PLASMA TREATMENT- A ROUTE FOR IMPROVED ADHESION BETWEEN PET AND EPOXY IN MULTIFUNCTIONAL COMPOSITE CAPACITORS?

T. Carlson[1*] and L. E. Asp[1,2]

[1]*Swerea SICOMP AB, Box 104, 43122 Mölndal, Sweden*
[2]*Luleå University of Technology, 97187 Luleå, Sweden*
* *tony.carlson@swerea.se*

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Abstract

This paper presents an approach towards realising novel multifunctional polymer composites. A series of structural capacitor materials made from carbon fibre reinforced polymers have been developed, manufactured and tested. The capacitors were made using three thicknesses of DuPont Mylar A thermoplastic PET as dielectric separator employing carbon fibre/epoxy pre-pregs as structural electrodes. Plasma treatment was used as a route for improved epoxy/PET adhesion employing a number of treatment times, 5, 10, 15, 20 and 25s. The manufactured materials have been mechanically and electrically tested to evaluate their multifunctional efficiency.

Plasma treatment have been shown to give some improvements to the interlaminate shear strength but not to any significant degree.

1 Introduction

To realise electric vehicles the mobile platforms must carry increasingly larger masses and volume of energy storage components such as capacitors, supercapacitors and batteries. This development counteracts the realisation of efficient electric vehicles, for which low weight is essential. One route to address this problem could be the development of multifunctional materials, in this case, materials that could store electrical energy and withstand mechanical loading.

More than a decade ago Chung and Wang [1] presented the idea of using the semi-conductive nature of the carbon fibre in “structural electronics”. Following this they were first to propose the use of a high dielectric constant material as an interface between CFRP laminas to make a structural capacitor. In a follow-on study Luo and Chung made thin structural capacitors from carbon fibre epoxy pre-pregs and different paper separators demonstrating structural capacitor materials for the first time [2]. More recently, Baechle and co-workers made structural capacitors employing glass fibre/epoxy pre-preg as the dielectric with metalized polymer films as electrodes [3].

Previous work [4-6] performed at Swerea SICOMP has investigated the use of different surface weight printing papers and polymer films dielectric separator with carbon fibre prepreg electrodes in the spirit of Luo and Chung [2]. The concept of making capacitors with

carbon fibre epoxy pre-preg electrodes separated by a thin polymer film was found to be most promising. This concept is further explored in this paper.
The objective of this follow-on study of previous work [4-6] has been to develop high performance multifunctional polymer composite capacitor materials. In this study thermoplastic PET-films of three different thicknesses, with and without surface treatment, are utilised as dielectric separator layers between carbon fibre epoxy pre-pregs. The mechanical and electrical performance is characterised and the overall multifunctional performance assessed.

2 Experimental

2.1 Materials

The structural capacitor materials were made from carbon fibre epoxy pre-preg woven lamina separated by a thermoplastic polyester (PET) film dielectric separator. The pre-preg was a 245g/m^2 2x2 Twill HS (3K) 0º/90º configuration, MTM57/CF3200-42% RW, supplied by the Umeco, UK.
PET is available in different thicknesses and is commonly used in capacitors, hence a good choice for a parametric study. A set of three film thicknesses 50, 75 and 125µm (DuPont Mylar A), thermoplastic polyester film supplied by Trafomo AB, Sweden were employed for evaluating separator thickness influence on performance.
Adhesion between PET and epoxy could be an issue and in addition to the neat polymer films, plasma treated PET-films were prepared. The treatment was performed in N_2 gas for a set of five treatment times, 5, 10, 15, 20 and 25s with 300W of power. The excited plasma gas breaks chemical bonds in the film surface generating active sites where chemical bonds can form for improved adhesion to the epoxy matrix [7]. Equipment used was a Technics Plasma 440G.
All CFRP reference specimens were manufactured for comparison of the mechanical properties of the structural capacitors and a single-functional composite.

2.2 Composites manufacture

Prior to manufacturing the laminates the pre-preg roll was taken from the freezer and cut to required size laminas. The laminas were allowed to reach room temperature before putting them in a vacuum chamber for 30 min to evaporate any leftover condensation. The pre-preg layers were stacked in a release agent coated mould. To achieve equal surface properties on both sides of the laminate the structural capacitor laminates were manufactured using peel plies on both top and bottom surfaces. The mould was sealed with butyl tape and a vacuum bag. A schematic of the bagged layup is shown in Figure 1. Vacuum was applied and debulking without heat for 30 min was performed. The mould was then placed in an oven and heated according to the supplier's recommendations (120ºC for 30 minutes) to achieve fully cured laminates.

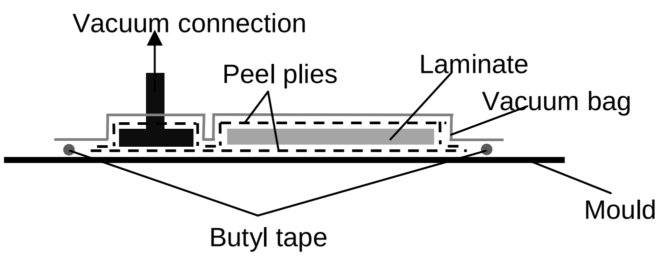

Fig. 1. Manufacture of the structural capacitor laminates.

For each type of material a set of five specimens was manufactured. Dimensions were chosen to follow Standards recommendations as closely as possible, alternating pre-preg/film for the tensile specimens and using a lay-up of [pre-preg$_{10}$/PET-film/pre-preg$_{10}$] for the ILSS specimens. These structural capacitor laminates where made from two pre-preg plies separated by one PET film. The specimen had a nominal electrode area of 0.010m^2. The dielectric material has an excess of approximately 25mm around carbon fibre plies to avoid edge effects and a copper mesh was used as electrical connection.

2.3 Experimental characterisation

2.3.1 Interlaminar shear strength

Interlaminar shear strength (ILSS) of the structural capacitor configurations was measured to expose any negative or positive effects of the dielectric, at mid-thickness, on the mechanical performance of the composite.
The interlaminar shear strength was evaluated at room temperature using the short beam three-point bending test according to the ASTM D2344/D2344 M standard [9]. The equipment used was a MTS 20/M with a 10kN load cell. A constant crosshead speed of 1mm/min was used.

2.3.2 Tensile testing

Tensile tests were made to examine the in-plane properties of the structural capacitors. Output from the test was Young´s modulus and ultimate tensile strength of the laminates. The tests were performed at room temperature according to the ASTM standard D3039/D3039 M [8]. The equipment used was an INSTRON 8501/H0162 with a 100kN load cell (INSTRON 2518-111). A constant crosshead speed of 2mm/min was used and strain was measured with a 25mm gauge length extensometer.

2.3.3 Capacitance

To characterise the structural capacitor materials the capacitance was measured by sweeping through 0.1-1000Hz at 1V while capacitance was recorded. The equipment used was a General Electric Programma IDA200 with Keithley 8009 electrode fixtures.

2.3.4 Dielectric breakdown voltage

Dielectric breakdown voltage (dielectric strength), of the capacitors was measured using the ASTM D3755 standard for direct current measurement of dielectric breakdown [10], as suggested by Baechle et al. [11]. The specimens were submerged in mineral oil to avoid any edge effects that may disturb the measurements. The test was stopped when breakdown was apparent by the voltage over the capacitor sharply dropping to zero. Equipment used was an AC transformer with a half wave rectifier. The sample voltage was measured with a resistive voltage divider connected to a DAQ-card on a stationary computer.

2.3.5 Specific energy

Evaluation of specific energy allows comparison between the different capacitor devices. Use of thin film dielectric separators usually results in capacitors with high capacitance but low breakdown voltage [11]. The specific energy is given by

$$\overline{\Gamma}_{sc} = \frac{\frac{1}{2}CV^2}{m_{sc}}, \qquad (1)$$

where $\overline{\Gamma}_{sc}$ is the specific energy of the structural capacitor, *C* the capacitance, *V* the voltage at dielectric breakdown and m_{sc} the mass of the structural capacitor.

3 Results and discussion

3.1 Mechanical properties

3.1.1 ILSS

Dielectric	ILSS [MPa]					
	No treatment	5s	10s	15s	20s	25s
PET-film 50µm	29.5±1.3	29.6±2.1	28.2±0.8	32.0±1.1	30.2±1.9	28.2±1.2
PET-film 75µm	30.6±1.7	31.2±0.9	32.9±2.5	30.7±1.6	30.9±2.4	28.9±1.9
PET-film 125µm	32.5±1.4	29.4±2.5	29.5±1.5	31.8±1.1	29.4±1.4	30.6±1.9
CFRP Ref.	54.4±1.5	-	-	-	-	-

Table 1. ILSS for all structural capacitor materials with and without plasma treatment and an all CFRP reference

As seen in table 1 all capacitor material specimens show significantly lower ILSS values then the CFRP reference. Note also that for 50 and 75 µm PET the most benefit from the plasma treatment occurs between 10-20 seconds of treatment time. Any improvements on performance lies within the scatter, hence, no significant improvement from the plasma treatment can be found. Therefore, the median treatment time, 15s, was chosen as the treatment time for further mechanical and electrical testing.

3.1.2 Tensile properties

Dielectric	E [GPa]	σ_{ult} [MPa]
PET-film 50µm	42.7±3.0	354±66
PET-film 50µm 15s PT	42.5±2.1	320±47
PET-film 75µm	44.6±0.8	377±15
PET-film 75µm 15s PT	41.7±5.2	344±35
PET-film 125µm	36.5±1.9	317±36
PET-film 125µm 15s PT	37.8±4.3	339±35
CFRP Ref.	56.1±1.7	631±73

Table 2. Tensile properties for non treated and 15s treated PET structural capacitors and a CFRP reference

Tensile measurements were made on as received and 15s plasma treated film capacitors and an all CFRP reference.

Young's modulus was calculated between 0.05-0.15% strain, and not between 0.1-0.3% strain as recommended in the ASTM standard [8]. This was due to the failure onset beyond 0.2% strain.

Considering the values of stiffness, there is a knockdown of approximately 15GPa regardless of film thickness. A small knockdown is expected from the interleaving of the CFRP with a less stiff material (PET).

Considering the ultimate tensile strength, there is a significant knockdown in the strength of the material compared to the CFRP reference.

3.2 Electrical properties

Dielectric	Capacitance* [nF/m^2]	Dielectric strength [kV]	Specific energy [J/g]
PET-film 50µm	447±3.8	14.6±2.3	0.06±0.02
PET-film 50µm 15s PT	442±2.6	15.4±1.7	0.06±0.01
PET-film 75µm	300±2.6	22.4±3.6	0.08±0.03
PET-film 75µm 15s PT	300±4.5	20.8±1.8	0.07±0.01
PET-film 125µm	193±4.6	29.4±4.1	0.09±0.02
PET-film 125µm 15s PT	195±1.6	29.8±4.8	0.09±0.03

* @ 1V and 0.1Hz

Table 3. Summary of electrical properties for various structural capacitors

The results from the capacitance and dielectric strength experiments are presented in Table 3. The results are measured average capacitance, dielectric strength and calculated specific energies with standard deviations, for respective dielectric. In an automotive application the frequency of charging/discharging will most likely be low. Hence the results measured at 0.1Hz are presented.

3.2.1 Capacitance

As expected the capacitance is highest for the thinnest dielectric, 50µm, and decreases with an increase in separator thickness. All results for capacitance are consistent, only small scatter in data indicating a stable electric response from the manufactured materials. An important result is that there is no significant difference in capacitance for as received and plasma treated films. This supports the assumption made in previous studies [4-6] that plasma treatment does not affect the dielectric properties of the film.

3.2.2 Dielectric strength and specific energy

Results from the dielectric breakdown voltage measurements are presented in Table 3.
As expected, structural capacitors with the thickest separator exhibit the highest breakdown voltage. However, considering the breakdown voltage divided by the separator thickness the thickest film presents the lowest breakdown strength per mm. This is also expected as a larger volume of material has a higher probability of flaws.
No adverse effects from the plasma treatment could be concluded from the tests. The small variations are most likely normal variations within a set of specimens.
The average capacitance, average breakdown voltage and average weight were used to calculate the specific energy according to Equation (1). The calculated specific energies are presented in Table 3.
The highest value of specific energy is 0.09J/g for the 125mm thick PET-film. Hence, the lower capacitance of the thicker film capacitors is compensated for by a higher breakdown voltage. The value is however lower than the 0.28J/g reported for structural dielectric separator capacitors developed by O'Brien et al. [11].

3.3 Multifunctional performance

Multifunctional performance is evaluated by assessment of measured specific energy vs. specific stiffness, specific strength and specific interlaminar shear strength.
Employing specific energy as the parameter to assess multifunctional performance allows us to compare the different structural capacitor designs for their applicability in a structural system, where energy needs to be stored, with respect to their potential to reduce system weight. Consequently, this approach allows us to evaluate the structural capacitors influence

on system weight, as described by O'Brien et al. [11]. This is important as even though the multifunctional element exhibits specific energy and strength and/or stiffness that usually are lower than those of the best monofunctional materials, at a system level the multifunctional material may still enable an overall mass saving. In the paper by O'Brien et al. [11] a procedure to evaluate multifunctional capacitor designs, following an approach suggested by Wetzel [12] is presented. O'Brien and co-workers [11] define a total system mass M equal to the sum of the mass of the capacitors m_c and the mass of the structure m_s. The design metric for capacitor performance is specific energy $\overline{\Gamma}$ (in J/kg) with overall system energy storage defined as $\Gamma = \overline{\Gamma} m_c$. Similarly, the mechanical performance, e.g. specific modulus or ILSS (J/kg), can be defined as $\overline{E}$ and $\overline{\tau}$. From these, the energy density and specific mechanical properties of the structural capacitors can be found as $\sigma^e \overline{\Gamma}$, $\sigma^s \overline{E}$ and $\sigma^s \overline{\tau}$. σ^e and σ^s are the structural capacitor's energy and structural efficiencies, respectively. An improved multifunctional design would maintain the same overall system energy and mechanical performance but reduce the total system weight. However, a structural capacitor will only enable such system level mass savings if

$$\sigma^{mf} \equiv \sigma^e + \sigma^s > 1. \qquad (3)$$

Multifunctional performance is depicted in Figures 5a, b and c. In the Figures, two lines are plotted, representing Equation (3) with a multifunctional efficiency, σ^{mf}, equal to one for two scenarios. The dashed line represents a target scenario where specific energy for a state of the art capacitor material set to 0.5J/g as reported in the literature as a maximum value for a electric field energy storage devise (aluminium electrolytic capacitor) [13] (1J/g, was used by O'Brien and co-workers [11]) and specific mechanical properties are set to those of the tested CFRP reference material. The solid line in figure 5a and 5b represents a second scenario where the specific energy is the same but the mechanical properties are the maximum values found for steel, which is a likely candidate material to be replaced by the multifunctional material. Values chosen are specific stiffness 25GPa/(g/cm^3) [14], and specific strength 150MPa/(g/cm^3) [13]. ILSS is not applicable for steel and hence there is no solid line in Figure 5 c.

In Figure 5a specific energy is plotted as function of specific stiffness. As seen in the figure, none of the manufactured materials are to the right of the dashed line. Hence, none of the manufactured materials will meet or exceed the target. However, all materials are to the right of the solid line meaning that compared to steel the multifunctional material would provide a weight saving. Comparing these results to those reported in previous studies [5, 6] it is obvious that the overall performance of the new materials are worse than those observed in the previous studies. However, it must be noted that the stiffness and density in previous studies [5, 6] were calculated while measured in the current study.

In figure 5b specific energy is plotted as a function of specific strength. As for stiffness the manufactured multifunctional materials will not meet the target values but will provide a weight saving when compared to steel.

In figure 5c specific energy is plotted as a function of specific ILSS. And as for the other mechanical properties the multifunctional materials are below the targeted line. Since ILSS is not applicable on steel there is no solid line. Comparing these results with those found in previous studies [5, 6] it is apparent that the performance of the current and old materials is of the same magnitude. The main reason that the new materials falls under the dotted line is the much improved performance of the reference material in this study compared to that found in previous studies [5, 6]. One reason for this could be an improved manufacturing procedure and more experienced personnel in this study.

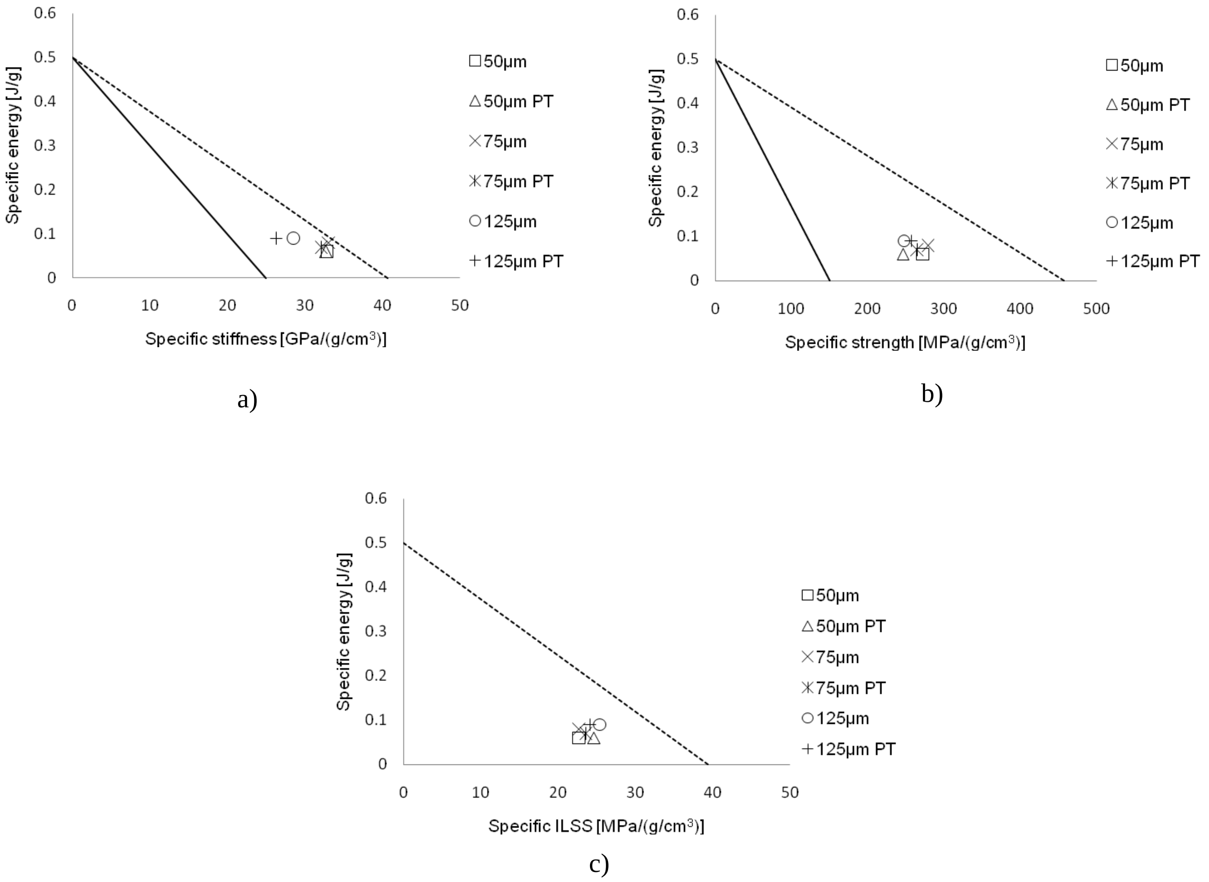

Fig. 5. a) Specific energy versus specific stiffness for the structural capacitors b) Specific energy versus specific strength for the structural capacitors c) Specific energy versus specific ILSS for the structural capacitors

4 Conclusions

In this study structural capacitor materials, using carbon fibre pre-preg electrodes and PET-film separator, have been developed and tested. The results indicate no significant mechanical benefits from plasma treating the PET separator. However, there seems to be no negative influence on the electrical properties of the multifunctional material which is preferable for any surface treatment to be used.

Considering the multifunctional performance, the materials fail to provide a multi-functional material that can compete with a mono-functional composite/capacitor combination. The developed materials could however compete with a steel/capacitor combination that might be found in some applications.

Further work could be aimed at finding thinner high dielectric constant films combined with plasma treatment and other chemical surface modification techniques to further develop the concept.

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References

[1] Chung DDL, Wang S. Carbon fiber polymer-matrix structural composite as a semiconductor and concept of optoelectronic and electric devices made from it. Smart Mater. Struct. 1999;8:161-166.

[2] Luo X, Chung DDL. Carbon-fiber/polymer-matrix compositors as capacitors. Comp Sci Tech. 2001;61:885-888.

[3] Baechle DM, O'Brien DJ, Wetzel ED. Design and processing of structural composite capacitors. Proceedings of SAMPE 2007, Baltimore, MD, USA, 2007.

[4] Carlson, T, Ordéus, D, Wysocki, M, "Load carrying composites for electrical energy storage" SICOMP TR08-02, Swerea SICOMP, Sweden, 2008.

[5] Carlson, T, Ordéus, D, Wysocki, M, Asp, LE, Structural capacitor materials made from carbon fibre epoxy composites, Comp Sci Techn, 2010;70(7):1135-1140.

[6] Carlson, T, Ordéus, D, Wysocki, M, Asp, LE, CFRP structural capacitor materials for automotive applications, Plastics, Rubbers and Composites, 2011;40(6-7):311-316

[7] Garbassi, F, Morra, M, Occhiello, E, Polymer Surfaces – From Physics to Technology, Revised and updated ed. pp. 226-229, 1998.

[8] ASTM Standard test method for tensile properties of polymer matrix composite materials and their laminates, Annual book of ASTM standards, West Conshohocken, Vol 15.03, 79-91. 2010.

[9] ASTM Standard test method for short-beam strength of polymer matrix composite materials and their laminates, Annual book of ASTM standards, West Conshohocken, Vol 15.03, 71-78. 2010.

[10] ASTM Standard test method for dielectric breakdown voltage and dielectric strength of solid electrical insulating materials under direct-voltage stress, STD no. D 3755 – 97 (Reapproved 2004).

[11] O'Brien DJ, Baechle DM, Wetzel ED. Multifunctional structural composite capacitors for U.S. army applications. Proceedings of SAMPE 2006, Dallas, Texas, USA, 2006.

[12] Wetzel ED, Reducing weight: Multifunctional composites integrate power, communications and structure, AMPTIAC Quarterly, 2004;8:91-95.

[13] Holm SR, Polinder, H, Ferreira JA, van Gelder P, Dill, R, A comparison of energy storage technologies as energy buffer in renewable energy sources with respect to power capability, IEEE Young Researchers Symposium in Electrical Power Engineering, Leuven, Belgium, 7-8 February, 2002.

[14] Ashby, MF, Materials selection in mechanical design, third ed., pp 50-60, 2005.