 80°C for 3 hours; 2 nd step: 140°C for 10 hours	27 ± 1	96
1 st step: 80°C for 3 hours; 2 nd step: 140°C for 20 hours	25 ± 1	94

Recently, O' Brien et al. [20] evaluated the electrical properties of GFRP dielectric capacitors by varying the cure condition of fabrication, as shown in Table 5. It is observed that the capacitance and energy density of GFRP dielectric capacitors increases with increasing the cure pressure. It could relate to the elimination of air, which has low dielectric permittivity, entrapped in the GFRP dielectric, leading to the reduction of void content in composite [26, 28, 33], as presented in Fig. 6. In addition, it is suggested that a uniform spacing between two conductive electrodes could be achieved at the high cure pressure condition due to the straightening of crimps presented in the woven fabrics, resulting in a smaller thickness of GFRP dielectric and thus improved capacitance.

To conclude, the influences of cure conditions of epoxy and GFRP dielectrics on the electrical properties of dielectric capacitors were investigated. It is supposed that the fabrication of structural dielectric capacitors, in which CFRP electrodes are employed for conductive electrodes, could also affect their mechanical and electrical properties.

Table 5 - Electrical performance of GFRP structural dielectric capacitors under different cure conditions [20]

Electrode material	Pressure (kPa)	Temperature (°C)	Duration (min)	Post-curing	Capacitance (nF)	\bar{E} (J/g)
Al-metallized polyimide	345	130	90	N/A	0.042±0.029	0.023±0.016
	1379	130	90	N/A	0.197±0.143	0.101±0.073
	1379	180	60	N/A	0.403±0.091	0.231±0.053
	1379	149	60	170°C for 60 min	0.575±0.201	0.332±0.116

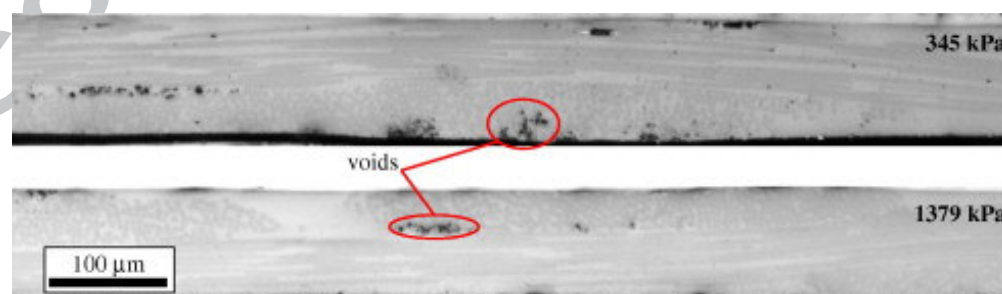


Fig. 6 - Micrographs of polished cross-section of autoclaved specimens [20]

3.5 Effect of nanoparticles on the multifunctional performance of dielectrics

Nanoparticle filled polymer dielectrics have been continuously developed for more than twenty years to possess their ultimately high EBD than those of micron-sized particle filled because of the high surface to volume ratio of nanoparticles [34-41]. In the dielectric capacitors, ceramics and polymers are mainly used for dielectric materials. However, the application of ceramic based dielectric capacitors are limited due to their relatively low EBD. For a polymer dielectric capacitor, it has a higher EBD but lower dielectric permittivity, ranging from 3-6, as compared to the ceramic based dielectric capacitor [38, 42-45].

Lovell [46] determined that the mismatch of dielectric permittivity between reinforcements and matrix reduced EBD of the reinforced epoxy polymers due to the formation of field enhancement. Therefore, the addition of nanoparticles into the matrix-phase of reinforced composite could rematch the dielectric properties between reinforcements and matrix and eliminate the local intensification, which initiates the dielectric breakdown, in the reinforced composite. Moreover, the dielectric permittivity of matrix could be increased by adding ferroelectric ceramic nanoparticles (e.g. Al_2O_3 , TiO_2 , BaTiO_3) with high dielectric permittivity, resulting in the high capacitance. However, a large quantity of ferroelectric ceramics is required to offer a high dielectric permittivity, which causes an increase in the mass of dielectric. In contrast, a little amount of conductive nanoparticles, including metallic powders and carbon-based materials, into polymer matrix can ultimately enhance their dielectric permittivity due to the effect of percolation threshold [34]. Therefore, conductive nanoparticles are proposed to replace the traditional ferroelectric ceramics. Typical dielectric nanoparticles and conductive nanoparticles, such as carbon nanotubes (CNT) and exfoliated graphite (EG), are commonly used for enhancing the dielectric permittivity of epoxy-based nanocomposites, as listed in Table 6.

On the other hand, the mechanical properties of nanoparticle reinforced composites have been investigated by other researchers [47-49]. It is shown that the flexural and tensile properties of nanoparticle reinforced composites were improved by adding a small portion of nanoparticles. Furthermore, the interfacial bonding between fibres and matrix could be significantly improved by using nanoparticles as the second reinforcement in the fibre reinforced composite, as presented in Fig. 7. Therefore, it is expected that the introduction of nanoparticles into structural dielectric capacitors could be an effective modification to improve their mechanical and electrical properties.

Table 6 - Dielectric properties of epoxy-based nanocomposites

Nanoparticle	Concentration	ϵ_r'	EBD (kV/mm)	$\sigma_{a,c}$ (S/m)	Ref.
Conductive nanoparticles					
Ag	0.03 wt%	4.6	36	-	[50]
Ag	23 vol%	300	1.25	5×10^{-5}	[51]
Al	40 vol%	450	23	-	[52]
CNT	0.2 vol%	3.75	-	-	[42]
CNT	0.50 wt%	1328	-	7×10^{-2}	[34]
CNT	1 wt%	5.5	-	-	[53]
EG	2 wt%	12.0	-	6×10^{-2}	[36]
Ferroelectric ceramic nanoparticles					
Al ₂ O ₃	0.1 wt%	4.6	-	-	[41]
Al ₂ O ₃	1 wt%	4.7	-	-	[44]
xAl ₂ O ₃ .ySiO ₂	40 wt%	6.0	-	1.25×10^{-9}	[54]
BaTiO ₃	5 phr	6.0	-	-	[55]
BaTiO ₃	7 phr	7.7	-	-	[38]
BaTiO ₃	30 vol%	10.9	200	2×10^{-11}	[45]
SiO ₂	0.1 wt%	4.5	-	-	[41]
TiO ₂	1 wt%	4.8	-	-	[44]
TiO ₂	5 wt%	5.3	30.15	-	[35]
TiO ₂	5 wt%	6.5	-	-	[56]
ZnO	5 wt%	5.0	-	-	[35]

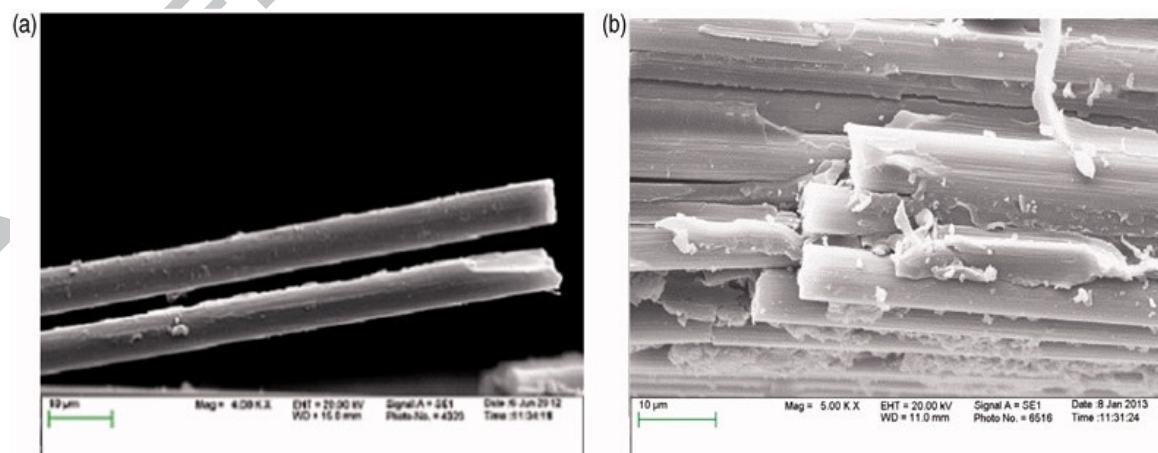


Fig. 7 - SEM micrographs of (a) neat; (b) CNT reinforced CFRP [47]

3.6 Effect of surface treatments of the interfacial bond between electrodes and dielectrics

The interfacial adhesion between electrodes and dielectrics is one of the most important factors in the mechanical characterization of structural dielectric capacitors. Therefore, the surface modifications on the fibre reinforcements and dielectrics are proposed to strengthen their interfacial bonding with the matrix. Typical surface modifications for polymers and fibres include abrasions, chemical methods [57, 58], and plasma treatments [59, 60]. For physical surface treatments, such as abrasions, their objectives are to remove contaminants on the surface of specimens, and to increase the mechanical interlocking between two contacting phases by increasing their surface roughness. Besides, the chemical treatments aim to improve the coupling of matrix with fibres by exposing reactive groups on the surface of fibres [61]. In physicochemical methods, such as plasma treatment, their purposes are to generate active sites on the surface of specimens, in which chemical bonds could be formed, and to provide specific interactions at the interface between two phases by using an ionized gas [22, 62].

Yavirach et al. [59] studied the shear strengths of different composites and polymers by using different plasma treatments, including oxygen, argon, nitrogen and a mixture of helium and nitrogen plasma groups. It is noticed that the polar functional groups could be generated on the surface of polymers, resulting in increasing their surface wettability and tensile-shear bond strength. For the structural dielectric capacitors, Carlson et al. [6, 15, 22] tried to modify the interfacial interaction between CFRP electrodes and PET-film dielectrics by using N₂ plasma activation. Table 7 shows that there is a drop in the ILSS of interleaved specimens as compared to the reference CFRP. It is due to the poor adhesive properties between CFRP electrodes and PET films. However, there is no noticeable improvement on the ILSS of interleaved specimens before and after the N₂ plasma treatment. It could be concluded that the N₂ plasma activation is not a proper method to modify the surface properties of PET films. Since the interfacial bond between electrodes and dielectrics is a critical parameter of the mechanical performance of structural dielectric capacitors, other possible surface treatments should be developed to enhance the surface adhesion between two phases.

Table 7 - Mechanical properties before and after plasma treatment of PET-film dielectric capacitors [22]

PET film (μm)	Young's modulus (GPa)		UTS (MPa)		ILSS (MPa)	
	Before	After	Before	After	Before	After
CFRP (Ref)	56.1	-	631	-	54.4	-
50	42.7	42.5	354	320	29.5	32.0
75	44.6	41.7	377	344	30.6	30.7
125	36.5	37.8	317	339	32.5	31.8

3.7 Effect of mechanical influences on the capacitive function of structural capacitors

The structural dielectric capacitors are the utilization of capacitive elements for a load-bearing structure. As a result, mechanical influences, such as tensile and compression loadings, on the structural dielectric capacitors in real-life applications could alter their capacitive functions. It is therefore important to analyze the effects of mechanical stresses on the electrical performance of structural dielectric capacitors.

Nishijima and Hara [63] investigated the dielectric properties of GFRP and PET dielectrics through compressive and tensile stress tests under various environmental conditions, including room temperature and cryogenic conditions, as presented in Fig. 8. In the compressive test, a mechanical stress was applied on the specimens in the thickness direction. It is shown that EBD of specimens firstly increases with increasing the compressive loading but decreases after reaching a maximum point. It is suggested that the decrease in EBD of GFRP and PET specimens at the high compressive stress could be caused by the formation of voids and cracks. On the other hand, EBD of GFRP and PET specimens decreased with increasing the tensile stress level. It is suggested that the difference of EBD under different types of stresses could relate to the change in the crack initiation and propagation. This is because the cracks, which are perpendicular to the applied stress direction, grow easier under the tensile loading as compared to the compressive stress. Therefore, EBD of specimens under the tensile loading is lower as compared to the compressive stress.

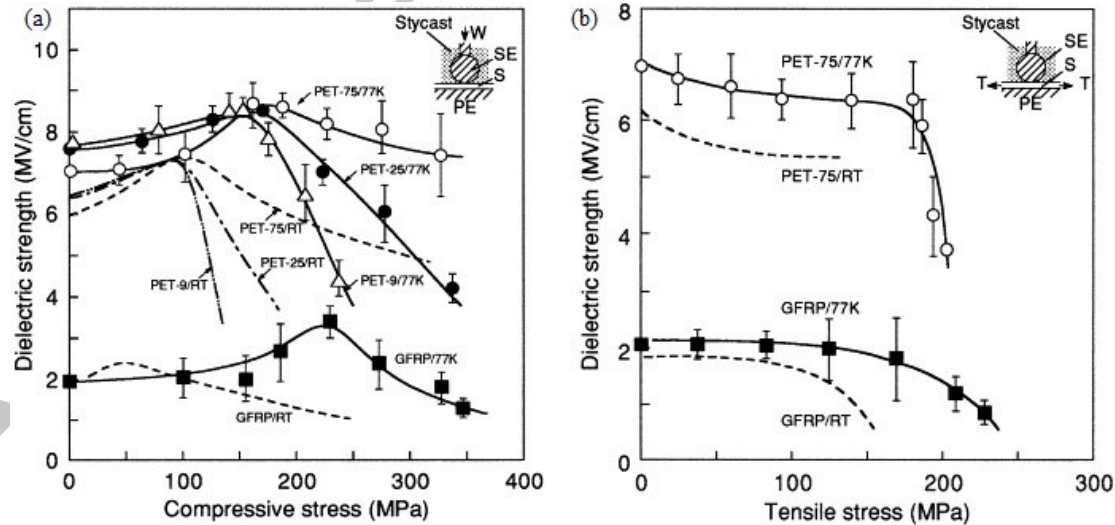


Fig. 8 - Effects of (a) tensile and (b) compressive stresses on EBD [63]

Furthermore, Carlson et al. [64] studied the effect of mechanical loads on the capacitance of PET-film dielectric capacitors. The capacitance measurements of specimens were taken before, during and

after the tensile loading, as presented in Table 8. The capacitance of specimens at the loaded state is 50% less as compared to the undamaged specimen due to air, which has the low relative dielectric permittivity, filled in the opening matrix cracks of specimens. Unexpectedly, the capacitance of unloaded specimens is recovered and even higher than that of undamaged specimens. It could be attributed to the permanent plastic deformation, which led to a reduction in the dielectric thickness, caused by the tensile loading on the specimens. More importantly, the result shows the ability of structural dielectric capacitors to retain their electrical function under a loading condition.

Table 8 - Capacitances of NaOH treated structural capacitor under a tensile loading [76]

PET-film thickness (μm)	Capacitance before loading ($\mu\text{F}/\text{m}^2$)	Capacitance under loading ($\mu\text{F}/\text{m}^2$)	Capacitance after loading ($\mu\text{F}/\text{m}^2$)
50	0.008	0.004	0.011

3.8 Challenges and further developments

For the GFRP dielectric capacitors (refer to Fig. 2 and 3), epoxy, which is a crosslinking polymer, is used as one of the dielectric materials as well as the supporting structure. Therefore, the structural properties of this kind of structural dielectric capacitor could be enhanced at the high crosslink degree of epoxy. However, there could be a loss in the polarizability of epoxy due to the formation of large polymer chains, which is more difficult to shift their equilibrium positions to cause the dielectric polarization, resulting in the low energy and power density. Therefore, there is a conflict between the mechanical and electrical properties of structural dielectric capacitors.

Besides, the energy density of structural dielectric capacitors is relatively low as compared to traditional capacitors. To achieve the high electrical performance, an alternative approach is to introduce nanoparticles into matrix as the secondary reinforcement for matching the dielectric properties between conductive electrodes and matrix. In addition, it is investigated that the integration of nanoparticles into matrix could improve the mechanical properties, such as interlaminar fracture toughness and compression-after-impact, of fibre reinforced composites [65]. Therefore, it is expected that the introduction of nanoparticles into matrix could be an effective method to enhance the overall performance of structural dielectric capacitors.

Moreover, it is indicated that there was no comprehensive study on the electrical performance of structural dielectric capacitors. In previous studies, researchers have focused on the capacitance, EBD and energy density of structural dielectric capacitors. However, a detailed evaluation on other electrical properties, such as rate response and cycle stability, of structural dielectric capacitors has not been conducted to-date. As a result, in-depth study on the electrical performance of structural dielectric capacitors are required.

Furthermore, delamination failure is the major concern in the laminated composites because the mechanical strength of fibre reinforced composites could be limited by the interfacial properties between laminates [65]. Therefore, the mechanical performance of GFRP and polymer film dielectric capacitors could be ultimately improved by strengthening the interfacial bond between laminates. For the GFRP dielectric capacitors, the interlaminar strength of GFRP could be enhanced by introducing nanoparticles into matrix as mentioned above [65, 66]. For the polymer film dielectric capacitors, other surface treatments should be selected to enhance the adhesion between CFRP electrodes and polymer film dielectrics.

4. Structural supercapacitors

4.1 Introduction

The supercapacitors can be divided into two groups, which are pseudo-capacitors and EDLC, basing on their energy storage methods. In the pseudo-capacitors, common materials used for conductive electrodes are transition-metal oxides, such as Ruthenium (Ru), Manganese (Mn) and Nickel (Ni), and conducting polymers, including polyaniline and polypyrrole [67-70]. The electrical energy is stored in the pseudo-capacitors by the redox reaction at the surface of electrodes, which is similar to the working principle of batteries. Therefore, there are chemical depletions at conductive electrodes in the charging and discharging process, resulting in a limited lifetime as compared to electrostatic energy storage systems. On the other hand, EDLC store electrical energy by the accumulation of electrostatic charges at the interface between electrodes and electrolyte [3]. The conductive electrodes are separated by an insulating separator and an ion-conductive but electrically insulating electrolyte is used for medium to allow the movements of ions in the EDLC, as shown in Fig. 9.

The movement of ions in aqueous or non-aqueous electrolytes is initiated by applying voltage on each side of conductive electrodes, resulting in the formation of electric field. After a period of time, two thin layers, as known as double layers, are formed due to the high concentration of ions at the interfaces between electrodes and electrolyte [71]. The charges are accumulated at the surface of electrodes and consequently electrical energy is stored. In EDLC, the charge separations are extremely short, ranging from 0.3 to 0.8 nm. In addition, conductive electrodes used for EDLC are usually activated to increase their surface area. As a result, more charges could be allowed to access into the pores on the surface of electrodes. Therefore, the high capacitance of EDLC could be achieved. Furthermore, the power density of EDLC is higher as compared to the batteries because only rapid ion-movement to and from the surface of electrodes is involved in their charging and discharging process [3]. However, the power density of EDLC is lower than that of dielectric

capacitors. Therefore, the role of EDLC is to provide a compromise between dielectric capacitors and batteries to balance the energy density and power density as well as other criterion, such as lifetime, when comparing different energy storage systems.

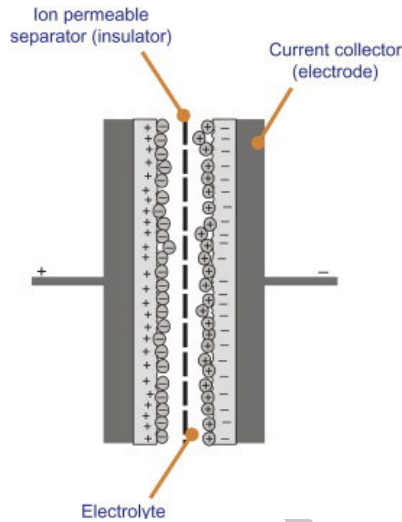


Fig. 9 – A schematic configuration of a EDLC [72]

With the continuous advancement of structural dielectric capacitors, more research works are focused on the development of structural EDLC [70, 73-77]. In EDLC, CFRP is employed for structural electrodes and an ion-permeable separator, such as a glass fibre mat, is used for separating two CFRP electrodes and containing various types of electrolytes, as presented in Fig. 10. Moreover, carbon fibre fabrics used for conductive electrodes of structural EDLC are usually activated to significantly increase their surface area due to the formation of pore in micro- or nano-scale, resulting in the enhanced capacitance. In the following sections, experimental findings on the surface treatments of carbon fibre, formulations of ionic electrolytes and development of insulating separators, which are conducted by other researchers, are presented.

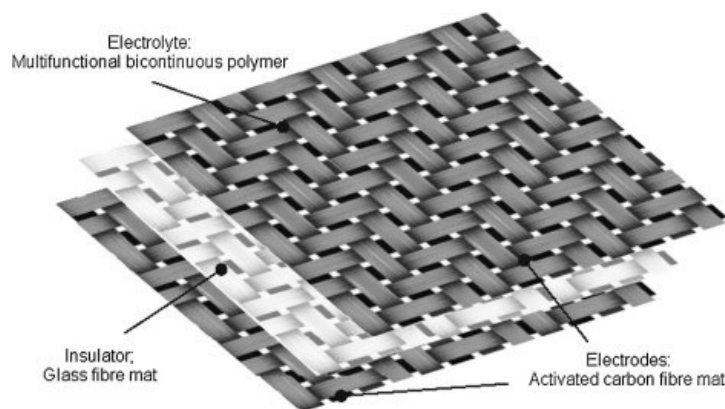


Fig. 10 - A schematic configuration of a structural EDLC [78]

4.2 Effects of surface treatments on electrodes

4.2.1 Activated carbon fibres (ACF)

To increase the capacitance of EDLC, commercial activated carbon fibres are usually used for conductive electrodes due to their high surface area to volume ratio and excellent electrical conductivity. As a result, the electrical performance of EDLC could be ultimately improved. However, most of the commercial activated carbon fibres are not suitable for structural applications since the heat treatment of carbonized materials are uncompleted, resulting in the weak mechanical properties of structural EDLC [73]. Therefore, research works are focused on developing more advanced surface treatments to the carbon fibres in order to increase their surface areas without weakening their mechanical properties [77].

The investigation on the mechanical and electrical properties of carbon fibres by using different surface modifications have been conducted by other researchers previously [3, 79-82]. The chemical activation is one of the most promising methods to introduce nanoscale pores on the fibre surfaces without significantly degrading their tensile properties, as shown in Fig. 11 [73, 78, 83]. In the chemical activation, carbon fibres are activated by immersing them into activating agents, such as potassium hydroxide (KOH) and sodium hydroxide (NaOH) [84]. The former shows a higher efficiency in activating carbon fibres with a low burn-off level, which is defined as the mass difference between untreated and activated carbon fibres, as compared with the latter [78, 85].

Shirshova et al. [78] compared the mechanical and electrical properties of structural EDLC, fabricated by using untreated carbon fibre fabric (CF), KOH activated carbon fibre fabric (ACF) and industrially activated carbon fibre fabric (IACF) for structural electrodes and poly(acrylonitrile) (PAN) gel electrolyte, poly(ethylene glycol) diglycidyl ether (PEGDGE) crosslinked electrolyte or epoxy based resin MVR444 (structural baseline) for matrix. In order to improve the electrical performance of structural EDLC, PAN polymer gel electrolyte was prepared by using propylene

carbonate (PC) for plasticizer, ethylene carbonate (EC) as solvent and lithium salts (LiTFSI). The effects of activation methods on the properties of carbon fibres, as shown in Table 9, and composites, presented in Table 10, were investigated. The electrochemical characterization on carbon fibres was performed by using a three-electrode system at room-temperature for cyclic voltammetry (CV) tests. Due to the high equivalent series resistance (ESR) of composites, charge-discharge tests were carried out, instead of CV tests, with 0.1V step voltage applied for 10s at room temperature.

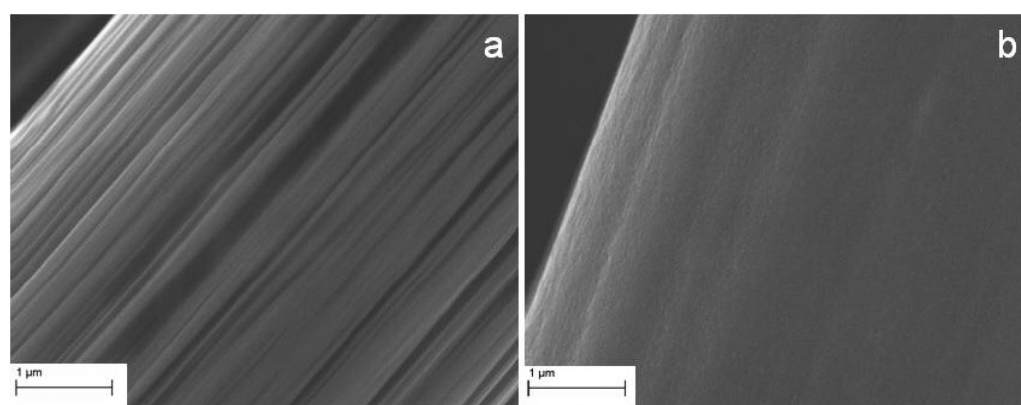


Fig. 11 - SEM images of (a) untreated and (b) KOH activated carbon fibres [83]

Table 9 – Electrical and mechanical properties of untreated and activated carbon fibres. The electrical properties was obtained using sweep rate of 5 mVs^{-1} within a potential window of $\pm 0.1\text{V}$. [78]

Carbon fibre	$S_{\text{BET}} (\text{m}^2 \text{g}^{-1})$	$d_{\text{pore}} (\text{nm})$	$\sigma_f (\text{MPa})$	E (GPa)	$\rho (\text{m}\Omega \text{cm})$	$C_{\text{sp}} (\text{Fg}^{-1})$
CF	0.21	5.6	3290	204	1.54	0.06
ACF	21.39	2.5	3960	207	1.79	2.63
IACF	1100	1.9	1100	40	329	0.10

S_{BET} : specific surface area; d_{pore} : average pore diameter; σ_f : mechanical single fibre strength; E: Young's modulus; ρ : electrical resistivity; C_{sp} : specific capacitance

Table 10 – Electrical and mechanical properties of various structural EDLC prototypes with the use of glass fabric as separator. Energy and maximum power densities were calculated by assuming a supplied voltage of 2.0V. [78]

Prototype	Electrolyte	C_{sp} (mFg ⁻¹)	\bar{F} (Whkg ⁻¹)	P (Wkg ⁻¹)	E_c (GPa)	X_c (MPa)
CF/PAN	PC/EC+0.1M LiTFSI	3.0	0.00087	90.40	-	-
ACF/PAN	PC/EC+0.1M LiTFSI	55	0.01054	71.63	-	-
CF/PEGDGE	0.1M LiTFSI	4.5	0.00020	8.82	24.57	19.44
ACF/PEGDGE	0.1M LiTFSI	1.4	0.000003	0.05	38.67	29.35
CF/MVR444	-	-	-	-	33.04	36.21
ACF/MVR444	-	-	-	-	51.07	49.84

\bar{F} : Energy density; P: maximum power density; E_c : compressive modulus normalized to $V_f = 55\%$; X_c : compressive strength

From Table 9, it is observed that the specific surface area of ACF increases from 0.21 m²/g (CF) to 21.39 m²/g. As a result, the specific capacitance of ACF increases from 60 mF/g (CF) to 2630 mF/g. In addition, the surface modification of carbon fibres enhanced the wettability of resin to ACF, resulting in the increased mechanical single fibre strength from 3290 MPa (CF) to 3960 MPa (ACF), which is consistent to the experimental results found by other researchers [77, 86]. Although the specific surface area of IACF is much higher than that of ACF, its specific capacitance is lower. It may contributed to the fibre breakage during handling because it is mechanically weak (Table 9), implying that IACF is not suitable to be the electrode material of structural EDLC.

The changes in electrical properties of prototypes using PAN and PEGDGE matrix, presented in Table 10, suggest ionic conductivity of matrix is significantly related to its state. For PAN-based prototype, the specific capacitance and energy density increases by using ACF, due to the increase in specific surface area of electrode, and electrolyte in the gel-state, due to the increase in ionic conductivity. However, both specific capacitance and energy density of PEGDGE-based prototypes decreases with the use of ACF. It could be explained by the poor accessibility of PEGDGE-based electrolyte, which is viscous, to pores on the activated surface in the composite fabrication, resulting in a high ESR and consequently poor capacitive performance [78]. On the other hand, the effect of fibre activation on the mechanical performance is positive. Both compressive strength and modulus are improved by using ACF instead of CF.

Nevertheless, the chemical activation is relatively complicated as compared to other surface treatments of carbon fibres because the critical damage on the microstructure of carbon fibres could be caused by the high burn-off level in the activation, resulting in the poor mechanical properties [73]. Since the soak times of carbon fibres and concentrations of activating agents used in the chemical activation are the significant influences on the burn-off levels of carbon fibres, the chemical activation of carbon fibres is therefore difficult to scale up.

4.2.2 Carbon nanotubes (CNTs)

Carbon nanotubes (CNTs) are usually introduced into conventional CFRP as a secondary reinforcement, which is in nanoscale, to form hierarchical composites with purposes of improving interfacial properties through surface modification [87]. Moreover, the applications of CNTs in electronic devices, especially supercapacitors, have been increased due to their excellent electrical conductivity [88-90]. Recently, Qian et al. [87] indicated the potential of CNTs to improve the electrical properties of multifunctional energy storage systems. As a result, more research works nowadays are focused on the development of CNTs reinforced CFRP electrodes for structural EDLC [12, 83, 91].

In general, there are two methods to introduce CNTs onto the surface of carbon fibres, which are (1) immersing the carbon fibres into CNT-containing sizing solutions and (2) allowing the direct in-situ growth of CNTs on the surface of carbon fibres, as shown in Fig. 12. The latter shows a better bonding between CNTs and fabrics as compared to the former due to the formation of intimate bond from CNTs to the host carbon fibres [12]. The comparison of specific surface area and capacitance of carbon fabrics between chemical activation and different CNTs modifications was compared by Qian et al [83] and presented in Fig. 13. Both specific surface area and capacitance increased after surface modifications and CNTs-grafting method had the best performance in improving the surface area and capacitance of carbon fabrics as compared to CNTs-growing modification and KOH activation. Besides, Qian et al. [92] showed that the interfacial bonds between CNTs-grafted carbon fibres and matrix were enhanced by the extension of CNTs into the surrounding matrix, resulting in the inhabitation of fibre micro-buckling [87]. Therefore, the delamination and compressive properties of CNTs reinforced CFRP could be significantly improved.

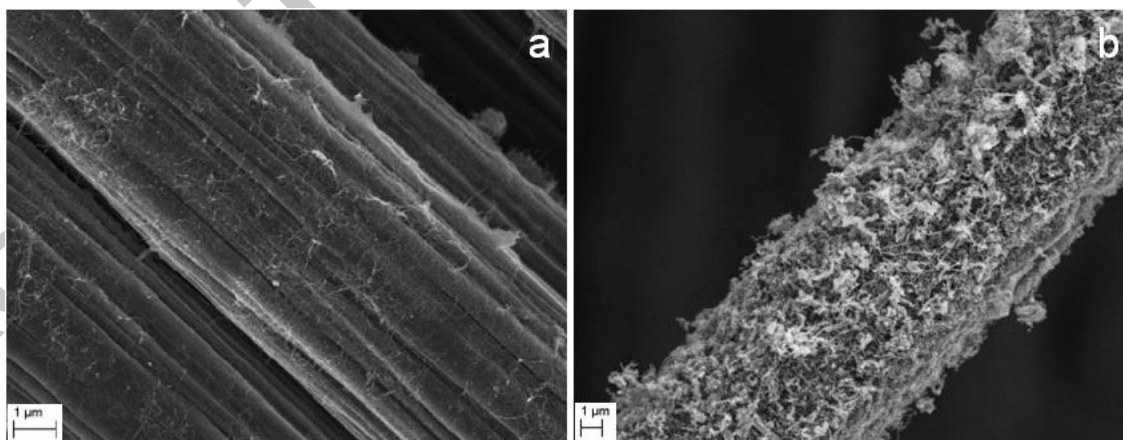


Fig. 12 - SEM images of (a) CNT-sized and (b) CNT-grafted carbon fibres [83]

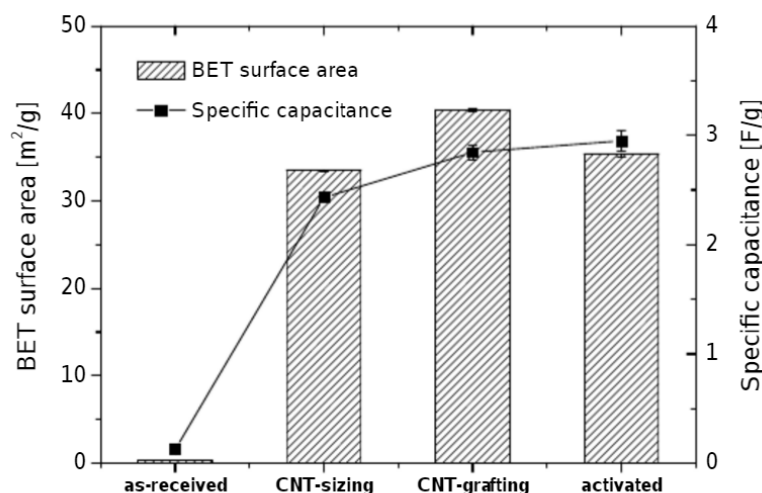


Fig. 13 – Specific surface area and specific capacitance of carbon fibre fabrics after different surface modifications [83]

Greenhalgh et al. [91] determined the mechanical and electrical properties of structural EDLC, made by using CNTs-modified carbon fibre for electrodes and epoxy (MTM57) for matrix, and their mechanical and electrical performance are summarized in Table 11. However, there was no information on the change in specific surface area before and after CNTs modifications. To enhance the ionic conductivity of specimens, epoxy resin was blended with ionic liquid (ILs) and LiTFSI. To characterize the electrical properties of structural EDLC, voltage chronoamperometry was used with an applied voltage of 0V to 1V for 4000s and 1V to 0V for another 4000s. From Table 11, it is obvious that there is a great knockdown in the specific capacitances of all specimens as compared to the typical graphene supercapacitors (100-250F/g) [93]. It is also unexpected that the specific capacitance of CNTs modified specimens (sets 3 and 4) are lower than that of multifunctional baseline (set 2). It could be related to the low accessibility of viscous epoxy based electrolytes to CNTs modified carbon fibres. For the mechanical performance, the shear strength and stiffness of multifunctional specimens (sets 2-4) are significantly reduced as compared to the structural baseline (set 1). It could be due to the presence of ionic electrolytes in the multifunctional specimens. However, there is the recovery of mechanical properties of CNTs reinforced multifunctional specimens (sets 3 and 4) by introducing CNTs onto the surface of carbon fibres.

Although the mechanical performance of structural EDLC could be improved by grafting CNTs on the carbon fibres, there are inverse effects on their electrical properties. It may be explained by the high viscosity of non-aqueous electrolyte (epoxy-based), which restrict the access of electrolyte into mesopores (pore diameters of 2 nm -50 nm) presenting on the surface of CNTs, used in the structural EDLC. Therefore, it can be concluded that the introduction of CNTs into CFRP electrodes are not recommended to apply in structural EDLC with the purposes of enhancing their multifunctional efficiency.

Table 11 - Summary of mechanical and electrical properties of CNT activated structural EDLC with the use of glass fabric for separator material [91]

Set	Carbon fibre	Matrix	Shear modulus (GPa)	Shear strength (MPa)	V_f (%)	Specific capacitance (mFg ⁻¹)
1	As received	MTM57	3.52 ± 0.16	106.04 ± 3.66	45	-
2	As received	MTM57:IL	0.41 ± 0.21	9.21 ± 1.18	51	6.98
3	CNTs-grafted	MTM57:IL	1.04 ± 0.08	25.48 ± 3.44	44	5.00
4	CNTs-sized	MTM57:IL	0.85 ± 0.18	22.48 ± 3.51	49	4.80

4.2.3 Monolithic carbon aerogels (CAGs)

Monolithic carbon aerogels (CAGs) are porous ultralight materials and consist of the three-dimensional network in their structure and they are usually used for creating hierarchical reinforcement structures [76]. CAGs are commonly synthesized by the poly-condensation of resorcinol and formaldehyde in the sol-gel process, followed by pyrolysis [3]. In general, CAGs have high electrical conductivity as compared to other activated carbon materials [94]. As a result, CAGs are one of the most typical electrode materials for EDLC [3, 94-96]. However, CAGs in thin sheets form are usually hard to handle and mechanically unstable. It is therefore not suitable for structural applications. To stabilize the mechanical performance of CAGs, it is suggested to integrate CAGs into the carbon fibre cloths [97, 98]. There are two common methods to coat CAGs onto the surface of carbon fabrics: (1) soaking carbon fabrics into resorcinol-formaldehyde (RF) solution and pressing them between two clean glass plates to form a thin film; (2) infusing RF solution into carbon fabrics. The cured specimens are then carbonized at 800°C for 30 minutes in a furnace under N₂ supply.

The effects of different CAGs modifications on carbon fabrics and composites have been evaluated separately by Qian et al. [76]. For electrochemical characterization of carbon fabrics, CV tests were conducted by using a three-electrode system at ambient temperature. The properties of untreated and CAGs modified carbon fabrics (CAGs-CF) are summarized in Table 12. The KCl aqueous solution was employed as electrolyte and different scan rates ranging from 1 to 100 mVs⁻¹ with potential window of ±0.2 V were adopted for CV tests. It is shown that specific capacitance increases with increasing the specific surface area of electrodes, made by carbon fibre bundles. CAGs-CF through pressing method provides the best performance in energy storage as compared to infusion method. However, from structural perspective, CAGs-CF by using the pressing method has relatively weak

mechanical strength because the weight percentage of CAGs in carbon fabric is relatively high. Also, the surface of CAGs-CF is not uniform by using pressing method. In order to balance the mechanical and electrical properties of structural EDLC, CAGs-CF made by infusion method, which can provide uniform and thin reinforced carbon fabric, are recommended for multifunctional applications.

Table 12 – Specific surface area and capacitance of carbon fabrics before and after modifications [76].

Type of carbon fabric	specific surface area (m^2g^{-1})	Specific capacitance (Fg^{-1})
As-received	0.209 ± 0.003	0.06 ± 0.01
CAGs-modified (pressing)	163.1 ± 1.8	14.3 ± 0.2
CAGs-modified (infusion)	118.0 ± 1.6	8.7 ± 0.3

Meanwhile, charge-discharge experiments with a 0.1V step voltage applied for 60s and tensile testing of a $\pm 45^\circ$ laminate, referring to the standard of ASTM D3518, were performed to determine the electrochemical properties and in-plane shear properties of specimens, as presented in Table 13. It is observed that both electrochemical and mechanical properties of CAGs-modified specimen are improved as compared to the specimen using untreated carbon fabrics for electrodes. The enhancement of electrochemical properties can be explained by the improvement on transverse conductivity between carbon fibres through the introduction of CAGs onto their surface, resulting in a reduction of interfacial resistance between the fibres and electrolyte [76]. By considering the microstructure of CAGs reinforced CFRP electrodes, carbon fibres provide mechanical supports to CAGs and CAGs, on the other hand, give a huge modification in the surface areas, as shown in Fig. 14, as well as the mechanical properties, such as compression strength and ILSS, of carbon fibres. Therefore, it could be concluded that the integration of CAGs into CFRP electrodes could effectively enhance the electrical and mechanical properties of structural EDLC.

Table 13 - Electrical and mechanical properties of CAG-modified (infusion) structural EDLC. Glass fibre fabric and PEGDGE with 10% IL, 1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide (EMITFSI) was used as separator material and electrolyte respectively. The applied voltage is 0.1V in the calculation of energy and power densities [76].

Specimen	V_f (%)	R_p ($\text{k}\Omega\text{cm}^2$)	R_p ($\text{k}\Omega\text{cm}^2$)	C_g (mFg^{-1})	Γ (μWhkg^{-1})	P (mWkg^{-1})	ILSS (MPa)	Shear Modulus (MPa)
CF/ Epoxy	47.2	255.7	23.7	10.7	14.8	2.64	5.36	276

CAGs- CF/epoxy	42.0	14.1	14.7	71.2	98.9	3.84	8.71	895
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V_f : fibre volume fraction of carbon fabrics; R_p : parallel resistance; R_s : equivalent series resistance; C_g : electrode mass-normalized capacitance; Γ : energy density; P : power density.

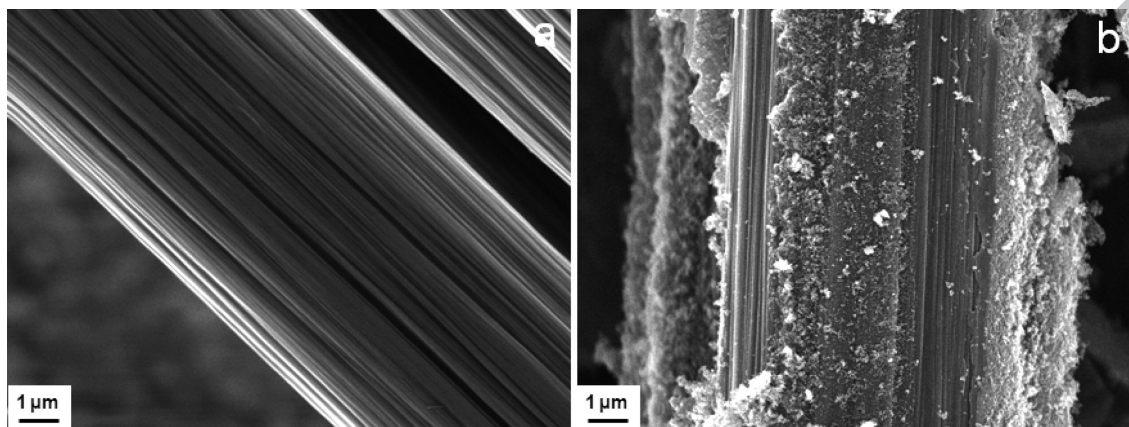


Fig. 14 - SEM images of (a) untreated and (b) CAG-modified carbon fibre [76]

4.2.4 Metal oxide nanowires

Transition metal oxide (TMO) nanowires, such as copper oxides (CuO), manganese oxides (Mn_xO_y) and zinc oxides (ZnO), have been commonly used for energy storage systems in recent years due to their benefits of availability, chemical stability, large surface area and enhancement of interfacial charge transmission [99-101]. Besides, nanowires reinforced woven carbon fibre composites are generally stiffer (higher strength and lower peak strain) as compared to the composites fabricated by using untreated woven carbon fibres [102-104].

CuO is one of the most advisable materials for conductive electrodes because of its high specific capacitance and good cycle stability [105]. Deka et al. [106] pointed out that the surface area of CRFP electrodes of structural supercapacitors could be increased by growing CuO nanowires onto the surface of carbon fibres through the hydrothermal process, as shown in Fig. 15. The schematic configuration of structural supercapacitor made by CuO nanowires reinforced woven carbon fibre (CuO/WCF) is presented in Fig. 16. Table 14 shows the comparison on mechanical and electrochemical performance of different structural supercapacitors, which were fabricated by using untreated woven carbon fibre (WCF), NaOH activated woven carbon fibre (AWCF) and CuO/WCF for electrodes and polyester resin (PES) as matrix. The electrochemical properties were obtained from CV tests with scan rate of 100 mVs^{-1} and potential window of $\pm 0.5 \text{ V}$. The specific surface areas of WCF, AWCF and CuO/WCF electrodes are $0.589 \text{ m}^2\text{g}^{-1}$, $41.365 \text{ m}^2\text{g}^{-1}$ and $132.852 \text{ m}^2\text{g}^{-1}$ respectively. The increased specific surface areas of AWCF and CuO/WCF electrodes, as compared with that of WCF, could enhance the interfacial strength between electrodes and multifunctional matrix to offers improved mechanical and electrochemical properties of structural supercapacitors.

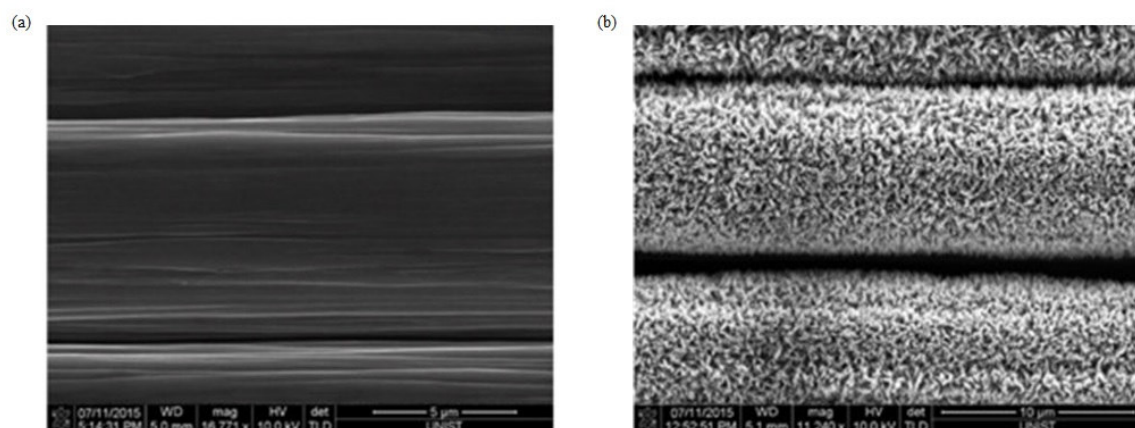


Fig. 15 - SEM images of (a) untreated and (b) CuO grown WCF [106]

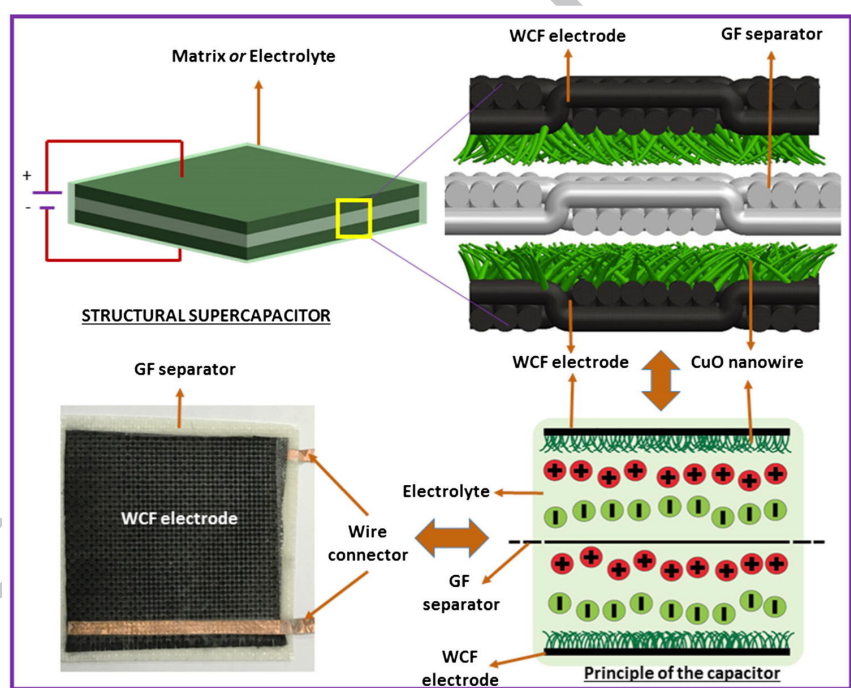


Fig. 16 - Schematic diagrams of structural supercapacitor by using CuO/WCF electrodes, woven glass fibre for separator and PES for matrix electrolyte [106].

Table 14 – Mechanical and electrochemical properties of various structural supercapacitors [106].

Specimen	V_f (%)	E (GPa)	σ (MPa)	τ (MPa)	C_g (mFg ⁻¹)	R_s (Ω)	R_p (Ω)	Γ (mWhkg ⁻¹)	P (Wkg ⁻¹)
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WCF/PES	39.4	11.817	149.640	57.914	150	730	1240	27.63	1.03
AWCF/PES	40.1	17.638	234.275	89.578	1170	724	1150	36.86	2.52
CuO/WCF/PES	45.6	20.912	270.275	102.439	2480	370	986	42.15	4.14

E: Young's modulus; σ : tensile strength; τ : in-plane shear strength; C_g : electrode mass-normalized capacitance; R_p : parallel resistance; R_s : equivalent series resistance; Γ : energy density; P: power density.

The specific capacitance of CuO-WCF composites increased from 150 mF/g to 2480 mF/g due to its significant increase in the specific surface area. To further enhance the capacitance of CuO-WCF composites, LiTFSI and ILs were introduced into the matrix. The capacitance increased from 2480 mFg⁻¹ to 6750 mFg⁻¹. It could be attributed to the use of TMO as electrodes, which could provide additional pseudocapacitance through rapid and reversible electrochemical reactions [107-109]. However, cycle stability is the most concern when using TMO based electrodes. It is because H₂O could be formed during the electrochemical reaction, which is harmful to electrodes, and the heat treatment in the fabrication of TMO nanowire reinforced electrode could have an inverse effect on its microstructure, which limited the electrochemical reactions [108]. Therefore, the study on the cycle stability of this kind of structural supercapacitor should be conducted.

Apart from the improvement of electrical properties of CuO-WCF composites, their tensile strength and Young's modulus also increased by more than 80% and 75% respectively. It could be associated by the presence of CuO nanowire on the surface of carbon fibres, resulting in improving the interfacial bonding between reinforcements and matrix. As a result, more energy is needed to break the CuO nanowires reinforced composites. To summarize, the surface treatment by using metal oxide nanowires, such as CuO, could be a promising method to enhance the multifunctional efficiency of structural supercapacitors.

4.3 Formulation of multifunctional electrolytes

Apart from the characters of CFRP electrodes, electrolytes used for structural EDLC also have a considerable influence on their overall performance. It is because the decomposition voltage of electrolyte defines the operating voltage window of EDLC, and consequently their power and energy density [110]. In addition, the mechanical performance of structural EDLC is greatly depended on the multifunctional electrolytes. Therefore, the selection of multifunctional electrolyte is a key to optimize the overall performance of structural EDLC. In general, the electrolytes used in the EDLC can be classified into three types, which are aqueous electrolytes, organic electrolytes and ILs. With regard to the structural requirement of structural EDLC, the organic electrolytes in the solid state is

advised to be employed because they have the good mechanical properties, long lifetime, short charging time, low internal corrosion, good reliability and wide potential window, resulting in a wide range of applications [111]. However, solid-state electrolytes have a relatively low specific capacitance as well as energy density as compared to liquid-state electrolytes. To enhance the electrical performance of structural EDLC, more research works are focused on the formulations of multifunctional electrolytes, aiming at enhancing the ion movements in the electrolytes without significantly degrading their mechanical properties [75, 111-115].

Generally, existing multifunctional electrolytes used for structural EDLC are usually single polymer based matrices and polymer-blend based matrices. Polymers commonly used to produce the multifunctional electrolytes are PEGDGE and diglycidyl ether of bisphenol-A (DGEBA). In the fabrication of multifunctional electrolytes, ionic salts, mainly LiTFSI, are firstly dissolved in the organic solvent and then mixed with the crosslinking polymer. This kind of multifunctional electrolyte is rigid to withstand mechanical loading but poor in the ionic conductivity. Therefore, bicontinuous networks are produced by adding a small portion of ILs in order to intensify the ion diffusion in the multifunctional electrolyte while retaining their good mechanical performance.

Shirshova et al. [115, 116] and other researchers [12, 117] studied the mechanical and electrical properties of structural EDLC by using various compositions of resin and ILs in the multifunctional electrolytes. The changes in the microstructure of multifunctional electrolytes were also investigated. It is observed that the multifunctional electrolyte shows a beadlike structure in the ILs rich region and cell porous structure in the resin rich region, as shown in Fig. 17 [12]. It is indicated that the porosity of multifunctional electrolyte decreases with increasing epoxy resin content due to the formation of continuous epoxy phases, and consequently its Young's modulus also increases. However, the formation of continuous epoxy phases could restrict the ion movements, resulting in decreasing the ionic conductivity of multifunctional electrolyte.

Another approach to improve the overall performance of structural EDLC is to employ the blend based polymer electrolytes. Javari et al. [77] studied the mechanical and electrical properties of structural EDLC by using DGEBA/ PEGDGE blend based multifunctional electrolytes. Although both DGEBA and PEGDGE are crosslinking polymers, the former has a higher crosslinking density as compared to the latter. As a result, the tensile stiffness of structural EDLC increases with increasing the content of DGEBA. Nevertheless, the high crosslinking density of DGEBA used in the multifunctional electrolytes could cause the hindrance of ion movements, leading to a low specific capacitance. Therefore, the conflict existing between tensile properties and ionic conductivity of multifunctional electrolytes becomes one of the most challenging issues in the development of structural EDLC.

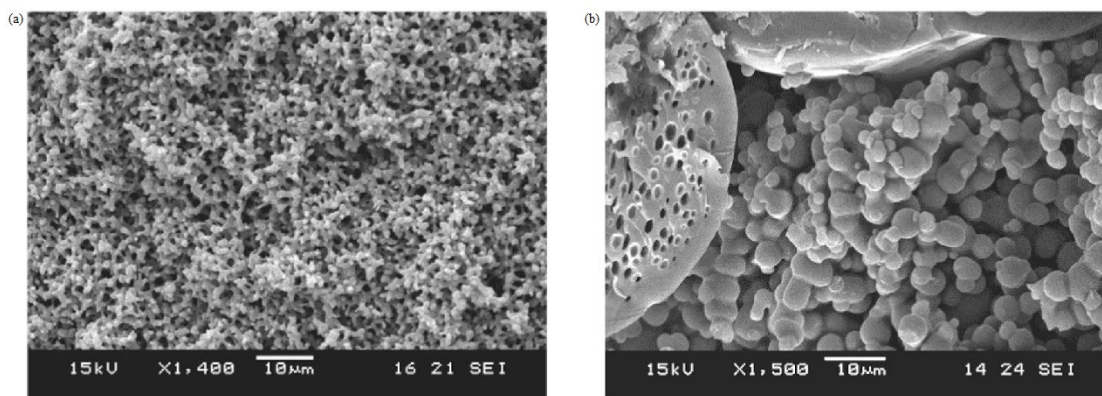


Fig. 17 - SEM images of (a) resin dominated and (b) IL dominated matrices [118]

4.4 Development of insulating separators

The functions of insulating separators for EDLC are to prevent electron transmissions between two conductive electrodes, to contain ionic electrolytes in its porous and to allow ion movements between electrodes. It is well known that ESR are highly depended on the distance between two electrodes, which is dominated by the separator thickness. In theory, ESR increase with increasing the separator thickness because the moving distance of ions from one side to another becomes longer, resulting in the reduction of power density of EDLC. Besides, the content of ionic electrolyte in the EDLC increases with increasing the porosity of separator. As a result, the high concentration of ions at the interface of electrodes could be obtained, resulting in the high capacitance of EDLC. Furthermore, the separator chosen for EDLC should be chemically resistant to other materials, especially acidic or alkaline electrolytes [119]. Therefore, the selection of insulating separators for structural EDLC is essential to their overall performance.

In the previous studies, major concerns have been focused on developing the superior electrode-electrolyte system with a large capacity for energy storage. Nowadays, the developments of insulating separator have been driven due to its influences on the electrical properties of EDLC. In general, cellulose (filter paper), woven glass fibres, polypropylene (PP) membrane, eggshell membrane and Teflon ring [78, 119-122] are commonly used for insulating separators for EDLC. Nor et al. [120] determined the relationship between nanoporous structures and electrical performance of EDLC by using different nanoporous separators, including PP membrane, egg shell membrane (ESM) and filter paper (FPW). It is proved that the high capability of electrolyte absorption as well as good ion infusion could be achieved by increasing the porosity, which is in nanoscale, of insulating separators. In addition, Laforgue and Robitaille [123] improved the power density and specific capacitance of EDLC by decreasing the thickness and increasing the porosity of insulating separators, resulting in the low ESR of EDLC, as presented in Fig. 18. It is observed that the ESR is directly proportional to the thickness and inversely proportional to the porosity of insulating separator.

Javadi [122] investigated the mechanical and electrical properties of structural EDLC by using different insulating separators, including glass fibre mat (GF), filter paper (FP) and PP membrane. Although FP specimens showed the highest shear modulus, its electrical performance was poorer as compared to GF specimens and PP membrane specimens. On the other hand, PP membrane specimens achieved the highest specific capacitance as compared to other specimens. It may attribute to the thinnest thickness of PP membrane as compared to those of GF and FP. Since GF specimens have the intermediate electrical and mechanical performance as compared to FP and PP specimens, GF are advised to be used in the further studies of structural EDLC.

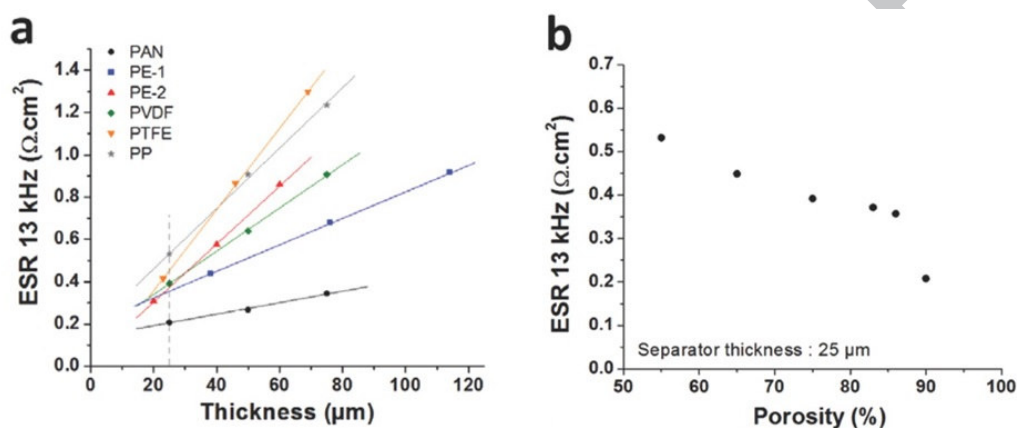


Fig. 18 - (a) ESR VS separator thickness; (b) ESR VS Separator porosity [124]

4.5 Challenges and further developments

The additional surface treatments of carbon fibres are needed to carry out to increase the surface area of CFRP electrodes. However, some surface activations of carbon fibres could show inverse results of improving the overall performance of structural EDLC (see Section 4.2). In addition, they could be difficult to be controlled for scale-up productions of carbon fibres. By comparing current approaches used for modifying the surface of electrodes, CAGs and TMO nanowires are the most recommendable choices to achieve the high accessibility of ions to the surface of CFRP electrodes, resulting in the high power density and improved tensile properties of structural EDLC.

The formulations of multifunctional electrolytes play a critical role in the overall performance of structural EDLC. The solid-state electrolytes provide the stiff structure but poor ionic conductivity while the blend based electrolytes have noticeably improved ionic conductivity but weak structure for structural EDLC. Therefore, the mechanical and electrical properties of multifunctional electrolytes are strongly conflicted. In the future, more research works are needed to find the optimum composition of ILs in the polymer matrices in order to optimize the mechanical and electrical performance of structural EDLC.

Moreover, common polymers used for the multifunctional electrolytes are not fully miscible with ILs. Hence, heterogeneous matrices could be formed in the blend based electrolytes and the mechanical behavior of multifunctional electrolytes could not be derived by the rule of mixtures of composites as easily as homogenous systems [118]. Therefore, a comprehensive study on the failure mechanism of multifunctional electrolytes is needed to conduct for a good understanding on the microstructure of structural EDLC in the further development.

Furthermore, the insulating separator is another significant constituent in the EDLC but it is also considered as an ohmic barrier because its thickness affects ESR and other electrical properties, including specific capacitance, power and energy density, of EDLC. Ideally, the high energy and power density of EDLC could be achieved by using extremely thin separators. However, GF, which is usually thick (160-250 μm) as compared to the ultra-porous membranes (20-40 μm), is commonly used for separator in the structural EDLC, resulting in the low energy density and power density [122, 123]. The reason of using a relatively thick GF is to prevent the contact between two carbon fibre fabrics and to protect the structural EDLC from the short circuits. Therefore, new materials should be developed for the insulating separator of structural EDLC in order to improve their overall performance.

Generally, structural EDLC have better performance on energy storage as compared to structural dielectric capacitors. However, the capacitance values of structural EDLC, ranging from 1.4 mFg⁻¹ to 6750 mFg⁻¹, mentioned in this review are relatively low as compared to those of traditional supercapacitors, which is around 100 Fg⁻¹ (activated carbon based electrodes) to 1715 Fg⁻¹ (TMO based electrodes) [125, 126]. The significant reduction in capacitance of structural EDLC, as compared to traditional supercapacitors, is due to the selection of polymer-based electrolytes, which have good mechanical properties but poor ionic conductivity, of structural EDLC. Although the capacitance of structural EDLC is low generally, they have strong structure to support mechanical loads in their applications, such as automotive industries.

There is a lack of discussion on other electrochemical properties, including rate response and cycle stability, of structural supercapacitors. As a result further studies on rate response and cycle stability of different structural supercapacitors should be conducted with the aims of evaluating their overall performance comprehensively. Nevertheless, the additional process of electrode activations and the use of ILs in structural EDLC ultimately increase their fabrication costs, which is one of the most important factors in their development, and it is expected that the costs could be reduced by mass production in the future.

5. Conclusion

The multifunctional composite materials have been continuously developed with the aim to reduce the energy and fuel consumption. The advanced energy storage system made by CFRP is one of the

typical examples of realizing the multifunctional composite materials. In this paper, the concept of multifunctional composite materials is introduced. Moreover, the introduction of structural dielectric capacitors, followed by the research works in terms of improvements on their mechanical and electrical properties, performed by other researchers are presented. On the other hand, the introduction of structural EDLC and parameters, which are the surface treatments of carbon fibres, formulations of multifunctional electrolytes and development of insulating separators, followed by challenges existing in their development are given.

To realize the multifunctional energy storage systems, the most difficult part is to fabricate the multifunctional dielectrics and electrolytes for optimizing their mechanical and electrical properties, especially interfacial properties. However, the mechanical and electrical requirements of multifunctional materials could be different in different applications. Therefore, the criterion of selecting materials for electrodes and dielectrics, including the mechanical and electrical properties, lifetime, cost and ease of fabrication of composites, should be taken into considerations comprehensively in every single application. Last but not least, it is expected that there would be more new multifunctional materials to be developed in the future to bring engineering fields to a higher level.

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