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Karakterisering av plasmabehandlad PET för lastbärande komposit kondensatorer

Master of Science Thesis

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Characterization of plasma treated PET for load carrying composites
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Abstract

This master thesis was carried out at Swerea Sicomp AB in Mölndal. The aim for this work was to evaluate plasma treated polyethylene terephthalate (PET) films for load carrying composite capacitors.

The main part of this work has been focused on different plasma treatment times (5, 10, 15, 20 and 25 seconds) on PET films with the thicknesses of 50, 75 and 125 μm , used as dielectrics in structural carbon fibre capacitors. Mechanical properties and surface analysis have been evaluated to observe any changes in adhesion properties. This work is a continuation and addition of the master thesis: Carlson T, Ordéus D. Load carrying composites for electrical energy storage, Chalmers University of Technology. Master thesis 2007:114, ISSN 1652-8913.

The experimental results indicated that plasma treated PET films shows a higher value of short beam strength in mechanical testing than regular none-treated PET film. Furthermore the PET-films plasma treated for longer than 15 seconds indicate absorption of nitrogen when surface analyzed. Surface analysis also shows a trend in increasing oxidation as a function of longer plasma treatment time, indicating an increased amount of functional groups on the surface of the PET-films, even though the amount of N_2 absorbed on the surface is small. This work has shown that it is possible to give a load-carrying composite increased mechanical properties by plasma treating the PET-films used as dielectrics for a longer time.

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Sammanfattning

Detta examensarbete har utförts på Swerea Sicomp AB i Mölndal. Målet med detta arbete har varit att utvärdera plasmabehandlade polyetylentereftalat (PET) filmer för lastbärande kompositkondensatorer.

Huvuddelen av detta arbete har fokuserats på plasma behandling av PET vid olika tider (5, 10, 15, 20 och 25 sekunder) bestående av olika tjocklekarna 50, 75 och 125 μm som används som isolatorer i strukturella kolfiberkondensatorer. Mekaniska prover och ytanalys har utvärderats för att observera förändringar i adhesionegenskaper. Detta arbete är en fortsättning och påbyggnad på ett tidigare examensarbetet av Tony Carlson och Daniel Ordéus, Load carrying composites for electrical energy storage, Chalmers University of Technology. Master thesis 2007:114, ISSN 1652-8913.

Experimentella resultat pekar på att plasmabehandlade PET filmer visar en högre interlaminär skjuvhållsfasthet jämfört med icke behandlad PET filmer. PET filmer som plasma behandlats visade även i ytanalysen ett högre upptag av kväve molekyler vid plasma behandlingen. Ytanalysen påvisade även en trend av ökad oxidation som funktion av ökad plasmabehandlingstid vilket indikerar en ökning av funktionella grupper på ytan av PET filmerna. Detta arbete har visat att det är möjligt att öka mekaniska egenskaperna hos lastbärande kompositkondensatorer genom att plasmabehandla PET filmerna som används som isolator.

Acknowledgement

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Table of Content

1	Introduction	8
1.1	Background	8
1.2	Aim and challenges	8
1.3	Goal	8
2	Theory	9
2.1	Composites	9
2.2	Capacitors	10
2.3	Polyethylene terephthalate (PET).....	11
2.4	Multifunctional Materials.....	11
2.5	Plasma treatment	12
2.6	ESCA/XPS.....	14
2.6.1	Basic principle.....	14
2.6.2	Chemical State and depth profiling	15
2.6.3	Quantitative analyses	15
2.6.4	Instrumentation.....	15
3	Experimental setup	16
3.1	Materials.....	16
3.2	Manufacturing and sample preparation.....	17
3.2.1	Laminate manufacturing	17
3.2.2	ESCA specimen preparation	17
3.3	Interlaminar shear strength.....	17
3.4	Sample preparation	18
4	Results.....	18
4.1	Short beam strength.....	18
4.2	Conclusions and discussions of the ILSS-test.....	20
4.2.1	Results.....	20
4.3	Surface analysis.....	20
4.4	ESCA/XPS.....	21
4.5	Conclusions and discussions from the ESCA/XPS and comparison with ILSS	22
4.6	Recommendations and future work.....	25
	References and appendices.....	

1 Introduction

This report covers the development of structural carbon fibre composites capacitors, and evaluation of plasma treated PET as dielectric insulator, a study to evaluate the potential of electrical energy storage in composite structures. This work is a continuation of the work Load carrying composites for electrical energy storage, Chalmers University of Technology. Master thesis 2007:114, done by Carlson T, Ordéus D. The study has been carried out at SWEREA Sicomp AB in Mölndal as a master thesis work (30 hp points) at Chalmers University of Technology.

1.1 Background

One of the major subjects of several decades has been focused on environmental issues and sustainable development as its solution. When considering vehicle components weight can be a liability. Weight that does not contribute to the load carrying or crash absorbing capacity is simply parasitic. Lighter vehicles made out of lightweight materials will certainly minimize our energy consumption. Scientists and engineers all around the world are working toward the goal to develop these materials that will have a great impact in our life and the future.

The ideal design for a vehicle would be to maximize the efficiency of individual components through advanced materials and new high performance technologies and maintain a low total weight. By implementation of the vehicles subsystems, such as power and sensors, electronics and structure this goal can be achieved.

1.2 Aim and challenges

The aim of this project is to evaluate plasma treated PET as dielectric in structural carbon fibre components in capacitors. One of the challenges of making a good capacitor is the choice of dielectric. The treatment is done to increase the adhesion between the dielectric film and matrix of a composite. In previous studies [1] PET films has found to be one of the more promising dielectrics. The challenge is to identify the parameters which give the best adhesion properties.

1.3 Goal

The goal of this project is to evaluate the use of plasma treatment as a route for improved adhesion but also to identify challenges and possibilities for further studies.

2 Theory

2.1 Composites

Composite materials exist both as naturally occurring and as man-made. They are made from two or more constituents that are different in chemical and physical properties and separated by a distinct interface. An example of a natural occurring composite is wood, which is made of cellulose and held together by lignin. “Graphite” tennis rackets, “fiberglass” bodies of cars and boats, hardmetal (tungsten carbide) tools, and reinforced concrete are all examples of man-made composites. One of the oldest and most used composites made by man is concrete. It contains cement and an aggregate that consists of sand (less than 2 mm in diameter) and larger particles of gravel and crushed rock. The smaller sand particles fit in to the spaces between the larger gravel. Cement flows into the remaining spaces and forms a continuous matrix. The materials used in composites are referred as constituent materials and composites are mostly made of two constituent materials called matrix and reinforcement. The matrix material surrounds and supports the reinforcement material and keeps it in place. The reinforcement material enhances the matrix material due to its chemical and physical properties. The bonding between fibres and matrix is created during the manufacturing phase of the composite material. This has fundamental influence on the mechanical properties of the composite material. The concurrence of these gives the composite other properties than of the constituent materials individually. The mixture of reinforcement/resin does not really become a composite material until the last phase of the fabrication. This makes the manufacturing process an important part when designing composite materials.

Polymers are practically divided into plastics, rubbers, adhesives and resins. Plastics are defined as materials that can be molded into shape; rubbers are characterized by large elastic deformations; adhesives are used to join materials (glues); resins serve as the matrix in composites. From a scientific viewpoint, one divides polymers into thermoplastics and thermosets. Thermoplastics soften and liquefy on heating and are processed in the liquid state by a variety of extrusion and molding processes similar to those used for glass. Polyethylene, polyvinylchloride, polypropylene, and polystyrene, in that order are the four most widely produced thermoplastics. Thermosets solidify by a chemical reaction; this reaction is accelerated by heating. Thermosets include phenolic resins, epoxies, unsaturated polyesters, and polyurethanes – substances that cannot be melted like thermoplastics and therefore cannot be recycled simply by heating. Their most important usage is found in adhesives and in composites.

The fibers used in composites have a diameter of as small as 5-10 μm . Such thin fibers are less likely to contain cracks or surface roughness to act as stress concentrators; therefore they resist high stress before breaking and possess great strength. Glass and polymers are suitable to be drawn into thin fibers because their viscosity increases rapidly as temperature decreases. [2,3,4]

2.2 Capacitors

A capacitor stores energy by an electric potential between two plates called electrodes. Capacitance [C] is a measurement of the amount of energy that is possible to store in a capacitor, larger value correlates to more energy. In between the two electrode plates there is a dielectric. The dielectric is also called separator, can be made of anything electrically insulative; commonly paper, polymers and air is used. It should ideally have a high dielectric constant (ϵ_r), a measure of the amount of electrostatic energy possible to store per unit volume. A low leakage current is also required, in order for the capacitor to maintain its charge over time. This requires the dielectric to have a large resistance.

In order to store a large amount of energy, in a capacitor with a given capacitance, a high voltage between electrodes is required. This in turn requires a large dielectric strength for the dielectric, simply the largest voltage drop possible over the dielectric, (a number, since the gradient is constant) measured in [V/m]. The energy of a capacitor is calculated using equation 2.1.

$$E = \frac{1}{2} CV^2 \quad (2.1)$$

Capacitance of a plate electrode capacitor with a single material spacer is calculated using equation 2.2. The capacitance is measured in Farads [F] and is usually in the range of 10^{-12} – 10^{-6} F. Capacitors with values of C in the range 1-1000 F are often called supercapacitors or ultracapacitors for the highest values of C.

$$C = \frac{\epsilon_r \times \epsilon_0 \times A}{t} \quad (2.2)$$

E = Energy [J]

V = Voltage [V]

C = Capacitance [F]

ϵ_r = Relative dielectric constant

ϵ_0 = Permittivity of vacuum = 8.854×10^{-12} [F/cm]

A = Total projected area of the capacitor [m²]

t = Dielectric layer thickness [m]

Considering equation 2.1, to achieve a large capacitance the area and ϵ_r should be large while t small. In other words, to achieve maximal capacity for a given A and ϵ_r , the two electrodes

cells, each of which contains oils and perspiration glands, sensory receptors, hair follicles, blood vessels and other components with functions other than providing the basic structure and protection of the internal organs. Scientists now want to mimic these multifunctional systems in nature by designing synthetic multifunctional materials by applying physics, chemistry and mathematics. Multifunctional materials are by necessity composite materials, and the strong growth in the use of composites has been greatly influenced by multifunctional design requirements. [8]

The idea of using carbon fibre reinforced polymers (CFRP) in structural capacitors was presented a decade ago by Chung and Wang [9]. They suggested that the semiconductive nature of carbon fibre composites could be used to make electric devices. They were the first to propose the use of a high dielectric constant material as an interface between CFRP laminae to provide a capacitor material. This was the true beginning of multifunctional materials, i.e. a material that can perform more than one function. Structural capacitors are made of materials that are stiff and strong to sustain mechanical loading and at the same time able to store electric energy. Another approach for structural capacitors was suggested by Baechle [10]. Baechle and co-workers made structural capacitors from dielectric glass/epoxy pre-peg with thin metal electrodes to achieve high energy density and maximum multifunctional efficiency. Since Chung and Wang [9] presented their idea a new research area has emerged. Recently, concepts for structural polymer composite batteries [11, 12] and supercapacitors [13] have been presented. [14]

The increased interest in multifunctional materials and structures is driven by the need for the development of new materials and structures that simultaneously perform (a) multiple structural functions, (b) combined non-structural and structural functions, or (c) both. One example of a multifunctional structure of type (a) would be a composite structure that has high strength, high stiffness, high fracture toughness and high damping. An example of type (b) would be a load-bearing structure that has the capability of providing its own noise and vibration control, self-repair, thermal insulation, and energy harvesting/storage, whereas an example of type (c) would be a structure combining the functions of both type (a) and type (b). Most of the recent developments in multifunctional materials and structures tend to be of type (b). [15]

2.5 Plasma treatment

In plasma treatment the surface of a substrate is exposed to plasma. Plasma is generated by electrical discharge in a gas feed, always including high energy photons, electrons, ions, radicals and other excited species. It is generally described as an ionized gas or as an electrically neutral medium of positive and negative particles. "Ionized" refers to the presence of free electrons which are not bound to an atom or molecule. Plasma is considered to be the 4th state of matter after solid, liquid and gas. The state of matter can be changed by adding enough energy. Plasmas can carry electrical current and generate magnetic fields and the most common method to produce plasma is to apply an electrical field to a gas in order to accelerate the free electrons. There are different kinds of

processes of plasma treatment such as Corona treatment, Gas Atmosphere Plasma, Flame Plasma, Atmospheric Plasma, Low Pressure Plasma, Vacuum Plasma, Glow-Discharge Plasma, Cold plasma and Etching Plasma all relying on the properties of the plasma. Each of the methods mentioned have differences and are chosen based on the desired surface effects and the qualities of the material. [16]

When the surface of a substrate is exposed to plasma, initiated in a gas e.g. N₂, as used in these experiments it may increase the adhesion between the specimen and matrix of a composite. Chemical bonds in the surface are broken and reactive groups and positions are generated. These could react either with each other creating crosslinking, or the N₂ could integrate into the surface creating new functional groups. In this work, the substrates were exposed to N₂ plasma, i.e. excited in a gas e.g. N₂ using a Technics Plasma 440G equipment. [3]

Plasma surface modification technology offers innovative solutions to adhesion and wetting problems in many industries. Component preparation using plasma is an important step prior to printing, bonding, painting, varnishing and coating processes. Plasma surface modification provides an economical solution for the cleaning and activation of component surfaces before further processing. [17]

Plasma treatment only affects surface properties, typically less than 50 Å and the important parameters are:

- Power
- Pressure
- Gas flow
- Reactor geometry
- Positioning of the sample

Influence of plasma on polymers:

- Crosslinking – Chain scissioning
- Etching – Removal of surface contaminants
- Functionalisation – Increase of surface energy

The equipment needed for plasma treatment is commercially available, and consists of a vacuum system, energy supply, gas supply, measurement and control equipment to adjust parameters. The advantage of the process is that no thermal or mechanical strains are introduced into the specimen. [18]

2.6 ESCA/XPS

ESCA (Electron Spectroscopy for Chemical Analysis) / XPS (X-ray Photoelectron Spectroscopy) is an analysing technique method that was developed in 1960's by Kai Siegbahn and his group of researchers in Uppsala Sweden. The technique is based on the Einstein theory of photoelectric effect, published in 1914. The technique is widely used because of its simplicity in use and data interpretation to analyse chemical samples. [19]

2.6.1 Basic principle

Bombarding a sample in vacuum with x-rays gives rise to emission of electrons. When the sample is irradiated with monochromatic x-rays it causes the electrons to be emitted from the surface of the sample.

Photons collide with electrons, transferring their energy to the sample. Emitted electrons (photoelectrons) acquire a kinetic energy which is equal to the difference between the energy of the incident photon and the binding energy of the electron to the nucleus. From the binding energy and intensity of a photoelectron peak, the elemental identity, chemical state, and quantity of an element are determined. If monochromatic x-rays are used with a photon energy $h\nu$, the kinetic energy of the emitted electrons K_e is given by:

$$K_e = h\nu - B_e - \phi \quad (2.5)$$

Where B_e is the binding energy of the atomic orbital from which the electron originates and ϕ is the work function. The work function is the minimum amount of the energy an individual electron requires to escape from the surface. Each element produces a unique set of electrons with specific energies. By measuring the number of these electrons as a function of kinetic (or binding) energy, and XPS spectrum is obtained. All elements can be detected except H (hydrogen) and He (helium). Figure 2.6 shows an example of a spectrum of a plasma treated PET.

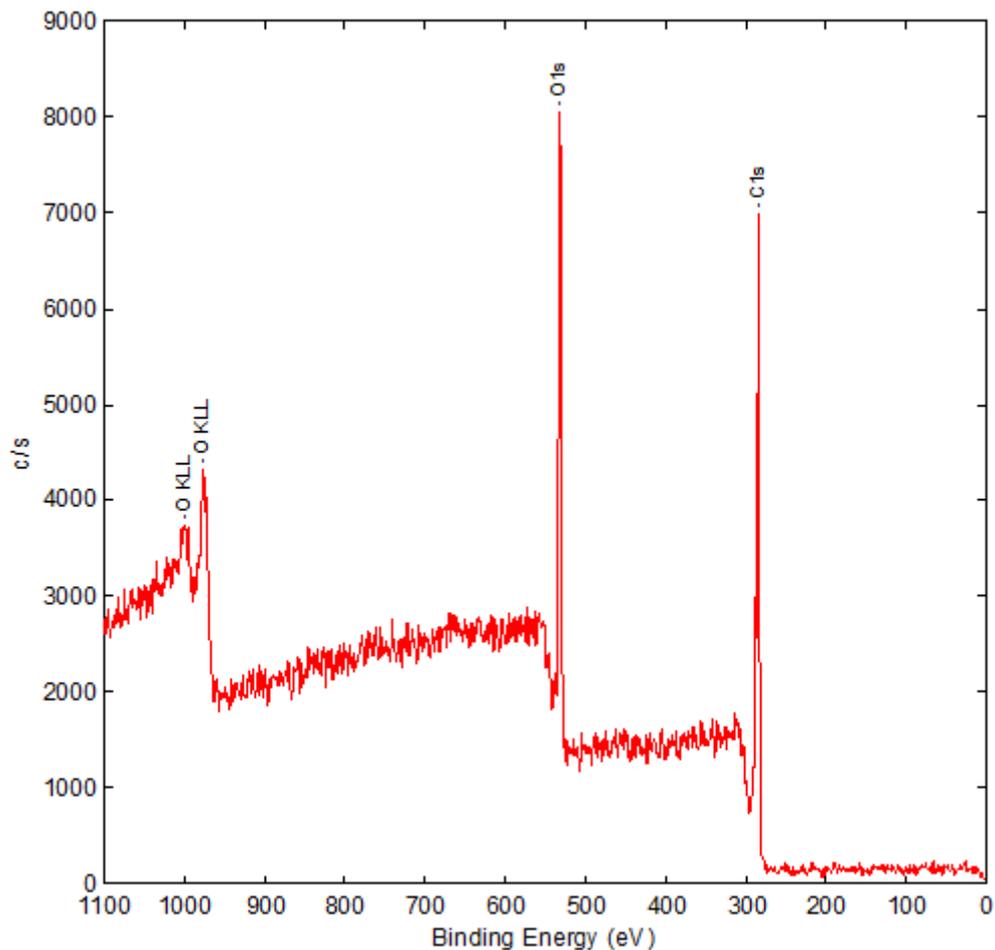


Figure 2.6 ESCA/XPS spectrum of plasma treated PET

2.6.2 Chemical State and depth profiling

Binding energies of photoelectrons depend on the chemical environment of the atoms. Accurate measurements of the exact peak position of the elements present gives information about the chemical state of these elements. To obtain information at larger depths (1-2 μm at most), concentration profiles can be recorded by alternating sputtering with Ar^+ -ions and spectrum collection. Typical sputter rates are 5-10 nm/min. A disadvantage of sputtering is that the sample will be affected in such way that the chemical state of the elements present may change due to the ion bombardment. In other words, the elemental composition will be influenced by sputtering.

2.6.3 Quantitative analyses

The number of detected electrons is a measure for the elemental concentration. In order to obtain quantitative results, peak areas are divided by standard sensitivity factors and normalized to 100 % to obtain atomic concentrations. [20]

2.6.4 Instrumentation

The instrument uses different pump systems to reach the goal of an ultra-high vacuum (UHV), and this happens in the UHV-chamber, as depicted below in figure 2.7. The ultra-high vacuum environment will prevent contamination of the surface and aid an accurate analysis of

the sample. A monoenergetic x-ray beam emits photoelectrons from the surface of the sample. The cylindrical mirror analyser (CMA) measures the kinetic energy of the emitted electrons. The spectrum is then plotted by a computer from the analyser signal. The binding energies can then be determined from the peak positions and the elements present in the sample are identified. [21]

1. UHV-chamber ($10^{-7} - 10^{-8}$ Pa)
2. X-Ray source
3. Electron analyzer

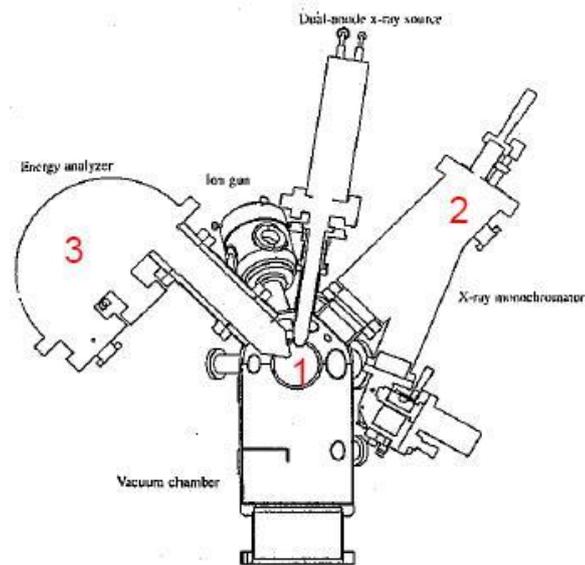


Figure 2.7 A schematic illustration of ESCA/XPS [19]

3 Experimental setup

3.1 Materials

Laminates were made from carbon fibre epoxy composites. The electrode layers were made from 0.25 mm thick pre-peg waves. The pre-peg was a 245 g/m² 2x2 Twill HS (3K) 0°/90° configuration, MTM57/CF3200-42% RW, supplied by the Advanced Composite Group, UK. They were cut out in the dimensions of 150 mm in length and 60 mm in width and stacked on each other with the stacking sequence; 10 prepreg /PET/ 10 prepreg. A dielectric layer in the composite separated the electrode layers. Different thicknesses of plasma treated PET films (DuPont Mylar A) supplied by Trafomo A/S Sweden were used as dielectrics. The different thicknesses of PET films used were 50, 75 and 125 µm, and plasma treated in 5, 10, 20 and 25 seconds. The results for 15 seconds are from previous work done by Tony Carlson [22]. In total 15 laminates were made, one for each combination of thickness and plasma treatment time.

3.2 Manufacturing and sample preparation

3.2.1 Laminate manufacturing

During manufacturing pre-peg 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 vacuum bag as shown in figure 3.1. The laminates were placed in an oven and vacuum was applied before heating. After debulking at room temperature for 30 minutes the temperature was ramped up to 120 degrees Celsius and held there for 30 minutes to achieve fully cured laminates. The vacuum was necessary to achieve void free, high quality composite laminates. The cured laminates were cut in the dimensions of two times the thickness in width and six times the thickness in length, resulting in specimens approximately 12 mm in width and 35 mm in length. The specimens were grinded and polished to correct dimensions according to the ASTM D2344 standards [23] for ILSS.

3.2.2 ESCA specimen preparation

Fifteen dielectrics consisting of PET films with the thicknesses of 50 μm , 75 μm and 125 μm were cut out in the dimensions of 150 mm in length and 70 mm in width were plasma treated. The PET-films were plasma treated for 5, 10, 15, 20 and 25 seconds for each thickness in the plasma chamber using 300 Watts of power. The treated PET films were protected in aluminium foils to avoid post plasma treated reactions before ESCA/XPS analyses.



Figure 3.1 Moulding process

3.3 Interlaminar shear strength

The interlaminar shear strength was evaluated using the short beam three-point bending test according to the ASTM D2344 standard [23]. In the test the specimen rests on two support rollers that allow lateral motion. The set-up is shown in figure 3.2. The displacement was applied at the centre of the specimen at a rate of 1.0 mm/min. As a result, maximum shear stresses appear at the specimen mid-thickness, i.e. at the position of the dielectric. In total 60 specimens were tested, five for each laminate. A span length of approximately 23.3 mm was used. Usually due to the complexity of internal stresses and variety of failure modes that can occur in this specimen, it is not generally possible to relate the short-beam strength to any one material property. However, failures are normally dominated by resin and interlaminar

properties, and the test result have been found to be repeatable for a given specimen geometry, material system, and stacking sequence. [23]

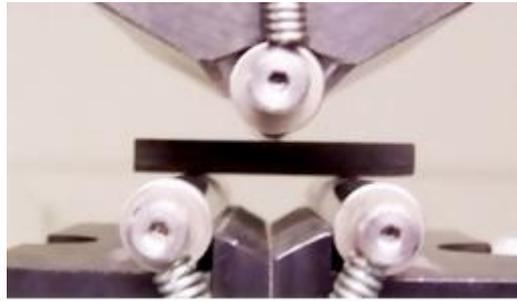


Figure 3.2 Short beam 3-point bending set up [4]

During the ILSS tests load and crosshead displacements were recorded. The interlaminar shear strength was calculated according to the standard. Short-beam strength determined by this test method can be used for quality control and process specification purposes. It can also be used to compare testing of composite materials, provided that failures occur consistently in the same mode. The method was chosen for this study being a very robust and easy to perform test.

3.4 Sample preparation

The chemical composition of the plasma treated PET films used as dielectrics were evaluated and analysed by ESCA/XPS. The plasma treatments were performed 24 – 48 hours before being analysed. After the plasma treatment all the samples were protected in aluminium foils to avoid exposure to reactive materials such as polymers and prevent any reaction to occur on the surface.

4 Results

The experimental was performed according to chapter 3; this chapter will present the analysis and results. The results are divided into parts according to testing methods. All results are presented in Appendix A.

4.1 Short beam strength

When calculating the ILSS, the following equation was used:

$$F^{sbs} = 0.75 \times \frac{P_m}{b \times h} \quad (4.1) [23]$$

Where:

F^{sbs} = short beam strength, MPa

P_m = maximum load observed during the test, N

b = measured specimen width, mm

h = measured specimen thickness, mm

Worth mentioning is that the ILSS calculations are the mean values from the results of five tests.

In the tables below the results are shown from the short beam strength experiments for the plasma treated PET films with the nominal thickness of 50 μm , 75 μm and 125 μm .

Treatment time [s]	Mean ILSS [MPa]	Standard deviation
REF	29,33	0,88
5	29,56	2,10
10	28,22	0,77
15	32,00	1,10
20	30,22	1,87
25	28,23	1,20

Table 4.2 short beam strength, plasma treated PET 50 μm compared to a reference

Treatment time [s]	Mean ILSS [MPa]	Standard deviation
REF	30,31	1,35
5	31,16	0,92
10	32,92	2,54
15	30,65	1,58
20	30,87	2,41
25	28,89	1,88

Table 4.3 short beam strength, plasma treated PET 75 μm compared to a reference

Treatment time [s]	Mean ILSS [MPa]	Standard deviation
REF	32,24	1,55
5	29,42	2,51
10	29,53	1,54
15	31,78	1,06
20	29,36	1,36
25	30,61	1,92

Table 4.4 short beam strength, plasma treated PET 125 μm compared to a reference

The results for 15 seconds for the short beam strength test are from previous work by Carlson T, Multi-functional composite materials, CRFP thin film capacitors, paper III, 2011, ISBN: 978-91-7439-335-4.

4.2 Conclusions and discussions of the ILSS-test

4.2.1 Results

When comparing all the results, one important conclusion can be drawn. All the plasma treated PET-films regardless of thickness or plasma treatment time have approximately the same values of short beam strength. Regardless plasma treatment for 5 seconds or 25 seconds, no trends can be observed in increasing values of ILSS as a function of increased plasma treatment time.

4.3 Surface analysis

This test is done in order to analyse and understand what happens on the surface of the PET films. All the plasma treated PET films with thicknesses of 50 μm , 75 μm and 125 μm were analysed and compared with a none plasma treated PET film as reference. It is of interest to understand the change in chemical composition and the atomic- rearrangements on the surface of the PET films when undergoing a plasma treatment process. The analysing method applied here is ESCA/XPS, as it is described in section 3.1. The ESCA/XPS analysing depth was approximately 5nm and the analysing area was 500 μm x 400 μm . Comparisons and

conclusions between the short beam strength test and ESCA/XPS results will be discussed in a later section, to see if interpretations can be made between the two different testing methods.

4.4 ESCA/XPS

In the tables below the results are shown from the surface analysis done on all the PET films by using ESCA/XPS. The results are also compared to a reference sample

Samples	C1s	O1s	S2p	Si2p	N1s
50 μm REF	71.37	28.63	-	-	-
50 μm , 5s	69.09	30.89	0.02	-	-
50 μm , 10 s	67.84	32.09	-	0.06	-
50 μm , 15 s	64.28	35.72	-	-	-
50 μm , 20 s	66.45	33.09	0.02	-	0.43
50 μm , 25 s	67.05	32.68	-	-	0.27

Table 4.5 Atomic concentration table of PET 50 μm in percent

Samples	C1s	O1s	S2p	Si2p	N1s
75 μm REF	72.89	27.11	-	-	-
75 μm , 5s	68.65	31.17	-	-	0.18
75 μm , 10 s	67.43	32.40	-	0.03	0.13
75 μm , 15 s	65.87	33.11	0.26	-	0.76
75 μm , 20 s	66.71	33.14	-	-	0.15
75 μm , 25 s	66.73	32.96	-	-	0.30

Table 4.6 Atomic concentration table of PET 75 μm in percent

Samples	C1s	O1s	S2p	Si2p	N1s
125 μm REF	70.63	29.37	-	-	-
125 μm , 5s	67.84	32.06	-	-	0.10
125 μm , 10 s	67.04	32.82	-	-	0.15
125 μm , 15 s	66.24	33.22	-	-	0.55
125 μm , 20 s	67.09	32.72	-	-	0.19
125 μm , 25 s	64.95	34.82	-	-	0.23

Table 4.7 Atomic concentration table of PET 125 μm in percent

4.5 Conclusions and discussions from the ESCA/XPS and comparison with ILSS

As seen in table 4.5 the reference sample of the PET film consists of 71.37 % carbon atoms and 28.63 % oxygen atoms. When the sample is plasma treated, the oxygen level increases while the carbon level decreases. This shows that oxidation has occurred thus the increase of oxygen concentration. Other elements showing to be present is sulphur (S) for the 5 second treatment and silicon (Si) for the 10 second treatment but this is very likely to be contamination either from the sample or the XPS/ESCA chamber. Tables providing information about which types of molecules found in the sample showed C-C bonds, C-O bonds and O-C=O bonds. This shows how the PET molecules bond structures and its respective atomic concentrations changes with longer plasma treatment time. [24]

A trend can be observed showing increased oxidation as a function of plasma treatment time except a drop in the last sample treated for 25 seconds. That drop can also be explained if considering the atomic concentration of nitrogen atoms formed from the nitrogen gas absorbed in the plasma chamber, both for 20 s and 25 s. The nitrogen concentration is far too low to have any actual function and significant role in the improvement of adhesion to the epoxy groups from the glue of the pre-pegs. However the increased oxygen concentration has created new functional groups on the surface of the PET film and allowed reaction with the epoxy groups resulting in better adhesion and higher values of short beam strength.

As seen in tables 4.6 and 4.7 same trends are observed, except that nitrogen can be seen to exist on the surface for both films with the thicknesses of 75 μm and 125 μm . Other elements like sulphur and silicon is most likely to be contamination and impurities and should not be present.

To get a better understanding of how efficient the oxidation has been, the method of oxygen – carbon ratio (O/C) is sometimes used when interpreting XPS spectra. By dividing the oxygen percentage by the carbon percentage for each plasma treatment a value is obtained. It is then easier to see a trend.

Samples	O/C-ratio
REF, 50 μm	0.401
5s, 50 μm	0.447
10s, 50 μm	0.473
15s, 50 μm	0.556
20s, 50 μm	0.498
25s, 50 μm	0.487

Table 4.8 O/C ratio for PET film with nominal thickness 50 μm

As seen in table 4.8 the O/C-ratio increases from 5s to 15s and later decreases. As mentioned before the plasma treated sample for 15 seconds, was surface analysed approximately 5 weeks earlier than the rest of the samples, but treated, tested and stored in the same way. Why this specific sample differs more than normal from the rest of the samples can be the cause of many variables, such as different atmosphere and circumstances in the ESCA/XPS UHV chamber, therefore it is hard to draw any certain conclusions.

Samples	O/C-ratio
REF, 75 μm	0.372
5s, 75 μm	0.454
10s, 75 μm	0.480
15s, 75 μm	0.503
20s, 75 μm	0.497
25s, 75 μm	0.494

Table 4.9 O/C ratio for PET film with nominal thickness 75 μm

Samples	O/C-ratio
REF, 125 μm	0.416
5s, 125 μm	0.473
10s, 125 μm	0.490
15s, 125 μm	0.502
20s, 125 μm	0.488
25s, 125 μm	0.536

Table 4.10 O/C ratio for PET film with nominal thickness 75 μm

Same trend is seen in table 4.10 as in table 4.8 and 4.9 except the increase in the last sample, which was a drop in previous figures. The O/C-ratios in table 4.10 seem to be higher than the other O/C-ratios in previous tables. The reason can be explained by considering volume-weight. All of the PET films were cut out in the dimensions of 150 mm in lengths and 70 mm in width, making the total area of each PET film 105 cm². The PET films have the density of 1.39 g/cm³. The films have different volumes depending on the thickness of the films, as shown in table 4.14.

Thickness of PET film (μm)	Volume (cm³)	Weight (g)	Intensity (W/cm³)
50	0.53	0.74	566.04
75	0.79	1.10	379.75
125	1.31	1.82	229.00

Table 4.11 film specifications

The PET films are plasma treated with the effect of 300 W for different periods of time. The intensity for each film is calculated as 300 Watts divided by the volume, as calculated and shown in table 4.11. The intensity is much higher for the film with the thickness of 50 μm but the weight is much less. A theory can be that less functional groups are created on the surface because of its low weight. The film with the largest thickness of 125 μm is exposed to a lower intensity but because of its higher weight more groups on the surface can react with the plasma and create more functional groups as seen in table 4.10, the O/C-ration is higher than the other films.

Worth mentioning is the procedure done directly after plasma treatment process to preserve and store the treated PET-films. The plasma treated PET films were earlier in the experiments preserved in sealed plastic bags directly after the treatment, before being analysed by ESCA.

The results of ESCA showed no absorbed nitrogen at all. This failure was due to the storage of the PET films in plastic bags. The plasma treated films had reacted with the sealed plastics and therefore did not show the expected changes. The plasma treatments were repeated but this time preserved in aluminium foils so no reaction could occur before being surface analysed.

4.6 Recommendations and future work

The short beam strength showed no significant change in plasma treatment time and the ESCA/XPS analysis showed small changes. Most importantly nitrogen was absorbed with longer treatment time, but not enough large amounts. In future studies oxygen plasma could be tested to see if there is any difference compared to nitrogen plasma, furthermore evaluation of longer plasma treatment times of PET is also recommended. After plasma treatment of the PET films it is recommended to store them in aluminium foil and not in any plastic containers of any kind. The plasma treated films can easily react with plastic containers and affect the results.

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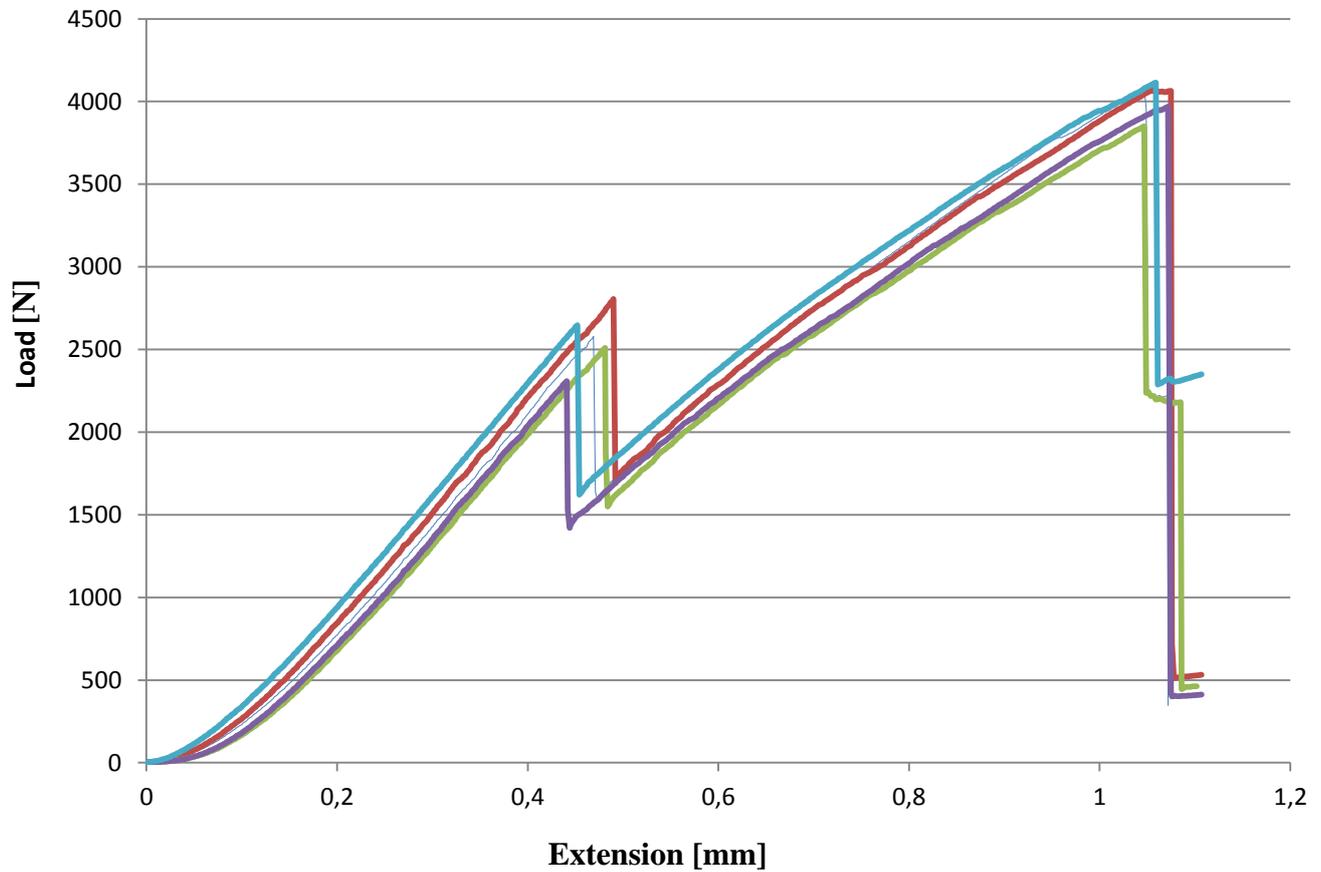
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INDEX OF APPENDICES

APPENDIX A-	3-POINT BENDING RESULTS
APPENDIX B-	SHORT BEAM STRENGHT RESULTS
APPENDIX C-	3-POINT BENDING: SPECIMEN DIMENSIONS
APPENDIX D-	ESCA/XPS RESULTS
APPENDIX E-	EQUIPMENT
APPENDIX F-	MATERIALS

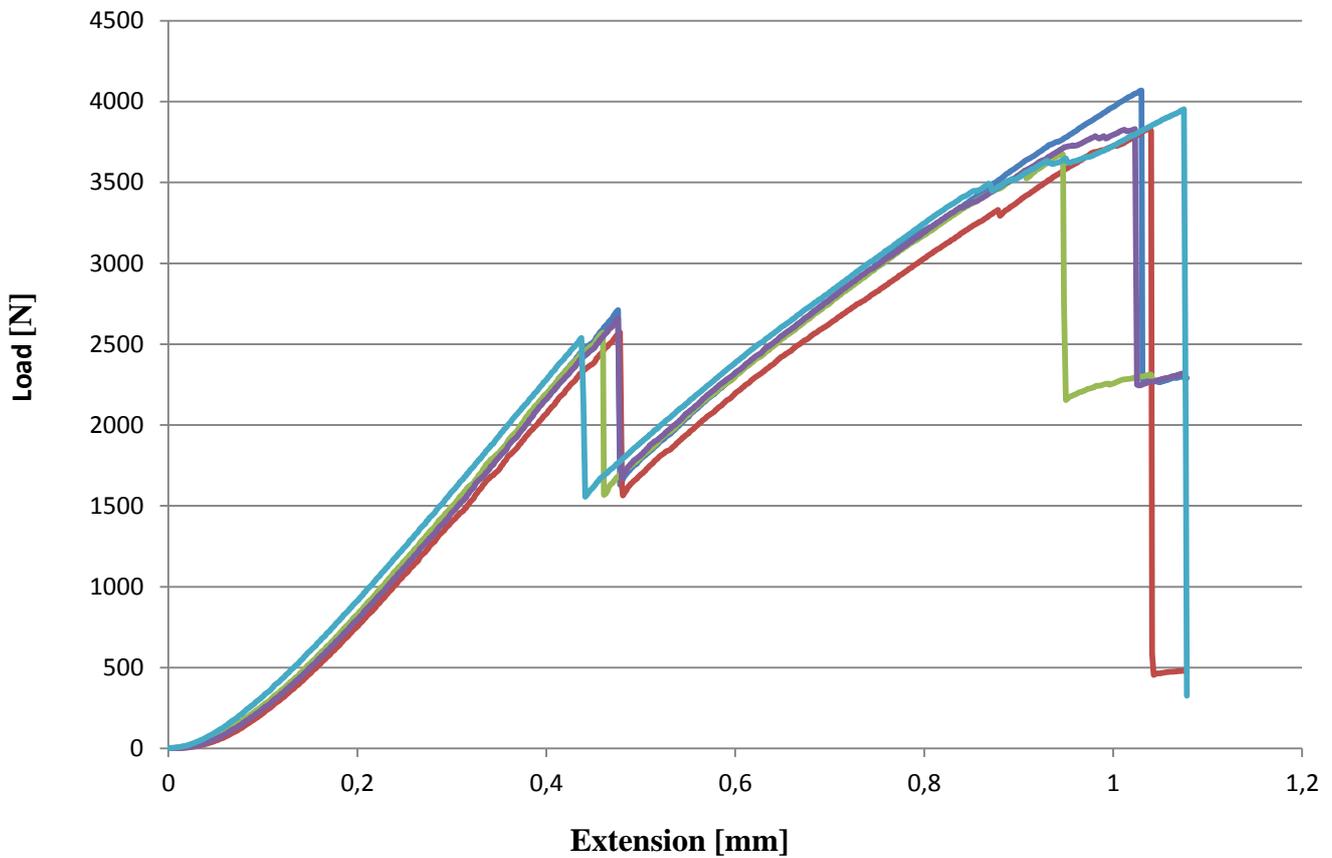
Appendix A: 3-POINT BENDING RESULTS

PET film, thickness 50 μm , plasma treated for 5 seconds



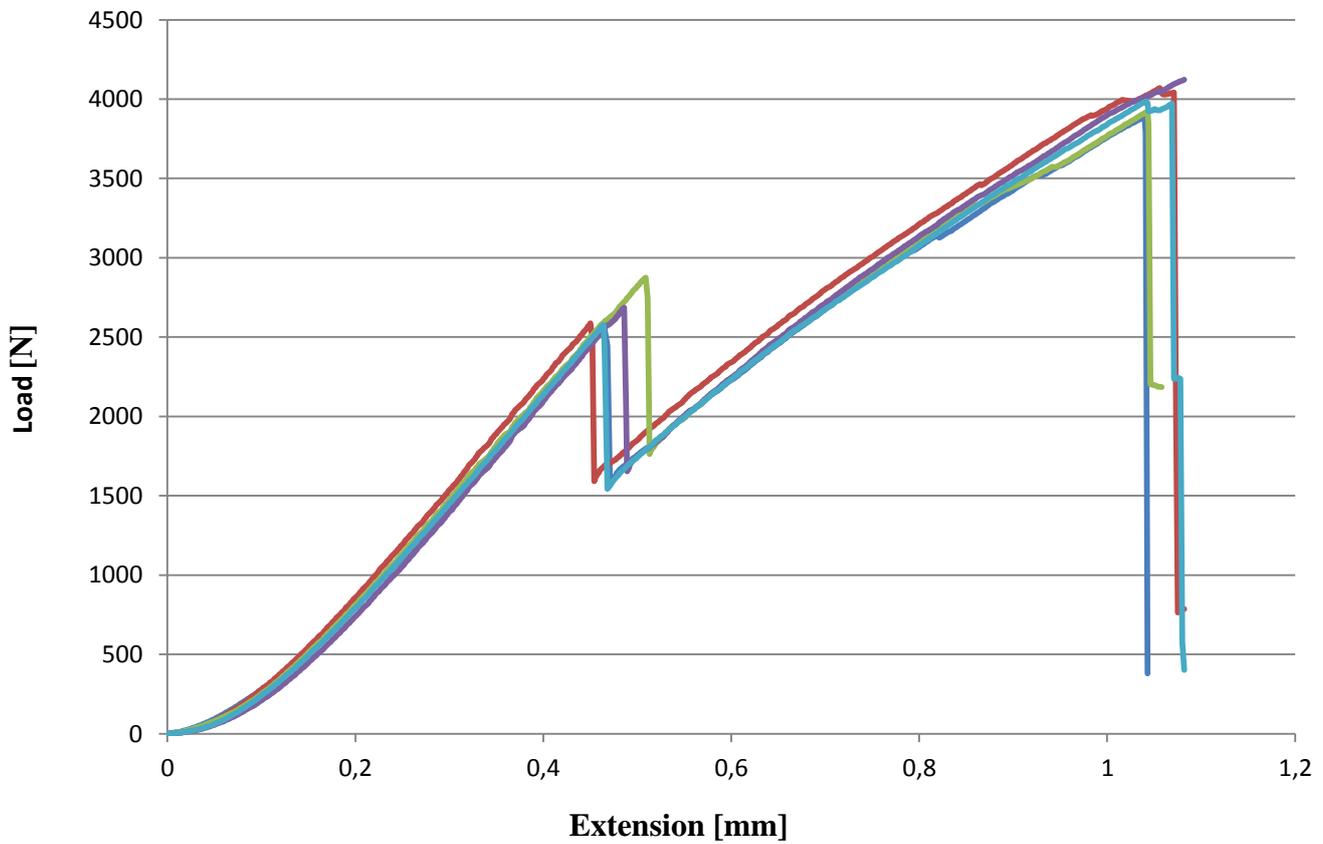
Specimen	Load at yield [N]
1	2580
2	2804,8
3	2509,8
4	2308,8
5	2646,9
Mean	2570,06
Std.Dev	182,34

PET film, thickness 50 μm , plasma treated for 10 seconds



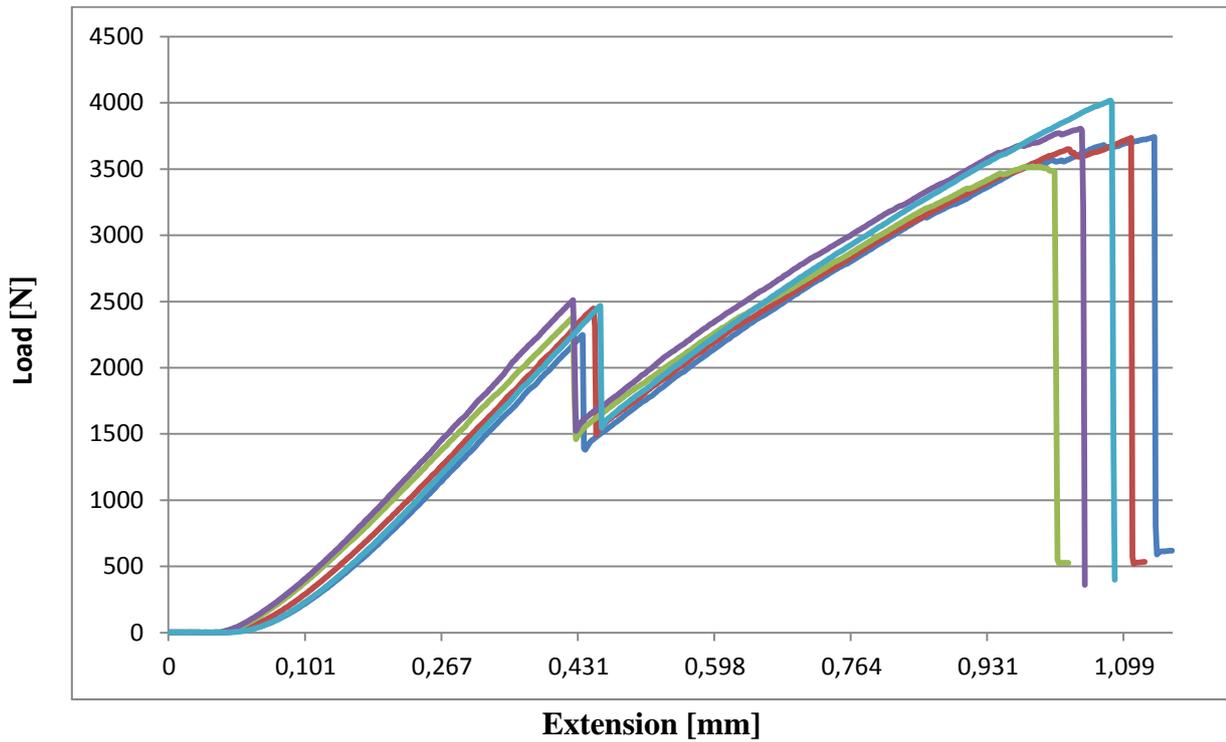
Specimen	Load at yield [N]
1	2710,4
2	2572,2
3	2571,4
4	2658,1
5	2539,1
Mean	2610,24
Std.Dev	71,31

PET film, thickness 50 μm , plasma treated for 20 seconds



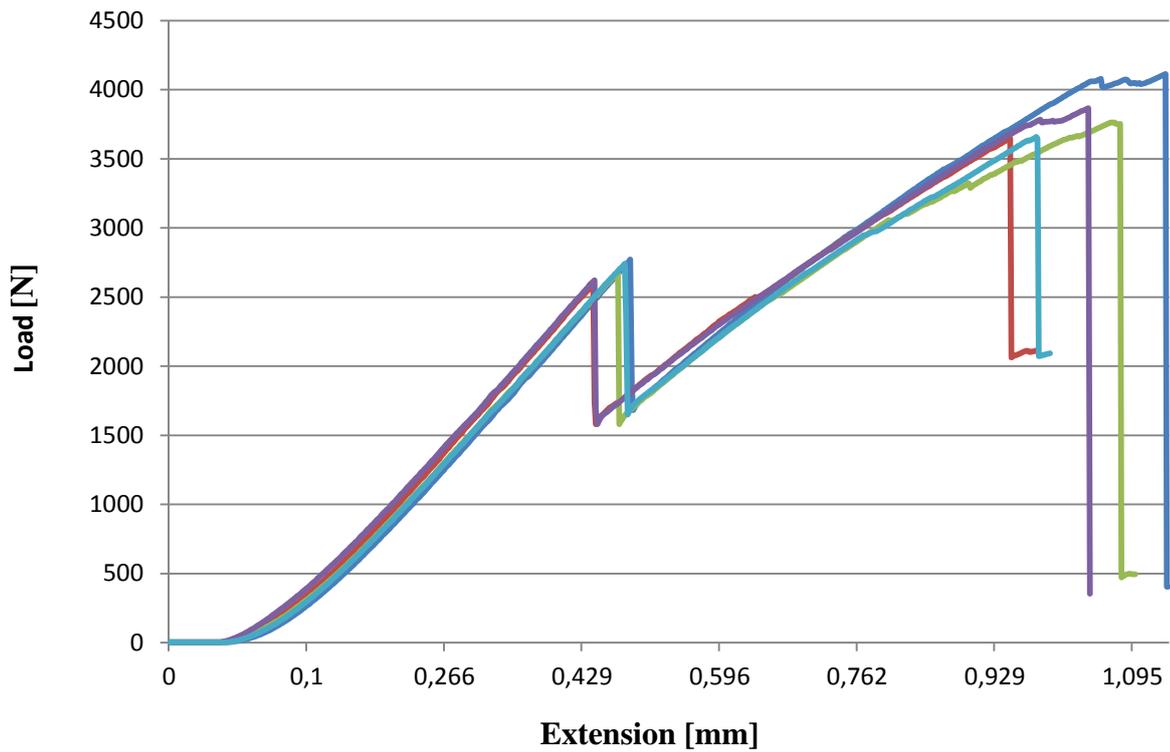
Specimen	Load at yield [N]
1	2445,8
2	2552,6
3	2875,2
4	2686,6
5	2577,7
Mean	2627,58
Std.Dev	162,75

PET film, thickness 50 μm , plasma treated for 25 seconds



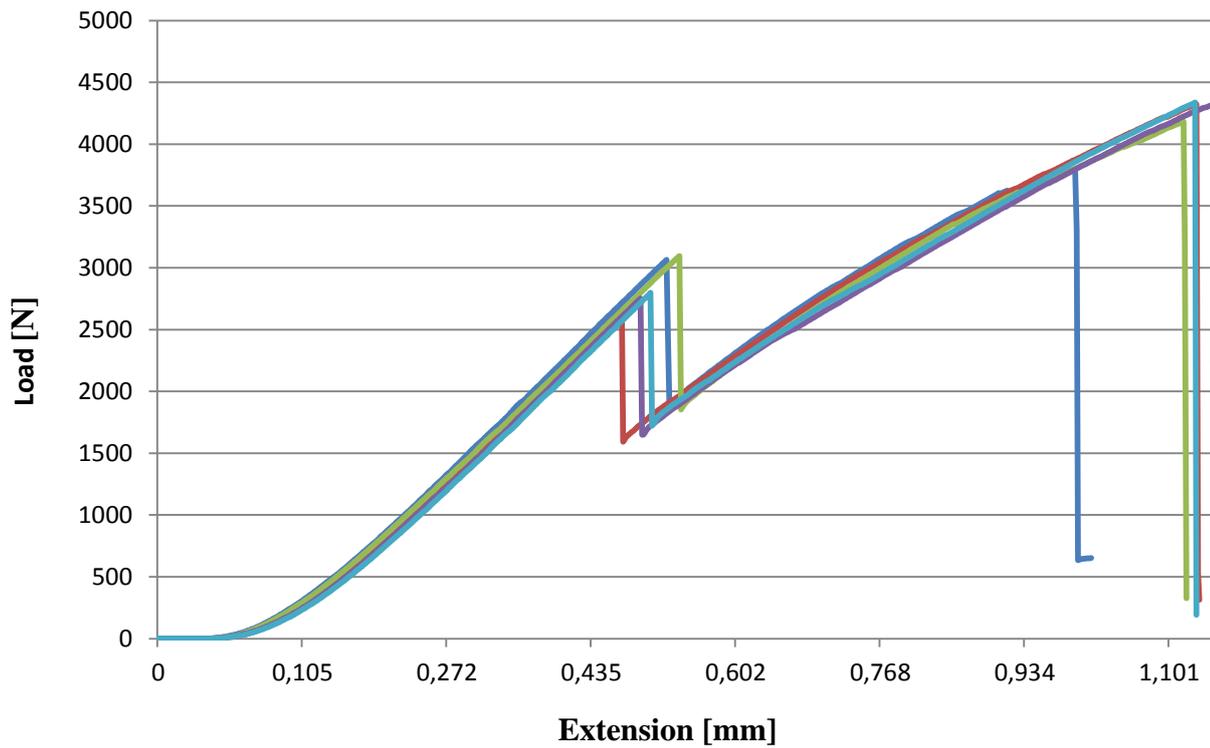
Specimen	Load at yield [N]
1	2247,5
2	2449,3
3	2383,8
4	2509,8
5	2468,6
Mean	2411,8
Std.Dev	102,49

PET film, thickness 75 μm , plasma treated for 5 seconds



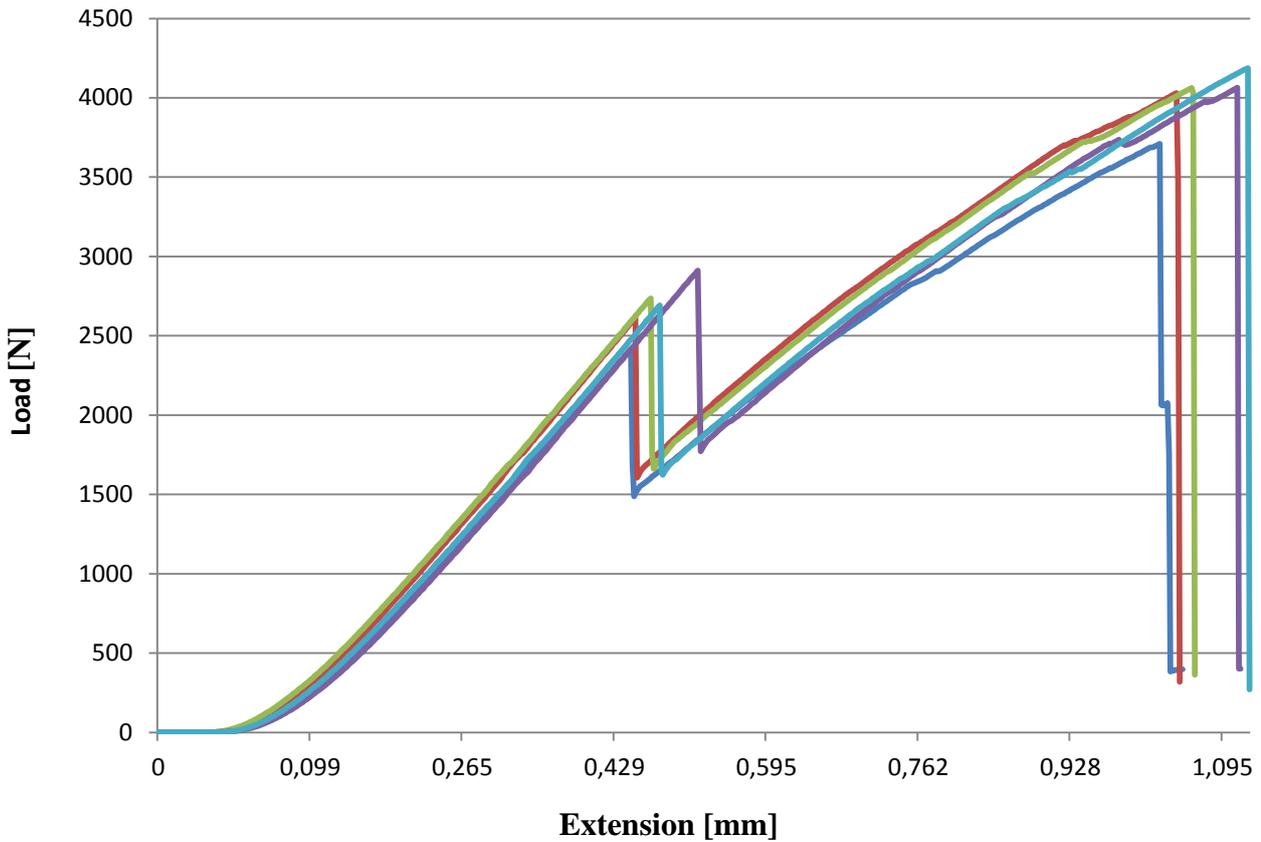
Specimen	Load at yield [N]
1	2770,9
2	2591,2
3	2678,6
4	2622,2
5	2741,7
Mean	2680,92
Std.Dev	76,31

PET film, thickness 75 μm , plasma treated for 10 seconds



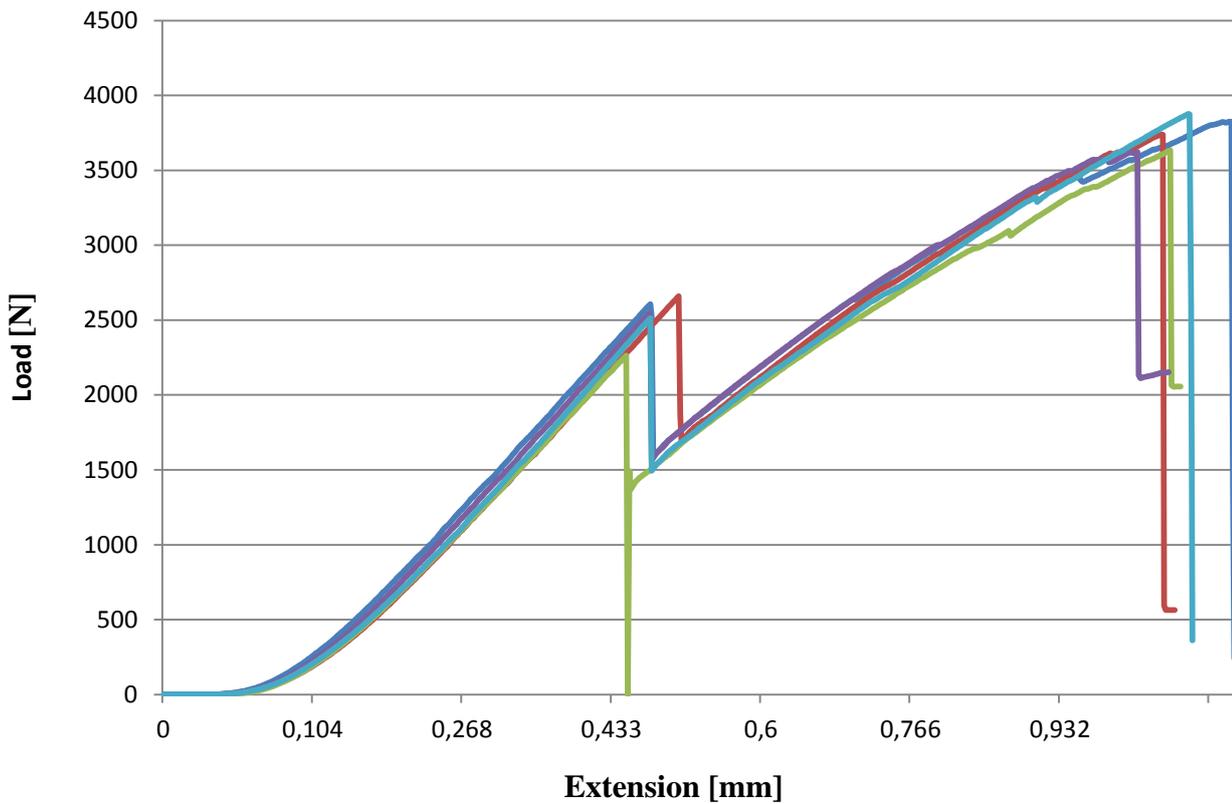
Specimen	Load at yield [N]
1	3063,5
2	2651,7
3	3095,1
4	2752,6
5	2798,4
Mean	2872,26
Std.Dev	196,63

PET film, thickness 75 μm , plasma treated for 20 seconds



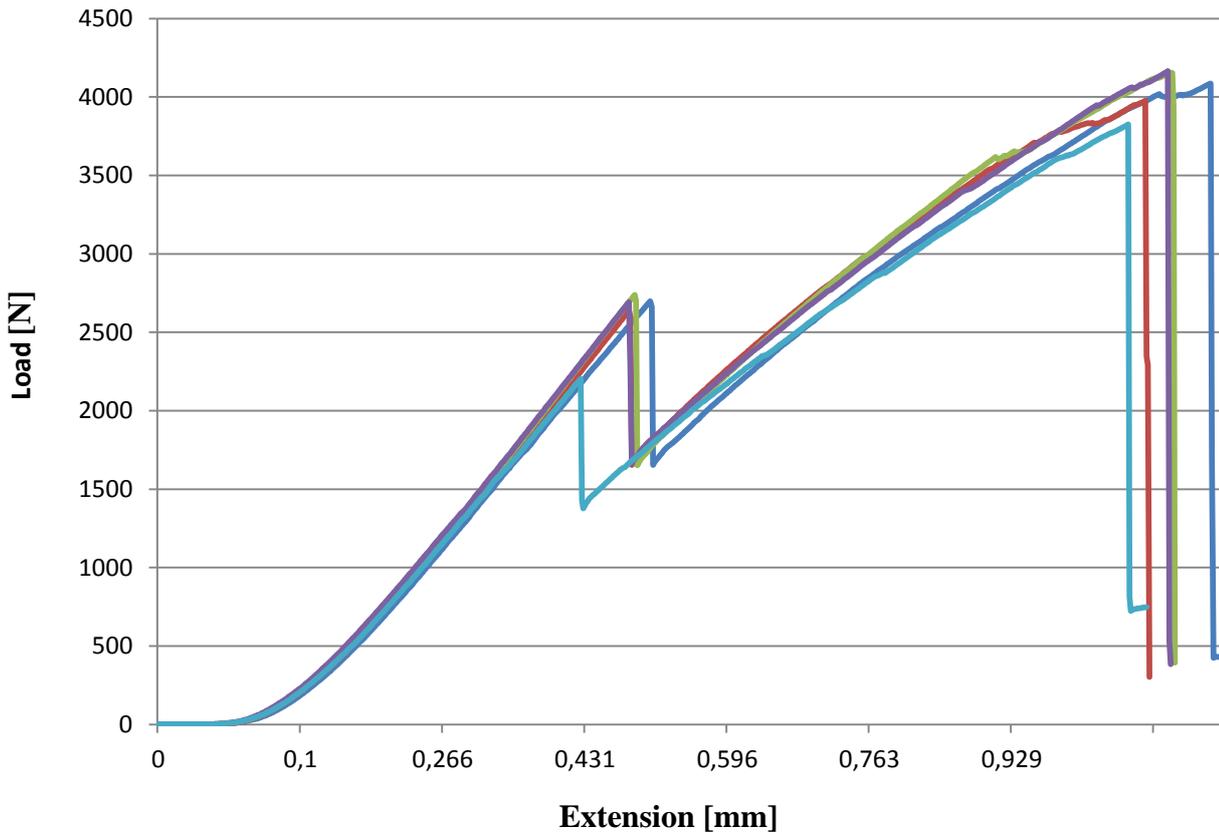
Specimen	Load at yield [N]
1	2416
2	2615,2
3	2737,2
4	2911,8
5	2691,6
Mean	2674,36
Std.Dev	180,88

PET film, thickness 75 μm , plasma treated for 25 seconds



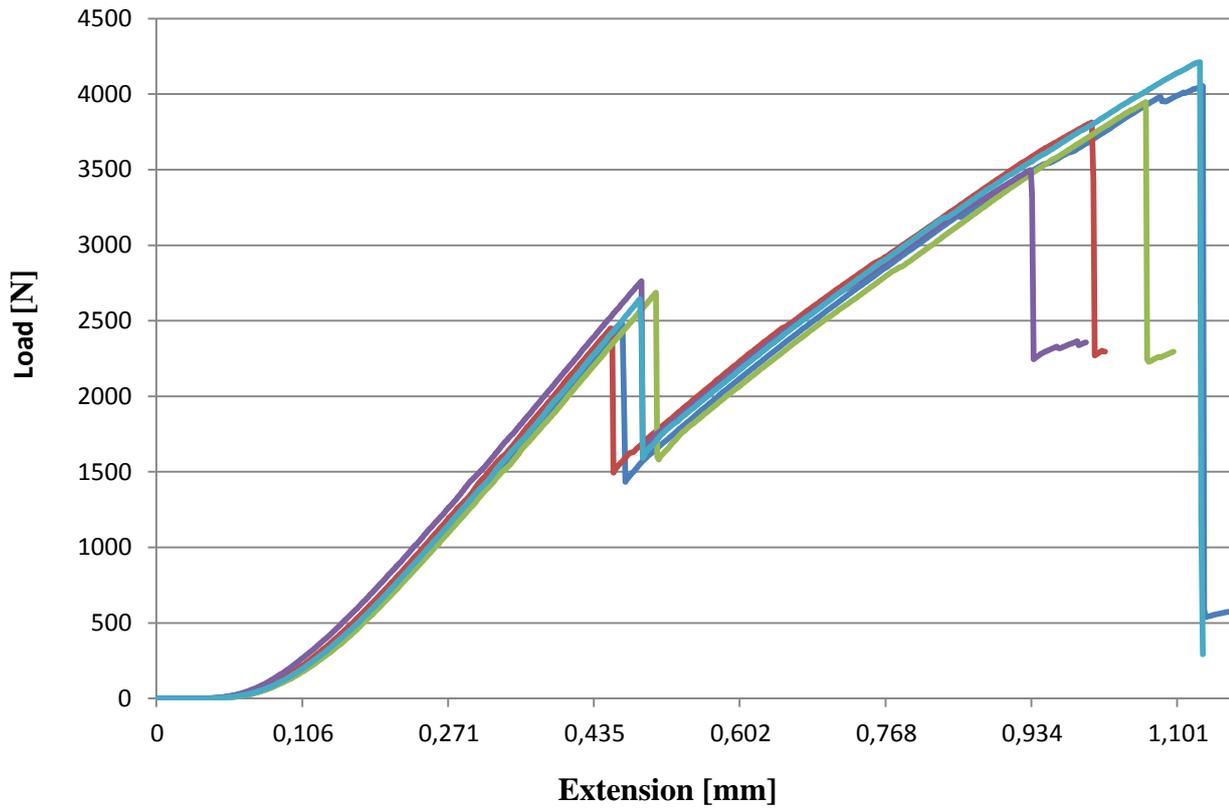
Specimen	Load at yield [N]
1	2525,8
2	2659,7
3	2273,8
4	2544,6
5	2512,8
Mean	2503,34
Std.Dev	140,92

PET film, thickness 125 μm , plasma treated for 5 seconds



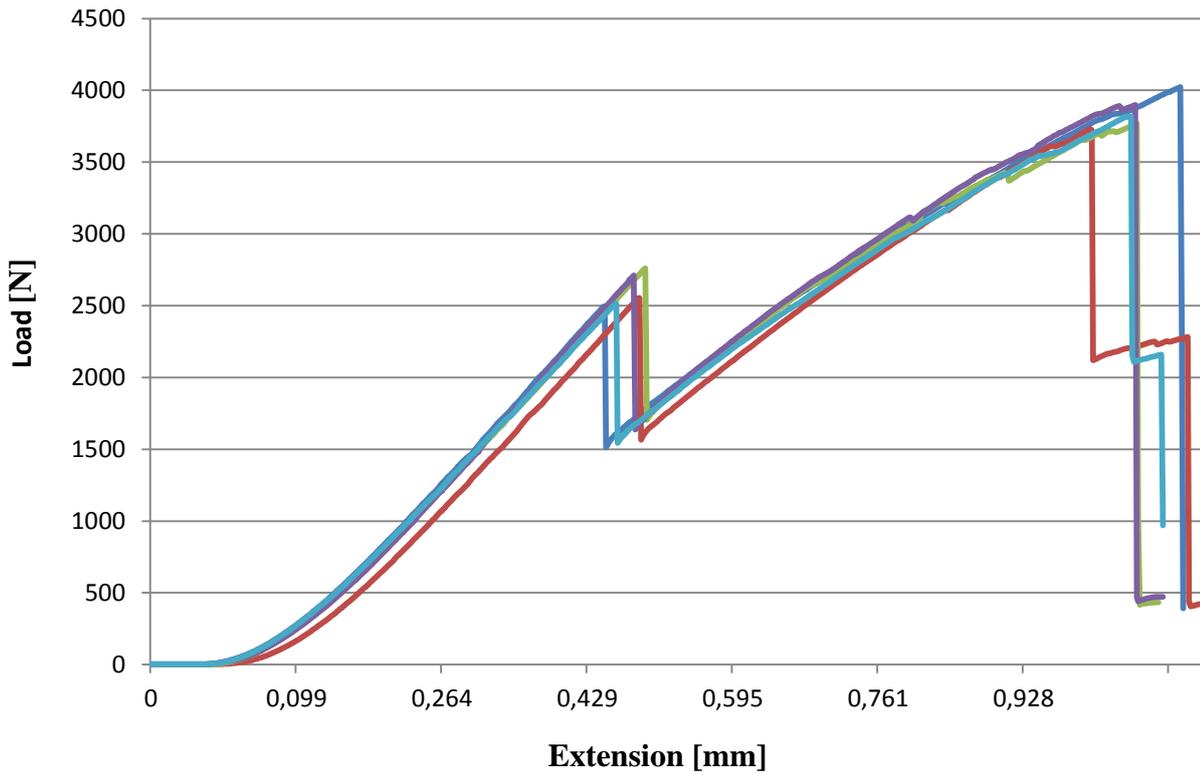
Specimen	Load at yield [N]
1	2698,4
2	2637
3	2738,8
4	2692,6
5	2203,3
Mean	2594,02
Std.Dev	221,41

PET film, thickness 125 μm , plasma treated for 10 seconds



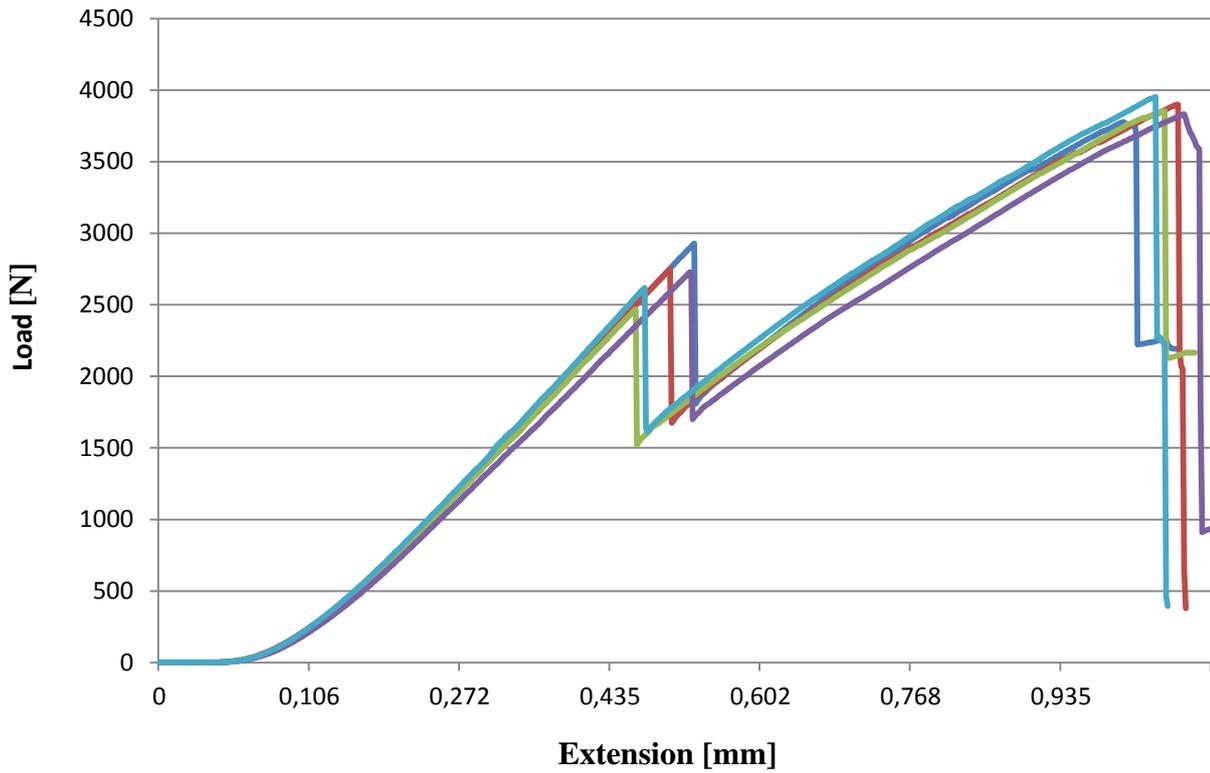
Specimen	Load at yield [N]
1	2477,1
2	2449
3	2686,4
4	2761,5
5	2643,4
Mean	2603,48
Std.Dev	135,35

PET film, thickness 125 μm , plasma treated for 20 seconds



Specimen	Load at yield [N]
1	2494,5
2	2552,7
3	2760,2
4	2710,9
5	2513,7
Mean	2606,4
Std.Dev	121,01

PET film, thickness 125 μm , plasma treated for 25 seconds



Specimen	Load at yield [N]
1	2927,8
2	2749,3
3	2469
4	2727,2
5	2618,6
Mean	2698,38
Std.Dev	169,59

APPENDIX B: SHORT BEAM STRENGTH RESULTS

Short beam strength [MPa]

Dielectric	1	2	3	4	5	Average	Std. Dev.
PET50μREF	28,04	30,04	30,05	28,81	29,72	29,33	0,88
PET50μ5s	29,67	32,26	28,87	26,55	30,44	29,56	2,10
PET50μ10s	29,30	27,80	27,80	28,73	27,45	28,22	0,77
PET50μ15s**	32,39	31,61	31,22	31,05	33,73	32,00	1,10
PET50μ20s	28,13	29,36	33,07	30,90	29,65	30,22	1,87
PET50μ25s	26,31	28,67	27,90	29,38	28,90	28,23	1,20
PET75μREF	28,62	28,85	30,80	31,28	32,01	30,31	1,35
PET75μ5s	32,21	30,12	31,13	30,48	31,87	31,16	0,92
PET75μ10s	35,11	30,39	35,47	31,55	32,07	32,92	2,54
PET75μ15s**	30,74	33,31	29,57	31,66	27,99	30,65	1,58
PET75μ20s	27,89	30,18	31,59	33,61	31,07	30,87	2,41
PET75μ25s	29,15	30,70	26,24	29,37	29,00	28,89	1,88
PET125μREF	32,49	33,19	30,70	34,16	30,64	32,24	1,55
PET125μ5s	30,61	29,91	31,06	30,54	24,99	29,42	2,51
PET125μ10s	28,10	27,78	30,47	31,32	29,98	29,53	1,54
PET125μ15s**	32,01	30,43	31,32	31,81	33,32	31,78	1,06
PET125μ20s	28,10	28,75	31,09	30,53	28,31	29,36	1,36
PET125μ25s	33,21	31,18	28,00	30,93	29,70	30,61	1,92

** The data is taken from reference [1]

APPENDIX C: 3-POINT BENDING: SPECIMEN DIMENSIONS

3-Point bending specimen dimensions [mm]

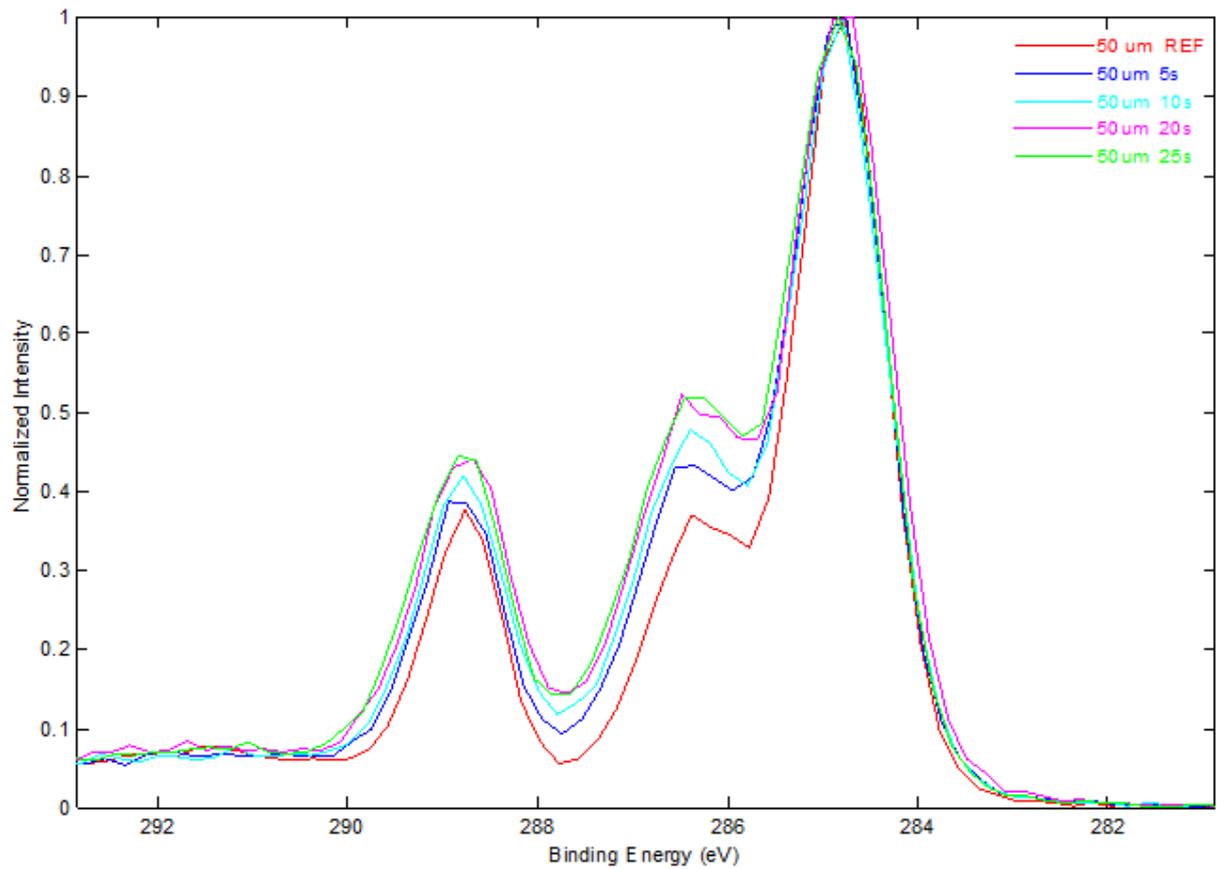
PET50μ5s	1	2	3	4	5	Average
Width	11,5	11,4	11,5	11,41	11,51	11,45
Thickness	5,63	5,59	5,68	5,65	5,63	5,64
Length	34,4	34,18	34,07	34,4	34,35	34,28
PET50μ10s						
Width	11,8	11,5	11,76	11,83	11,85	11,75
Thickness	5,6	5,63	5,59	5,59	5,62	5,61
Length	35,09	34,61	35,11	35,23	35,27	35,1
PET50μ15s**						
Width	-	-	-	-	-	11,5
Thickness	-	-	-	-	-	5,7
Length	-	-	-	-	-	33,3
PET50μ20s						
Width	11,49	11,5	11,59	11,81	11,32	11,54
Thickness	5,68	5,54	5,61	5,59	5,63	5,61
Length	34,32	34,39	34,25	34,07	33,84	34,17
PET50μ25s						
Width	11,34	11,34	11,37	11,38	11,45	11,38
Thickness	5,62	5,6	5,62	5,51	5,66	5,6
Length	33,35	33,3	33,78	33,91	33,64	33,6
PET75μ5s						
Width	11,54	11,34	11,36	11,29	11,33	11,37
Thickness	5,63	5,61	5,6	5,6	5,66	5,62

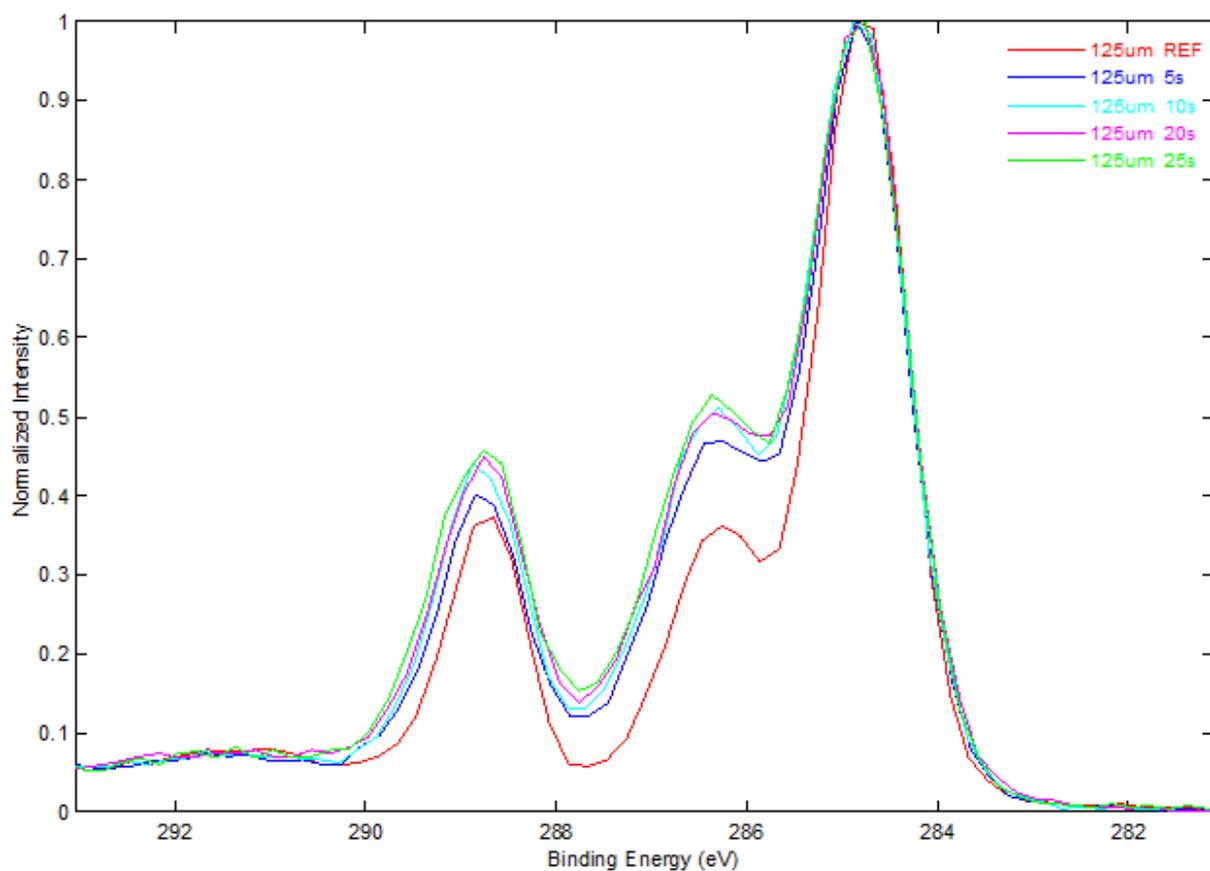
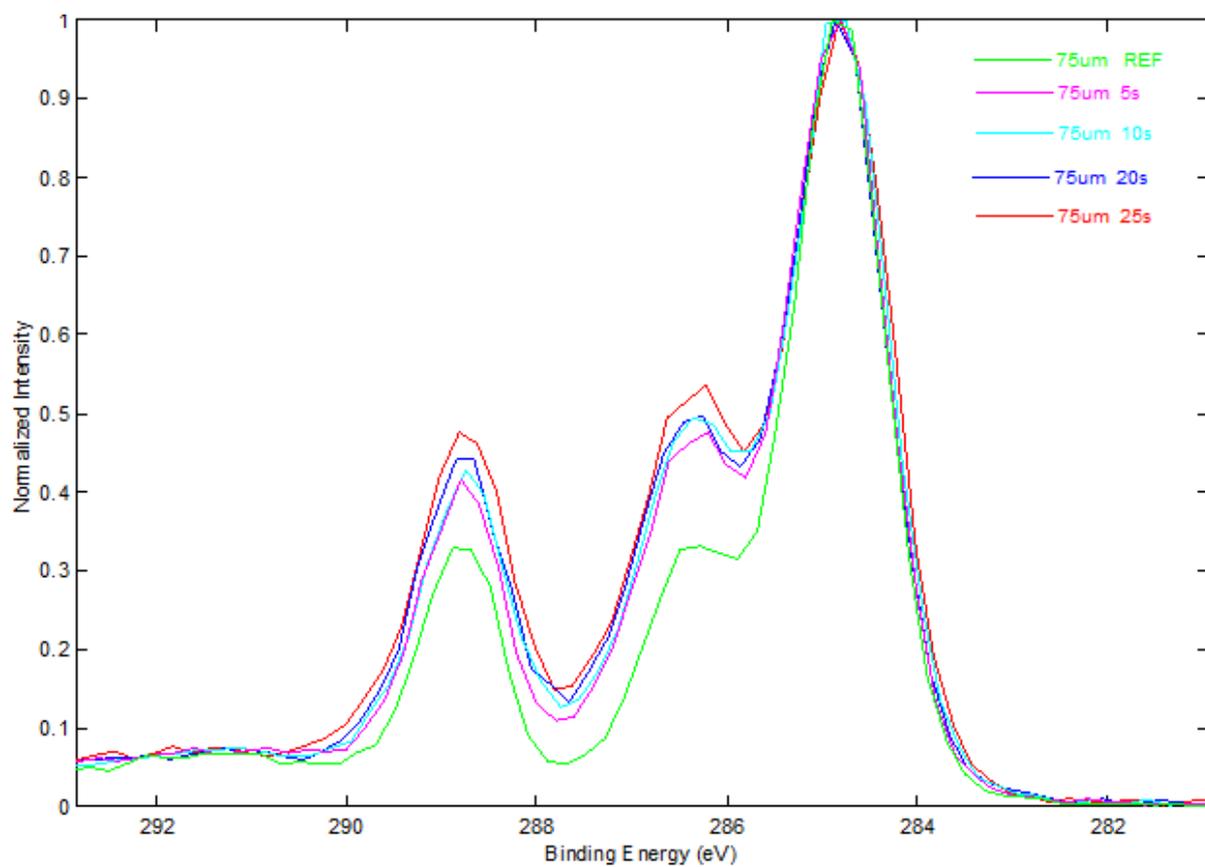
Length	33,73	33,9	34,11	33,92	34,0	33,93
PET75μ10s						
Width	11,3	11,46	11,31	11,4	11,35	11,36
Thickness	5,63	5,71	5,71	5,69	5,71	5,69
Length	34,33	34,0	34,3	34,0	34,03	34,13
PET75μ15s**						
Width	-	-	-	-	-	11,5
Thickness	-	-	-	-	-	5,8
Length	-	-	-	-	-	34,6
PET75μ20s						
Width	10,89	11,4	11,46	11,21	11,2	11,23
Thickness	5,62	5,71	5,7	5,7	5,68	5,68
Length	33,68	34,03	34,09	34,04	34,1	33,99
PET75μ25s						
Width	11,4	11,45	10,96	11,17	11,33	11,26
Thickness	5,72	5,73	5,71	5,74	5,61	5,7
Length	34,15	34,09	34,04	34,07	33,88	34,05
PET125μ5s						
Width	11,39	11,47	11,53	11,47	11,5	11,47
Thickness	5,73	5,76	5,76	5,71	5,74	34,3
Length	34,36	34,34	34,49	33,94	34,39	5,74
PET125μ10s						
Width	11,5	11,46	11,36	11,46	11,44	11,44
Thickness	5,57	5,71	5,75	5,66	5,73	5,68
Length	34,45	34,58	34,3	34,42	34,49	34,45
PET125μ15s**						

Width	-	-	-	-	-	11,4
Thickness	-	-	-	-	-	5,7
Length	-	-	-	-	-	34,4
PET125μ20s						
Width	11,44	11,29	11,51	11,47	11,37	11,42
Thickness	5,69	5,71	5,78	5,77	5,71	5,73
Length	34,47	34,53	34,56	34,65	34,43	34,53
PET125μ25s						
Width	11,49	11,35	11,46	11,25	11,51	11,41
Thickness	5,74	5,74	5,73	5,74	5,67	5,72
Length	34,4	34,36	34,54	34,1	34,43	34,37

** The data is taken from reference [1]

APPENDIX D: ESCA/XPS RESULTS





APPENDIX E: EQUIPMENT

Vacuum injection moulding

Vacuum pump (used for VIM and prepegs): Leybold SA SOGEVAC (8V25 10903, 395 12 00126)

Consolidation of prepeg

Degasser: Bel-Art

Overflow vessel: Unknown make and model.

Oven: TRIAB, Eurotherm 2408, Nr: 5854

ESCA/ XPS analysis

Equipment: Quantum 2000 scanning ESCA microprobe from Physical Electronics

X-ray source: Al K α (1486.6 eV)

Beam size: 100 μm

The analysed area: approximately 500 x 500 μm

Take-off angle was 45° with respect to the sample surface

The information depth: approximately 4-5 nm.

Mechanical characterization

Polish equipment: Struers Labopol – 5

Mechanical tester: MTS 20/M with Testworks 4.04 B

Plasma treatment

Technics Plasma 440G

APPENDIX F: MATERIALS

Carbon fibre prepeg

Advanced composite group MTM57/CF3200

Carbon fibre fabric

Unspecified maker and model

Polyester film

DuPont Mylar A, supplied by Trafomo A/S Sweden