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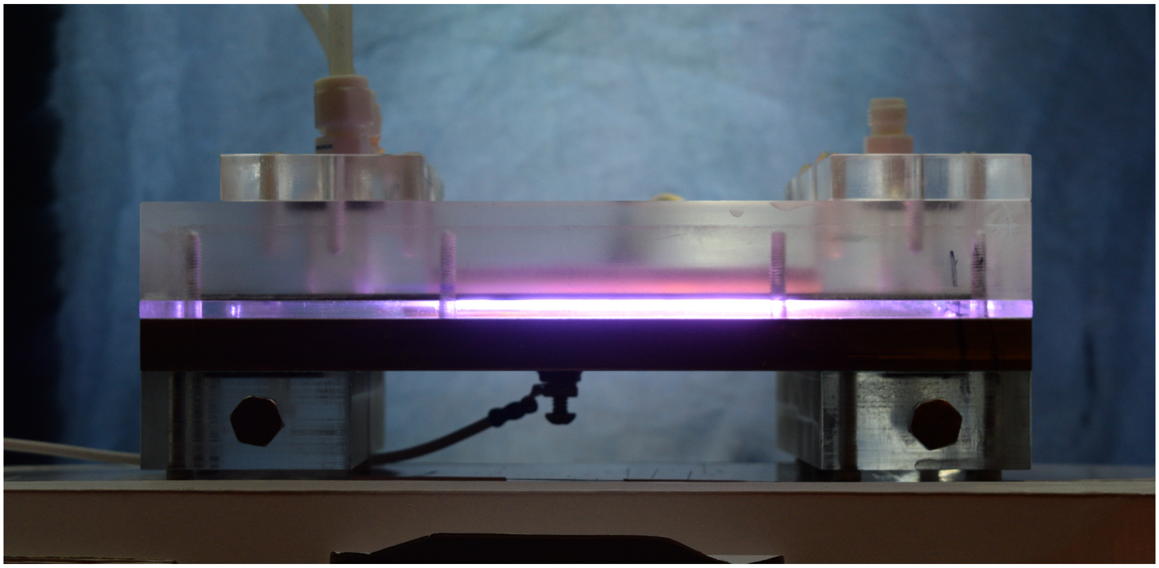

Atmospheric pressure plasma deposition of thin organic films for improved adhesion in polymer composites

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TABLE OF CONTENTS

1 Abstract

Composite polymers in the form of multilayer laminates are used to produce multifunctional surfaces such as food packaging, pool linings, or automotive interiors. Individual sheets provide antimicrobial properties, water resistance, or mechanical properties and require a sound union for robust composite performance. Current industrial processes use toxic isocyanate containing adhesives to bind the multiple layers together, which could be replaced with plasma deposition of nitrogen-rich organic adhesive coatings. Here, atmospheric-pressure dielectric barrier discharge (DBD) plasma is shown to enhance adhesion between a Thermoplastic Polyolefin (TPO) substrate and Polyurethane (PU) coating in an industrially suitable process. Sample production begins by treating TPO with two stages of DBD, operating at 18.7 kHz and 9.9 kV_{pp}. Initial plasma treatment within a simulated air mixture achieves surface activation of TPO through oxidative reactions. A nitrogen-rich organic film is then deposited in the form of a plasma polymer through further DBD treatment using a mixture of Nitrogen and either Ethylene or Butadiene. XPS characterization of samples at this stage showed up to 25 at% Nitrogen incorporated in produced plasma polymers. Following plasma treatment of TPO, solvent based polyurethane is then twice brush coated onto the modified substrate and cured in an oven at 95 ℃. Samples are finally assessed for the quality of adhesion between TPO and PU layers by qualitative and quantitative peel testing. Analysis of peel tests has shown clear improvements over samples without plasma polymer deposition, but lower delaminating loads than for samples produced with PECVD. Significant improvements including additional steps for quality control are required at lab scale to meet industrial standards. Nevertheless, the demonstrated adhesion enhancement, using an atmospheric pressure DBD plasma system, is a promising concept for polymer production.

2 Abrégé

Les polymères composites sous la forme de multicouches stratifiées sont utilisés pour produire des surfaces multifunctionelles telles que des revêtements de piscine et des intérieurs d'automobiles. Les feuilles individuelles confèrent aux propriétés antimicrobiennes appropriées, à la résistance à l'eau ou aux propriétés mécaniques, et nécessitent une union solide pour des performances composites robustes. Les procédés industriels actuels utilisent des adhésifs contenant des isocyanates toxiques pour lier les multiples couches, ce qui pourrait être remplacé par un dépôt par plasma de revêtements adhésifs organiques riches en azote. Ici, un plasma à décharge sur barrière diélectrique à pression atmosphérique (DBD) montre l’amélioration de l'adhérence entre un substrat de polyoléfine thermoplastique (TPO) et un revêtement de polyuréthanne (PU) dans un procédé convenant à l'industrie. La production d'échantillons consiste à traiter un substrat de TPO avec deux étages de DBD fonctionnant à 18,7 kHz, 9,9 kV_{pp}. Le traitement initial au plasma dans un mélange d'air simulé permet d'obtenir une activation de surface de la TPO par des réactions oxydatives. Un film organique riche en azote est ensuite déposé sous la forme d'un polymère de plasma par un autre traitement au DBD en utilisant un mélange d'azote et d'éthylène ou de butadiène. La caractérisation XPS des échantillons à ce stade a montré jusqu'à 25% d'azote incorporé dans les polymères plasmatiques produits. Après le traitement au plasma de TPO, le polyuréthane à base de solvant est ensuite appliqué deux fois au pinceau sur le substrat modifié et cuit dans un four à 95 ° C. Les échantillons sont ensuite évalués en fonction de la qualité de l'adhérence entre les couches TPO et PU par des tests de pelage qualitatifs et quantitatifs. Ces tests de décollement ont montré des améliorations claires sur les échantillons sans dépôt de polymère plasma, mais des charges de délaminage plus faibles que pour les échantillons produits avec PECVD. Des améliorations importantes, notamment des étapes supplémentaires de contrôle de la qualité, sont nécessaires à l'échelle du laboratoire pour répondre aux exigences industrielles. Néanmoins, l’amélioration de l’adhérence démontrée avec un système plasma DBD à pression atmosphérique est un concept prometteur pour la production de polymères.

3 Acknowledgements

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4 Introduction

A person's average day carries heavy exposure to a variety of imitation plastics such as polyurethane bike seats or sofa cushion covers that are made to resemble more desirable leather. These "forgeries" are typically produced from multiple components, with a superficial layer providing a desired aesthetic and one or several underlying layers providing intrinsic mechanical properties. More complex plastic composites might include layers for antimicrobial or water resistant properties, as is common in food packaging[1].

A variety of multi-layer plastics are currently produced using isocyanate-containing adhesives. While use of these adhesive is inexpensive, time efficient, and provides mechanically sound unions between a range of materials, exposure to isocyanate compounds has been linked to dangerous medical conditions such as bronchitis, emphysema, and asthmatic syndrome[2]. A non-toxic adhesion process that maintains the currently achievable mechanical and chemical properties of available adhesives is therefore of interest. Due to widespread corona treatment of materials in the polymers industry, additional plasma deposition of an adhesive layer could be an option.

Past work with a Plasma Enhanced Chemical Vapor Deposition (PECVD) system has demonstrated significant adhesion enhancement between a Thermoplastic Polyolefin (TPO) substrate and Polyurethane (PU) coating. First, an oxidative plasma was used to increase the substrate surface energy. This treatment increases substrate affinity for subsequently deposited plasma polymer thin films and is therefore often referred to as "pretreatment". Next, a 200 nm thick nitrogen rich plasma polymer was deposited using a mixture of nitrogen and either butadiene or ethylene. Adhesion tests between TPO and the ultimately applied PU layer have demonstrated the efficacy of PECVD pretreatment followed by nitrogen rich plasma polymer deposition. [3]. While low-pressure plasmas are known for high uniformity in their treatment, vacuum generation becomes expensive when considering scale up and significantly complicates operation. In contrast, atmospheric pressure systems can operate in an open environment, given necessary safety precautions, allowing for easy integration with popular roll-to-roll production setups; large surface areas can be rapidly treated at low cost. Here it is proposed to develop an atmospheric pressure plasma process that achieves an adhesion strength comparable to what was attainable using both the toxic adhesive and the low-pressure plasma system. A capacitively coupled Dielectric Barrier Discharge (DBD) reactor was selected for all sample production, to allow for rapid treatment of large polymer sheets upon eventual industrial application.

This thesis will start by outlining the relevant theory behind polymer adhesion, the plasma processes to be used, and past work concerning plasma polymer coatings for polymer adhesion. An experimental approach consisting of a plasma pretreatment process, a subsequent plasma polymer deposition process, and a final curing process is outlined as the optimal solution. XPS characterization is presented to establish the effect of plasma pretreatment and polymer deposition on substrate surface chemistry. Samples are additionally tested for adhesion quality between TPO and PU layers by qualitative and quantitative peel testing. Peel test results are discussed, and conclusions are made regarding the potential of the process outline here.

5 Project Objectives

This project aims to improve current industrially used atmospheric pressure plasma processing in multilayer polymer laminate production. The standard substrate surface activation step, accomplished through oxidative plasma treatment, would be followed by a novel plasma polymer deposition stage. This could replace conventional adhesives, primers, and crosslinkers used for laminate production. Previous results have shown that low pressure plasma enhanced chemical vapor deposition of nitrogen rich organic thin films onto sheets of TPO substrate can enhance PU top finish adhesion. Here it was proposed to demonstrate similar adhesion enhancement through an industrially suitable, atmospheric pressure process.

The following project objectives were stipulated and considered throughout testing.

1. Accomplish deposition of an adhesive nitrogen rich plasma polymer using an atmospheric pressure dielectric barrier discharge system and non-toxic gas mixtures, to allow for eventual operation in open atmosphere.
2. Demonstrate adhesion enhancement between a TPO substrate and PU top finish using deposition of non-toxic nitrogen rich thin films
3. Produce samples of PU adhered to TPO with a minimum strength of 1.3 kg_f (production standard specified by Canadian General Tower)
4. Minimize sample production time and overall power requirements

These objectives will be assessed for completion throughout the Discussion and Conclusion sections.

6 Background

6.1 Adhesives

A range of products and applications use adhesives to join multiple, otherwise non-adhering, surfaces together. An adhesive's primary function is displacement of the air separating target surfaces, after which the surfaces must be immobilized by sufficient force[4]. Binding to surfaces is achieved through both chemical and physical methods. Pressure sensitive adhesives, such as tapes, are simple and practical in their use, but have limited applicability. Other options require evaporation of a solvent or chemical reaction between two separate components (as in an epoxy) to initiate adhesion but have increased performance interfacing with typically "non-stick" materials (metal, wood)[5], [6].

Adhesives are typically composed of a bulk polymer, termed either the base or binder, that determines the adhesive's main properties such as durability, stiffness, and surface energy. Additional components, or additives, such as fillers, hardeners, solvents, plasticizers, tackifiers, and antioxidants are dispersed throughout the binder to adjust properties as needed for production and application[7][8]. Consideration of the adhesive's eventual application is important when selecting additive components. For example, adhesives used in food packaging will require limited concentrations of solvents or low molecular weight components, due to their increased mobility and potential to contaminate edibles[8],[9]. In instances where production requires exposed workers, adhesives require a design that limits toxicity.

Isocyanate containing adhesives face widespread application due to their versatility. Application is effective in both hot and cold melt processes, and reactivity is high towards a range of materials[10][11]. Toluene diisocyanate (TDI) and diphenylmethane diisocyanate (MDI) are used on the largest scale[10]. As synthetic adhesives, their use is economically efficient, facile, and new developments are rapid. However, continuous exposure to isocyanate compounds can result in medical conditions such as bronchitis, emphysema, and asthmatic syndrome[2]. Natural adhesives have been developed based on proteins, starch, or lignin, and provide a potential alternative due to their low toxicity. These options are poor for applications requiring robust adhesion, as water and thermal resistance are limited and the timeframe for application is therefore reduced[10].

Another alternative to conventional synthetic adhesives is the deposition of an adhesive plasma polymer thin film. Plasma deposition for adhesive applications is often preceded by an oxidative plasma treatment, to increase substrate surface energy and ensure chemical compatibility with deposited plasma polymer films[7], [12]–[16]. The deposition of an adhesive plasma polymer layer can improve unions between a variety of polymeric and metallic surfaces [13], [17], [18]. Operation with non-toxic feed gases ensures a process that can operate in open atmosphere without harming workers. This alternative, similarly to natural adhesives, is limited by lower adhesion strength than standard synthetic adhesives.

6.2 Adhesion Theory

There are several parallel schools of adhesion theory. The Griffith-Irwin Theory of fracture mechanics is based around the energy required to form a crack of critical length, and implies that interfaces with stiff adhesive layers and cracks of small size will adhere more firmly[19].

Electrostatic and Chemical Interaction Theory attempts to explain adhesion in terms of charge transfer across the interface or covalent bonding. While charge transfer between polymeric surfaces should be negligible, the potential for strengthening adhesion by covalently bonding two plastics together or to an intermediate layer remains an attractive option[20].

Wetting Theory is based on the surface chemistry of materials used, and the difference in surface energy, as follows:

$$W_A = \gamma_1 + \gamma_2 - \gamma_{12}$$

Where W_A is the work of adhesion, γ_1 and γ_2 are the different material surface energies, and γ_{12} is the interfacial tension[20]. Materials of similar chemistry will require less work for adhesion due to negligible interfacial tension, allowing the process to proceed more favorably. This theory establishes increased importance of compatible chemistry at the interface.

Finally, Diffusion Theory applies almost exclusively to polymers or materials with long functional chains. Two polymers joined at an interface can have chain diffusion across into the other polymer, effectively binding the two together. The thermodynamic relationship describing the spontaneity of a mixing process, and therefore the miscibility of specific materials, is given as:

$$dG_{Mix} = dH_{Mix} - TdS_{Mix} < 0 \qquad [21]$$

Despite the long chains available for interdiffusion between polymers, this relationship illustrates the occasional difficulty in adhering polymers. The enthalpy of mixing for most polymer combinations is a positive quantity, while the entropy of mixing is far smaller than for smaller molecular weight materials. Most copolymer systems require elevated temperatures to promote chain diffusion across an interface, and therefore mixing. Indeed, it has been observed that polymers will generally not mix below their glass transition temperature[20].

A basic understanding of the latter three schools of adhesive theory discussed above can be used to promote maximum adhesion. The surface energies at the polymeric interface should be similar for compatibility, and this will be achieved using a plasma pretreatment process known to adjust contact angle[22][23]. Any covalent bond formation between polymer surfaces will further promote adhesion, and carefully selected process chemistry can achieve this[24]. Finally, joining the two polymeric surfaces at an elevated temperature in the eventual curing stage will help promote polymer chain diffusion.

Whether an adhesive is applied in liquid or solid form has significant implications on the theory describing failure mechanics. Separation of materials joined by a solid adhesive depends on surface, or topical, properties, while the same process completed with liquid adhesive becomes a rheological phenomenon dependent on bulk liquid properties (namely viscosity)[4].test iExtensive research regarding adhesion has resulted in the development of many test methods. [25], [26]atomic force microscopyTestsof this nature Figure 1

cldrTable 3

6.3 Plasma Processes

Plasma, a partially or fully ionized gas, is perhaps the most diverse state of matter in terms of characteristic properties: temperatures can range from 10^{-2}-10^{4} eV, while particle densities range from 10^{9}-10^{25} m^{-3}[13], [16]. This large range in properties provides versatility, and has led to industrial plasma applications from rocket propulsion to nanoparticle production[35]–[38].

A plasma's effect is dependent on its classification as either local thermal equilibrium (LTE) or non-local thermal equilibrium (non-LTE) plasma. If particle collision frequency is comparable to the system's rate of photon adsorption, a plasma will equilibrate. The high temperature, low-mass, electrons of the system will reach equilibrium with the initially low temperature, high-mass heavy species. Thus, a key difference between LTE and non-LTE plasmas is the fraction of system energy carried by heavy species, which has direct implications for material processability and therefore industrial applicability.

LTE plasmas often occur in the form of an arc and are applied where a high temperature, or ion and radical rich, environment can provide useful reaction catalysis or rare material synthesis. These plasmas are typically used in applications requiring high energy flux, or power. Arc treatment of metals is widespread in both the automotive and aerospace industry[39][40]. Temperature sensitive materials such as organic or polymeric materials typically dictate non-LTE use to prevent material degradation. Non-LTE plasmas are applied in less energetic processes requiring lower activation energies, such as surface functionalization either through small particle addition or removal or thin film deposition.

Whether plasma treatment will have an additive or subtractive effect is determined by the process gas composition. High concentrations of electronegative species such as oxygen and fluorine will promote ablation and oxidation of the surface, while high concentrations of hydrogen or carbon molecules promotes surface polymerization or thin film deposition[7], [41]. Both of these methods have been heavily investigated[8], [26]–[28].

6.3.1 Non-LTE Atmospheric Operating Conditions

Preventing thermalization, maintaining Non-LTE or "cold" plasma, at atmospheric pressure requires strict parameter control. The practical options to regulate particle collision frequency and avoid local thermal equilibrium are pressure, precursor, and power control. Operation at lower pressure is common for most glow discharge plasmas, used in the semiconductor industry, but becomes expensive for large areas of treatment. For atmospheric pressure operation, it becomes common to select a process gas with a low breakdown voltage, such as Argon or Helium[13],[16],[45]. nWhen the application provides further constraints regarding process gas, limiting power is the only alternative. Thus, atmospheric pressure LTE plasmas require either pulsed or high frequency power supply (as in corona or DBD) or gas flow rates high enough to avoid equilibrium (effectively lowering the power per molecule, seen in torches).

Operating at high frequencies, above 1 MHz, prevents heavy species from migrating in phase with the electric field and therefore equilibrating [16]. Providing pulsed power also attenuates equilibrating. Insulation is additionally used to prevent direct arcing from occurring. A recently popular configuration, the pencil-like torch, modifies the classic torch configuration by coupling it with a low power, high frequency power source. This produces non-LTE plasma, with a low effective temperature but high electron density, making it suitable for polymer or otherwise delicate material processing[13].

The Paschen Law famously describes the required breakdown voltage for an atmospheric plasma as follow

$$V_{Breakdown} = \frac{B \times p \times d}{C + \ln{(p \times d)}}$$

where p is operating pressure, d is the inter-electrode distance, and B and C are constants dependent on gas and electrode compositions[46]. It's clear from this equation that increasing either pressure or electrode spacing requires higher power operation, which is undesirable for industrial polymer processing. It is therefore intuitive to operate at the smallest gap spacing that still allows for sufficient and even gas flow through the void. Figure 2Figure 2Figure 3 Table d

6.3.2 Thin Film Deposition

Plasma deposition involves a wide array of materials. Plasma polymer composition and structure is determined by precursor gas flow rates and kinetics set by operating conditions (power, frequency, voltage). Hybrid coatings have additionally been developed, where small nanoparticles are embedded in a plasma polymer film. Thin films with compositional gradients can be produced by varying precursor flowrates throughout deposition. A list of various thin films deposited by atmospheric pressure plasma processes has been organized by Merche et al.[16].

Deposition is initiated by the formation of an activated species through repeated collision with high energy particles. Propagation of radical species formation, reaction, and random recombination drives the polymerization process, and distinguishes the resulting coating from a conventional polymer. The random radical recombination produces a branched and disorganized polymer structure when compared to the ordered, linear, forms resulting from conventional step growth polymerization. The chemical regularity of the produced plasma polymer is dependent on the Yasuda factor, determined as follows[16]:

$$E = \frac{W}{FM}$$

Where E is the Yasuda factor, W is the deposition power (J/s), F is the monomer flow rate(uL/min), and M is the monomer molecular weight (kg/mol). At low values of E, the produced plasma polymer coating will have a structure similar to the conventional polymer form and deposit at a low-rate. At high values of E, a random polymer structure is deposited at increased rates.

Film deposition alters the surface chemistry and energy of a material and can be used to multiple effects. Amine rich plasma polymers deposited using low pressure radio frequency discharge can achieve selective cell or protein adhesion, relevant for different medical applications, through precise control of surface chemistry and energy [43][22]. Plasma polymer thin films can also promote adhesion between otherwise incompatible surfaces[44], [53]. Incorporating metal ions into an intermediate layer through plasma processes has demonstrated improvements in otherwise weakly adhered systems. Titanium ion bombardment of a substrate generating an intermediate Ti_2N layer strongly promotes adhesion enhancement to TiN films[54].

DBD glow discharge has been used to deposit adhesive layers onto both insulative (polymeric) and metallic substrates with similar results [13]. Deposition of epoxide containing plasma polymers, specifically, generates highly reactive and versatile surfaces that strongly adhere to a range of substrates [55]. Adhesion is significantly enhanced here due to the formation of covalent bonds, which can be orders of magnitude stronger than the electrostatic interactions dominating other interfacial unions. Covalent bond formation can be further favored through deposition of thin films of complementary chemistry, such as opposing epoxide and amine rich coatings. PGMA Microfluidic devices coated in epoxide rich polymer have been joined with amine rich plasma polymer coated substrates through a mild curing process[56].

6.3.3 Hydrophobic Recovery

A significant challenge in surface functionalization is a material's subsequent thermodynamically driven, time dependent, reorganization to minimize surface energy. When considering polar coatings, this is termed hydrophobic recovery. The extent of material reorganization and therefore loss of functionality is dependent on material bulk and surface properties, as well as the environmental conditions and age of the sample. When samples are stored in the absence of solvent, recovery is largely due to polymer chain reorientation at the material surface[57], [58]. Reduction of chain mobility therefore reduces material recovery, and has been demonstrated by increased crosslinking of deposited films[22], [59]. Reduced temperature should have a similar effect. Alternatively, saturating the material surface with the desired chemistry reduces the effect of chain reorientation[59]. As outlined in the Experimental section, this project will use both an oxidative plasma treatment followed by a plasma polymer deposition process. Rather than vacuum storage, samples could be maintained under nitrogen for practical mitigation of aging. The time between pretreatment and deposition will additionally be minimized. Once plasma polymer deposition has occurred, the cross-linked nature of this layer should prevent further aging.

6.3.4 Weak Boundary Layer Formation

Adhesion to polypropylene, polyethylene, and other polymer surfaces can be reduced by the presence of a weak boundary layer consisting of small and poorly attached molecules. This formation can be the result of unwanted polymerization impurities, additives like antioxidants or plasticizers, mold release agents, or post fabrication contamination[60]. Crosslinking this layer using discharge treatment can increase attachment to bulk polymer and increase adhesion, but excessive treatment ("overtreatment") achieves the opposite. Polymer surfaces treated with oxidative corona, or other discharge, are often further coated in Low Molecular Weight Oxidize Materials (LMWOM), as a result of chain scission by reactive plasma species. Formation is promoted through increased treatment power, and suppressed through increased relative humidity, with power being the dominant factor. Heavily coated substrates begin to display a "frosted" appearance, due to agglomerated LMWOM[61].

The effect of a weak boundary layer, and any produced LMWOM, on adhesion is dependent on whether these compounds are incorporated into the adherate. Sufficient substrate – adherate interaction can displace or incorporate small surface compounds[60]. Studies have shown increased adhesion when this is the case, and decreased adhesion otherwise. LMWOM are typically polar, and soluble in water, alcohols, and ketones. Potential "overtreatment" is therefore defined with respect to adherate chemistry, and of more concern when working with alkane or aromatic based materials. Unwanted boundary layers can be removed simply by wiping a covered surface[61].

6.3.5 Corona Discharge

Corona discharge is a popular industrial tool for plasma oxidation or polymerization[46]–[48]. A pulsed DC signal of relatively low frequency (<1MHz) is run through either a wire or planar electrode to generate plasma[49], [50]. Induced electric fields accelerate electrons and generate plasma, and so the simplest coronas require geometries that amplify field strength. Sharp points and small radii of curvature and are commonly used to this effect[51]. Depending on the selected process parameters, one or more discharge regimes may be observed. The four common discharges are illustrated in Figure 1[50]. If the voltage applied surpasses a critical value dependent on process gas, total breakdown and arcing can occur, as shown in Figure 1d[13].

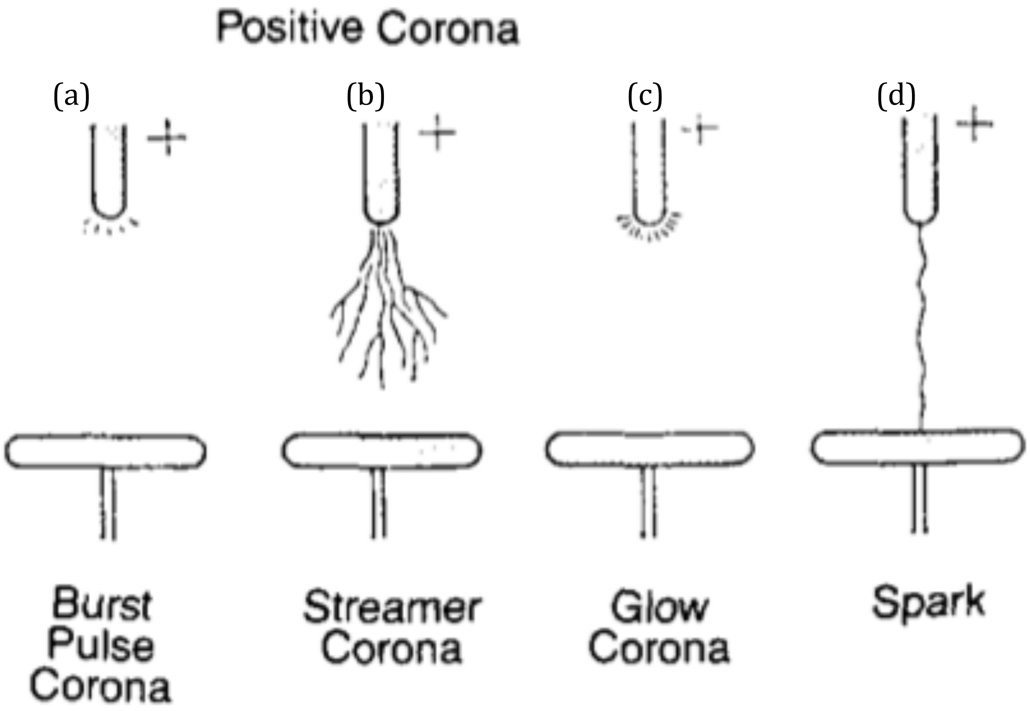


Figure 1: The four attainable corona discharge regimes: (a) burst, (b) streamer, (c) corona, and (d) spark

Corona treatments are some of the most widespread industrial uses of plasma due to key practical advantages. Operation at atmospheric pressure means that no pumps are required for vacuum generation, which provides an economic advantage when considering scale up. The opportunity for an open system provides the means for treating increased surface areas and operating as a continuous process, without time requirements for vacuum pump down or sample removal. A notable disadvantage of corona treatments is their heterogeneous nature. Streamer nucleation occurs at set points along the electrode, and so parts of the treated workpiece will receive high concentrations of plasma treatment while others receive low concentrations. DBD systems were developed as solutions to this problem[13].

6.3.6 Dielectric Barrier Discharge

DBD differs from corona due to the inclusion of a second electrode as well as one or two dielectric layers that separate the electrodes from the process gas mixture. A single dielectric configuration is shown in Figure 2 below[13]. The electrically insulating layer promotes diffuse electron accumulation across the electrode, rather than at defined nucleation points as is the case in a non-insulated corona system. DBD is typically supplied with a pulsed or sinusoidal signal of low frequency (<1 MHz). Streamer duration is 100 [ns] for most systems, meaning rapid renucleation at new points. Given a processing time that is orders of magnitude greater than nucleation duration, the process achieves homogeneous treatment that is not achievable using corona. The dielectric additionally increases the overall gap resistance, preventing sparking or direct arcing[13].

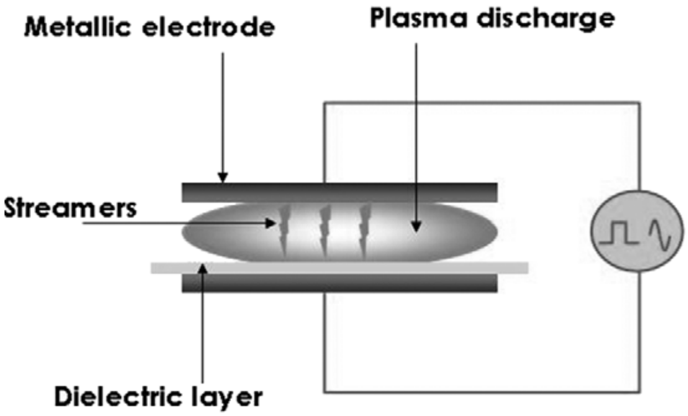


Figure 2: DBD System, Pulsed or Sinusoidal

Similar to corona, a range of different discharge regimes can be accomplished depending on process conditions such as gas mixture, voltage, and signal frequency applied. Table 1 provides characteristic properties of the different attainable DBD regimes, as well as one low-pressure regime (labeled RFGD)[35]. Filamentary Dielectric Barrier Discharge (FDBD) plasma is composed entirely of microdischarges and streamers, resulting in harsh process conditions evidenced by the power, current, and ion density. Glow Like DBD (GLDBD), Glow DBD (GDBD), and Townsend DBD (TDBD) are all initiated via Townshend breakdown and don't contain filamentary discharges, and as a result are pretty comparable to low pressure radio frequency plasmas. The advantage of operation in this regime is increase treatment homogeneity, although the uniformity of the generated plasma is still notably lower than in a low-pressure system. Operating within this regime requires tight parameter control, and is achieved best using Helium[16].

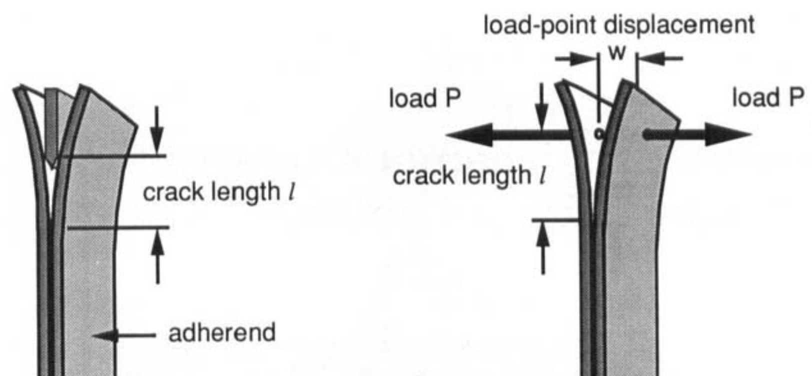
Discharge	Discharge duration	Max current density	Max power density [W cm^{-2}]	Max electron density [cm^{-3}]	Max metastable density [cm^{-3}]	Max ion density [cm^{-3}]
FDBD	10–100 ns	1–10 A cm^{-2}	10	10^{14}	10^{13}	10^{14}
GLDBD	200 ns	0.1–1 A cm^{-2}	5	Not available	Not available	Not available
GDBD (APGD)	1–5 μs	1–10 mA cm^{-2}	1	10^{10}–10^{11}	10^{11}	10^{11}
TDBD (APTD)	Half of the period	0.1–5 mA cm^{-2}	5	10^{7}–10^{8}	10^{13}	10^{11}
RFGD	Always ON	50 mA cm^{-2}	5	10^{12}	10^{12}	10^{11}–10^{12}

Table 1: Operating conditions for various DBD regimes

6.4 Adhesion Characterization

Adhesion is most commonly characterized by the force or work required to separate two surfaces. Figure 3, below, shows a double-cantilever beam specimen (DCBS) subjected to two differing adhesion tests. To allow theoretical analysis of each test, it is assumed that the adherends in question do not experience plastic deformation[52].

The Boeing Wedge Test is typically used for comparing adhesive performance under adverse conditions of high temperature or humidity. It is



$$\boldsymbol{G_1} = \left[\frac{\boldsymbol{3h^3Ew^2}}{\boldsymbol{16l^4}}\right]$$

where h is the adherend thickness, E the elastic modulus, l the crack length, and w the load-point displacement (typically assumed to be the sample width in the case of the Boeing Wedge Test and half the sample width for Constant Load-point Displacement Rate Tests). Evaluating sample strength, or the crack extension force, requires an estimate of crack length. As the crack tip location can be difficult to determine, this measurement carries significant uncertainty and therefore so does evaluation of sample strength[52]–[54].

A more precise adhesion test requires a Constant Load-point Displacement Rate applied to separate a DCBS. The crack extension force, G, can be implicitly written in terms of the load applied, P, the load point displacement, w, the adherend thickness, h, and the adherend width, b as follows[52]:

$$\boldsymbol{w} = \left[\frac{\boldsymbol{Eh^3G_1^3b^4}}{\boldsymbol{27}}\right]^{\frac{1}{2}} \frac{\boldsymbol{1}}{\boldsymbol{P^2}}$$

While crack velocity can be written as[52]:

$$\frac{dl}{dt} = \frac{1}{8l}\left[\frac{3Eh^3}{G_1}\right]^{\frac{1}{2}} \frac{dw}{dt}$$

A practical alternative for determining whether a set of adhered surfaces are generally adequate in terms of adhesion quality is described by the ASTM D3359-09 standard adhesion by tape test. This test is designed for characterizing thin film application to a metallic substrate, but the method is useful for a variety of substrates. A series of crosshatching cuts is made to the surface, a strip of pressure sensitive tape is applied, and allowed to adhere for a period of time. The tape is then rapidly peeled from the substrate, after which the quantity of thin film removal is assessed[55]. Table 2 outlines the classification standards based on the quantities of film removed.

6.5 X-ray Photoelectron Spectroscopy

X-ray photoelectron spectroscopy (XPS) is an analytical tool for material surface chemical and structural determination. The sample surface is probed by irradiated with a monochromatic x-ray source of known energy, and the energy of resulting emitted electrons is measured. An energy balance of the process shows:

$$E_{hv} = E_k + E_\theta + E_B(i)$$

With E_{hv} as x-ray energy, $E_k$the emitted photoelectron kinetic energy, E_θ as a known correction factor specific to the sample material (work function), and finally E_B as the electron binding energy. Measuring the photoelectron kinetic energy of all emitted electrons therefore provides binding energies of the chemically distinct regions within the probed surface. As binding energies are directly related to an atom's chemical state, comparing literature values to obtained data can provide sample surface chemical structure. Relative intensities of measured signals can further provide relative abundance of different chemical states [62]. Charge determination can be accomplished by one of several established methods: (a) Pauling, (b) Hückel molecular orbital[63], or (c) the CNDO molecular orbital[63][64].

XPS analysis is normally limited to within 10 nm of a sample's surface, making it an excellent tool for characterizing material coatings or thin films of material. It is possible to perform deeper surface analysis and attain information such as depth dependent compositional profiles through sputtering. Molecules such as Ar^+, Cs^+, and C_{60}^+ are mostly used for this purpose. Single ion sources such as the former two examples can damage soft materials and change their chemistry. Cluster ion sources such as C_{60}^+ cause less damage due to energy transfer occurring at the sample surface, resulting in cleaner depth profiling, but are expensive to produce[65].

Sample damage as a result of analysis becomes increasingly relevant when considering polymeric surfaces. Prolonged x-ray exposure can reduce relative oxygen:carbon peak ratios, especially the carboxyl peak around 289 eV. When analyzing polymers, the C(1s) peak is particularly informative in terms of attached functional groups and structure [66]. This unwanted chemistry change can be avoided by selecting appropriate spot size, dell time, and pass number parameters for minimizing exposure while satisfying desired resolution[67]. Additionally, use of monochromatic light with a high sensitivity detector can additionally reduce damage to samples [67].

Lastly, sample charging is of particular concern when analyzing polymeric samples with monochromatic light. Around .1-20 nA steady current passes through the analyte during XPS analysis. Insulating materials such as polymers eventually develop surface charging as a result, which can shift the measured binding energies and broaden peaks over regions experiencing inhomogeneous charging. Polymer analysis therefore requires the use of a flood gun, which delivers electrons to balance charge. This should be accomplished without heat transfer, and at the same current density as the measured photocurrent density emitted by the sample. Excessive flooding can produce negative charging on the sample surface which once again skews results [66][68].

7 Materials and Methods

7.1 Raw Materials

Raw materials for sample production were provided by CGT. Thermoplastic Polyolefin (TPO) was used as a substrate for all sample production and tested for adhesion with a polyurethane based top finish (Leatheroid LU-840-GPL).

High purity nitrogen (99.99%), oxygen (99.99%), ethylene (99.9%), butadiene (99.98%), and ammonia (99.99%) were purchased from MEGS Inc. (Calgary, Alberta, Canada) for sample pretreatment and deposition of nitrogen rich coatings. Adhesive tape (Scotch Transparent 600, 3M) is used for peel tests outlined in section 7.5, while high strength bonding tape for plastic (transparent, 3M, ¾") is used for tests outlined in section 7.6.

7.2 Experimental Setup

7.2.1 Power Supply

A parallel plate DBD reactor was used for pretreatment and deposition of nitrogen rich plasma polymer. The G2000 plasma generator was obtained (Redline Technologies, 52499 Baesweiler, Germany) to serve as a power supply. Connection to an external high voltage transformer generates a sinusoidal signal with 4-500 kHz and 0-9.9 kV_{pp}, with a maximum delivered power of 500 W. The power supply delivers an intermediate voltage of up to 300 V, which is further stepped up through the transformer's 1:33 winding ratio. In addition to operating voltage and frequency, the power supply allows duty cycle control between 0 and 45% and adjustment setting of t_{on}/t_{off} parameters between 0 and 5000 ms for pulsed plasma.

Both the external transformer and the reactor units are located under a fume hood to vent potentially hazardous species. A schematic of the setup can be seen in Figure 4 below.

7.2.2 Reactor Setup and Characterization

The reactor has a 5mm capacitor gap between the insulated electrodes. This gap is reduced to approximately 4 mm by the presence of a 1mm thick aluminum spacer plate, for the purpose of promoting low power breakdown. The remaining gap between alumina plates is 2.4 mm (2 plates of 0.8 mm thick each). The electrodes have an area of 7.5 x 10 cm^2. The top electrode is attached directly to the alumina dielectric with a thin layer of silicone gel, while the bottom dielectric is attached with silicone to a spacer plate of aluminum that sits on the grounded electrode.

Generating an evenly distributed dielectric barrier discharge is necessary for homogenous thin film deposition. All operation with nitrogen and

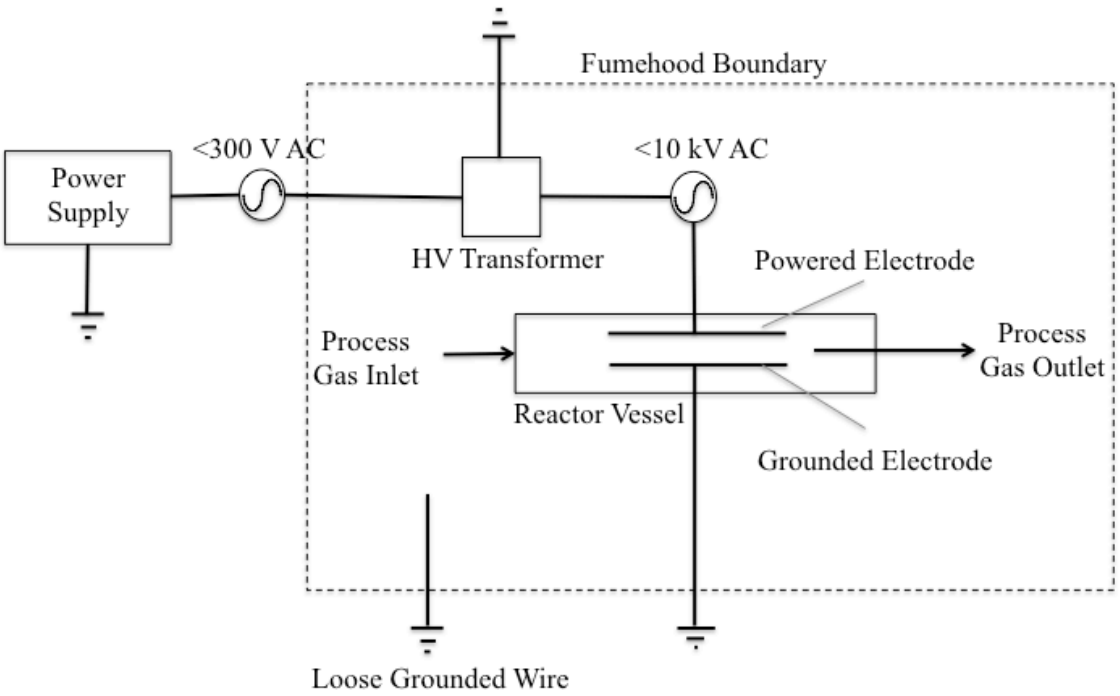


Figure 4: Experimental Setup, consisting of a power supply connected to an external transformer and the reactor. Power supply, external transformer, and reactor are all grounded separately. A loose, grounded, wire is used to ground top electrode and any suspect objects after operation, as a safety precaution

ethylene/butadiene or air feeds generated Filamentary Dielectric Barrier Discharge (FDBD). DBD reactor insulation directly effects homogeneity and dispersion of the observed filaments. The best efforts to evenly insulate both electrodes still maintained small amounts of bubbles in the silicone dielectric, which exacerbated the effects of imperfectly distributed silicone insulation. The insulation was strongest at the inlet of the reactor, evidenced by concentrated discharge towards the reactor outlet. Combined with the observed filamentary nature of the DBD, deposition was heterogenous and required impractical methods to produce even coatings, discussed in later sections.

Reactor operation at or above 150kHz supplied power increased DBD homogeneity at the cost of unwanted temperature increases. Pyrometer measurements taken from dielectric plates following 30-second operation showed an average temperature of 67.3 °C across the plate (over 10 second sampling time) and a maximum temperature of 73.0°C. Observed filaments, at higher temperatures than the investigated plates, degraded TPO samples exposed to discharge at this frequency. Reducing the operating frequency below 30 kHz resulted in reduced heating rates and average and maximum pyrometer measurements of 24.6 and 36.5 °C, respectively, following 60-second operation. TPO samples were then successfully treated for up to 180 seconds under continuous plasma without damage.

7.2.3 Oxidative Plasma Treatment and Plasma Deposition

For all DBD treatment of TPO, samples were immobilized on the bottom alumina dielectric with 0.5 mm thick double-sided tape, ensuring the sample remains flat, and allowing for even gas flow over its surface. Unless otherwise specified, pretreatment, or surface oxidation of TPO films was accomplished over 2-minute sample treatment with a feed approximating the composition of air (2 SLM nitrogen and 0.5 SLM Oxygen). Reactor operating conditions were maintained at 9.9 kV_{pp} and 18.7 kHz.

For thin film deposition, operating parameters of 9.9 kV_{pp}, 18.7 kHz. Unless otherwise specified, deposition experiments were completed over 4 periods of 2 minutes while appropriate gas mixtures were fed to the reactor. Between treatment periods, samples were additionally rotated 90°. Samples were produced with these operating conditions under various different feed mixtures for production of thin films of variable chemistry. A typical feed was 30 SCCM ethylene diluted with 5 SLM nitrogen.

others are conducted with “continuous plasma”.Following deposition experiments, the dielectric plates were heavily stained from plasma polymer. Steel wool and other abrasives scratch the dielectric surface, so cleaning is accomplished with soft materials and solvents, typically acetone soaked delicate task wipes.

7.2.4 Pulsed Plasma Treatment and Sample Rotation

In an attempt to increase treatment homogeneity, some experiments were completed using pulsed plasma. Adjustment t_{on}/t_{off} parameters at the power supply generates a pulsed plasma, further interrupting established microstreamers and effectively dispersing plasma treatment over the sample surface. This was applied for both pretreatment and deposition processes. Operating parameters of t_{on}=100 ms and t_{off}=400 ms were selected after numerous tests, while the duty cycle setting remained at the maximum 45%. These experiments are described as “pulsed plasma” in the discussion section, while all others are conducted with “continuous plasma”.

7.3 Sample rotation, throughout pretreatment and plasma polymer deposition, was additionally employed as a tactic for increasing treatment homogeneity. All samples described as receiving treatment under rotated plasma received 4 periods of deposition, between which the sample was rotated 90 degrees counterclockwise. Each period of deposition lasted 120 seconds, unless noted otherwise.

7.4 Polyurethane Application – Top Finished Sample Production

TPO substrate (typically sized 8x5 cm^2) was cut from a bulk roll of TPO and cleaned with water and isopropyl alcohol to remove any dust or oils from the surface. While the exact chemical formula of the TPO has not been provided, elemental composition of TPO was determined through XPS (8.3). After appropriate plasma treatment, samples are twice coated in polyurethane top finish and dried in an oven at 95°C. Either increased temperature or extended curing times resulted in some sample deformation, while decreased temperatures lead to an undesirable top finish whitening.

The top finish was applied via paint brush, which is temporarily stored in a beaker of Methyl Ethyl Ketone (MEK) solvent to prevent top finish accumulation or caking. The solvent was pressed out of the brush before a new coating was applied, so as not to dilute the top finish. Whitening of the applied coating could be reduced by minimizing the time a newly top finished sample remained outside the oven. Samples were therefore coated and cured one at a time.

7.5 Sample Naming Convention

Samples discussed in the later sections are named based on the plasma treatment received. A prefix of “o-“ indicates an oxidized or pretreated sample, having been exposed to air discharge pretreatment for a period of time. The following acronym represents the plasma polymer coating received, either PPB:N or PPE:N for plasma polymer produced with butadiene and nitrogen or ethylene and nitrogen, respectively. In the case of samples produced using PECVD, N represents Ammonia as the nitrogen source. A DBD produced sample labeled “o-PPE:N” received pretreatment and subsequent deposition of plasma polymer deposition under a feed of ethylene and nitrogen.

7.6 X-ray Photoelectron Spectroscopy (XPS)

A Thermo Scientific K-Alpha XPS was used to characterize sample surfaces for elemental composition. Sample size was limited to under $3\,\text{cm}^2$ in total to avoid increases in analysis chamber pressure due to sample degassing. Flood gun use prevented charge accumulation over the dielectric samples. All samples were analyzed using 200 μm spot size. Each sample was first surveyed for the presence of various elements, over 3 passes with 50ms dwell time. High resolution scans were then completed for key elements over 10 passes with 50 ms dwell time. Typically, oxygen, carbon, and nitrogen content were of interest, and estimated using O1s, C1s, and N1s peaks.

Control TPO samples were first cleaned with isopropyl alcohol and water for dust removal than allowed to dry in a petri dish for an hour to ensure clean and dry surfaces. Coated TPO samples were analyzed as soon as possible after production, within a maximum of 3 hours. Samples were analyzed at 2 different points. Oxygen to carbon ratios were calculated for each sample from the averaged atomic percent values of the two analyzed points per sample.

7.7 Qualitative Peel Test

Initial peel testing followed the ASTM D3359-09 procedure. This peel test is performed for the purpose of generally assessing adhesion quality, as well as for comparison to past samples that had been tested using this procedure.

11 intersecting perpendicular horizontal and vertical cuts, within a square centimeter, are made into the polyurethane top finish. A strip of transparent scotch tape is adhered to the surface, with firm top pressure applied to remove air bubbles and areas of poor contact. After 90 seconds, the tape is rapidly stripped from the surface at a 180-degree angle to the sample surface. The sample is then assessed for the quantity of material delaminated, according to the classifications outlined in Table

3[34]. Samples with good top finish adhesion are expected to undergo little to no delamination of polyurethane. When no produced samples maintained top finish adhesion following this peel test method, other variant peel tests were adopted to better differentiate sample quality.

7.8 Quantitative Peel Test

An Instron Peel Tester is used to characterize produced TPO/PU laminates for adhesion strength. This is an automated, quantitative, peel test method. Sample preparation is shown in Figure 5 below. A thermally activated adhesive test strip is adhered onto the sample surface (160-204C, applied for 25 seconds with preheated iron), with one end of the strip remaining detached for later peeling. After samples have cooled for 1 hour, the adhesive strip is peeled from the sample surface at a constant 200 mm/min, applied by the peel tester, while the load for removal is recorded.

A similar quantitative test was completed using a different adhesive material. Here, adhesive bonding tape for plastic (transparent, 3M, ¾”), a tape with higher adhesion values to PU than scotch tape, was used instead of the thermally activated adhesive strip required for the initial test. The peel test is completed using a uniaxial Shimanzu tensile tester, with 200N load cell. Sample preparation is shown in Figure 6 and Figure 7 below. The surface to be tested for adhesion is covered by a strip of tape. Tape is fastened to back of TPO sample at left end, and adhered to cardboard tab at right side, for mounting in top tensile tester clamp. Placing ruler over end of sample before applying tape keeps a strip of TPO uncovered, required for mounting in lower tensile test clamp. The Shimanzu tensile tested records the load required to maintain a constant peel speed of 200 mm/min. The peel speed was selected to allow for comparison between results obtained using the thermally activated tape and the adhesive bonding tape.

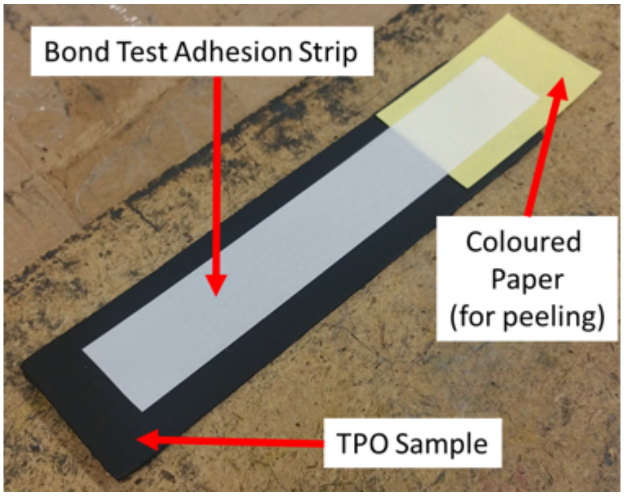


Figure 5: Sample preparation for quantitative peel test completed by personnel at CGT

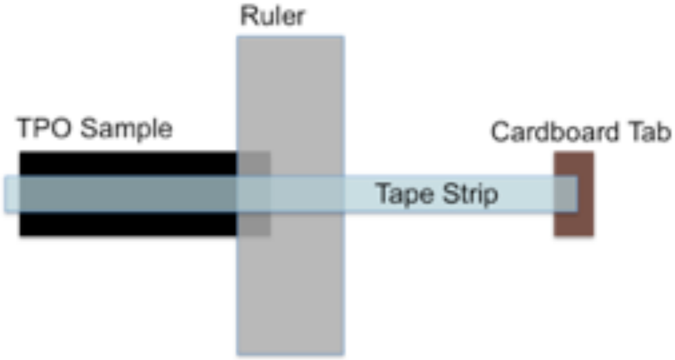


Figure 6: Sample preparation for automated peel test.

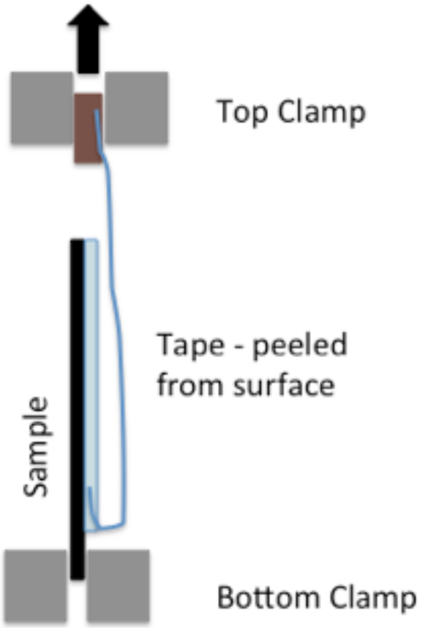


Figure 7: Automated peel test arrangement. Sample mounted in bottom clamp at tape free end. Cardboard strip mounted in top clamp.

8 Results

8.1 Oxidative Plasma Treatment - XPS Characterization

XPS characterization was completed in an attempt to understand the effect of oxidative plasma treatment on substrate surface chemistry. The atomic percent of oxygen and carbon for all TPO samples is shown in Table 4 below, along with the relative carbon to oxygen atomic percent ratios. The extended air plasma treatment shows a large increase in oxygen content, but the treatment does not appear consistent as the standard deviation increases compared to control samples.

The inconsistent oxidation of TPO samples emphasized the need for a steady feed of air throughout pretreatment. This should reduce resulting concentration gradients and may additionally serve to disperse established microstreamers for increased treatment homogeneity. A feed of 500 SCCM oxygen and 2 SLM nitrogen feed was now used for all experiments. Again, control TPO and samples treated in the noted mixture for 30 and 60 seconds were analyzed with XPS. The results are shown in Table 5 below, and survey peaks are shown in Figure 19 located in the Appendix.

There is still no clear change in sample surface chemistry after 30-second treatment. 60-second treatment remained inconsistent over the sample surface, again with increase standard deviation compared to control samples. However, 60 second treatment showed the same significant increase in oxygen content that had been observed without a reactor feed (Table 4). It is possible that hydrophobic recovery is responsible for negligible effects of shorter treatment times, as sample analysis occurs up to three hours after preparation. The uneven change in surface oxygen content observed across all tests results from filamentary discharge treatment of samples.

Measurement	Oxygen at%	Carbon at%	[O]/[C]
Control	**9.5** (10.5, 8.4)	**90.3** (89.5, 91.0)	**0.11**
30 seconds	**8.4**	**91.0**	**0.092**
60 seconds	**16.0** (20.9, 11.0)	**79.7**(71.4, 87.9)	**0.200**

Table 3: XPS results for untreated (control) TPO and samples treated with air plasma for 30 and 60 seconds. Operating conditions of 8 kV$_{pp}$ and 16.9 kHz. No feed to reactor throughout treatment

Measurement	Oxygen at%	Carbon at%	[O[/[C]
Control	**8.2** (9.9, 6.4)	**86.5** (85.0, 87.9)	**0.095**
30 Seconds	**9.0** (8.7, 9.2)	**88.9** (91.3, 86.4)	**0.10**
60 Seconds	**15.3** (18.8, 11.8)	**81.3** (78.4, 84.2)	**0.188**

Table 4: XPS results for untreated (control) TPO and samples treated with oxygen and nitrogen mixture for 30 and 60 seconds. Operating conditions of 8 kV$_{pp}$ and 16.9 kHz. 2 SLM nitrogen and 500 SCCM oxygen fed to reactor throughout treatment

8.2 Nitrogen Rich Organic Thin Film Characterization

Promoting uniform plasma treatment over the whole sample surface became an immediate concern, after early samples showed concentrated areas of deposited plasma polymer. Figure 8 shows TPO samples coated in ethylene and butadiene-based plasma polymers. Deposition under butadiene appeared to readily coat the entire sample surface with visibly improved uniformity. Butadiene has repeatedly been demonstrated as carcinogenic, with links to both lymphatic and hematopoietic cancers, as well as being a developmental and reproductive toxicant[69][70][71]. It is therefore less suitable than ethylene as a carbon source for open atmosphere industrial plasma processes. Producing results with an Ethylene based plasma deposition process is consequently more meaningful. Changes were therefore made to the production process until similar substrate coverage could be accomplished using Ethylene for plasma polymer deposition.

Feed flow rates were a major factor, with total flow rates ranging from 1-5 SLM producing uniform coatings and flow rates above 10 SLM producing striated, oriented, coatings similar to Figure 8, right, but with extended deposition streaks.

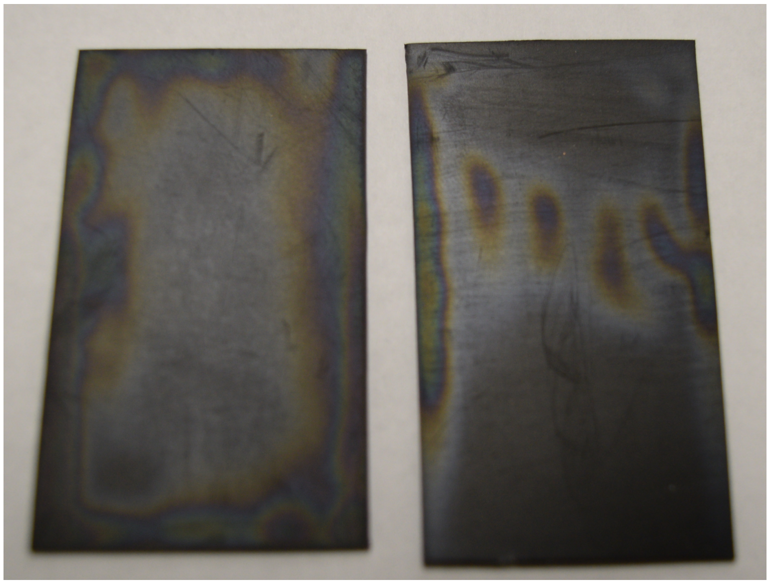


Figure 8: Coating produced with Nitrogen and Butadiene (Left)) and Nitrogen and Ethylene (right). No oxidative pretreatment was applied before plasma polymer deposition

Moderate flow rates, <6 SLM total flow, were therefore selected for initial sample production and XPS characterization. Nitrogen rich plasma polymer was deposited onto both silicon wafers and TPO substrates, for subsequent XPS analysis (results shown in Figure 9).

The deposition process seems to coat TPO and silicon wafers similarly, with the resulting organic films containing approximately 70% carbon, 25% nitrogen, and 5% oxygen. Without any oxygen fed during the deposition process, the high oxygen content is likely the result of surface oxidation reactions upon exposure to ambient air, following plasma treatment. Coatings produced using low pressure plasma processes had nitrogen content ranging from 2-6.5%. The significantly higher nitrogen content of the atmospheric pressure coatings is the result of the higher proportion of nitrogen fed. The flow rates selected for nitrogen were required to

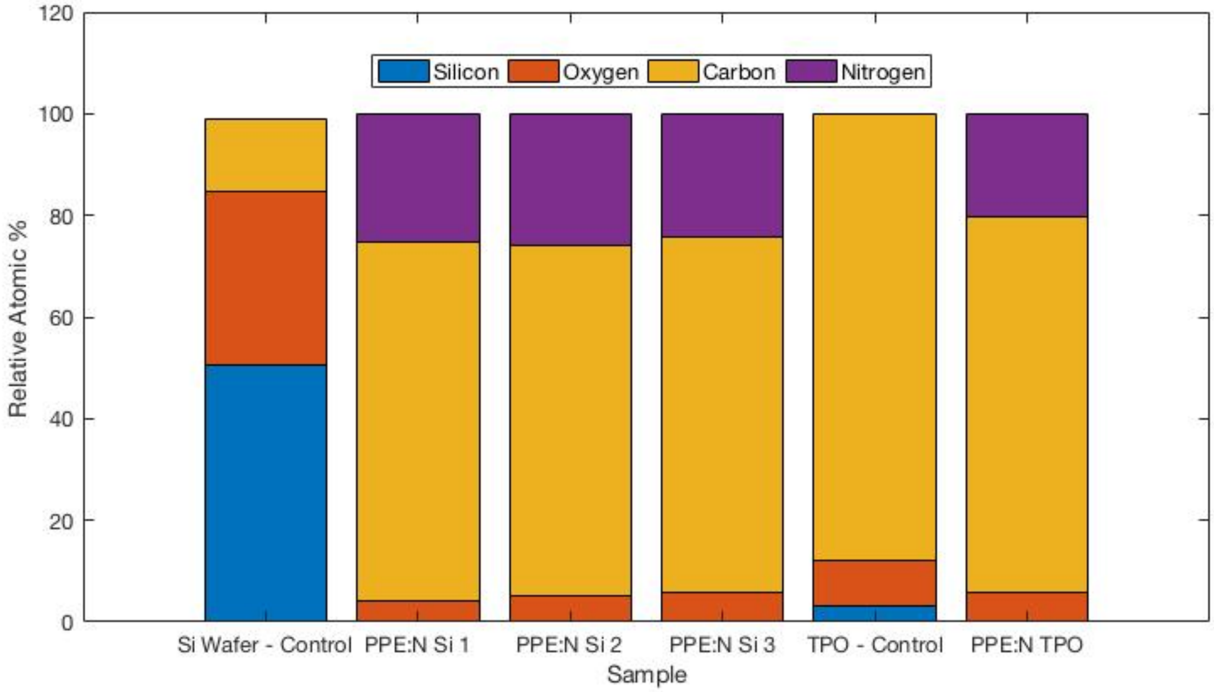


Figure 9: XPS results for 2 uncoated and 3 plasma-polymer coated silicon wafers, and a control and coated TPO sheet. Deposition completed over 60 seconds, with 3 SLM Nitrogen / 20 SCCM Ethylene, at 7.9 kV_{pp} and 16.9 kHz, under continuous plasma. No pretreatment.

maintain even deposition over the whole sample surface when using Ethylene as a carbon source. With less than 1 SLM nitrogen fed together with Ethylene, deposition became limited to sample edges. Increased nitrogen content, and therefore amine groups, is thought to promote top finish adhesion through amide bond formation with polyurethane functional groups. It was therefore expected that the high nitrogen content translates to favorable peel test results.

Production and characterization of these samples achieves the first two outlined project objectives, namely successful atmospheric pressure plasma deposition and deposition of a nitrogen rich thin film using non-toxic precursors.

8.3 Characterization of Thin Films Deposited Using Pulsed Plasma and Sample Rotation

Following poor peel test results obtained from qualitative peel tests conducted on samples produced under continuous plasma without sample rotation (outlined in

5.4), pulsed plasma and sample rotation was investigated for improving treatment homogeneity. This change produced the most visibly uniform sample coatings to date. Figure 10 shows TPO samples coated in plasma polymer, and the grid-like appearance that is characteristic of samples produced with rotation between 4 deposition periods.

Sample rotation was additionally tested as a means for improving pretreatment homogeneity. Samples treated continuously for 60 seconds in air plasma were compared to samples treated for 4 periods of 20 seconds with 90-degree sample rotation in between. Results are shown in Table 5, and XPS analysis of oxygen content is shown in Appendix Figure 20. While the average oxygen content increased, this is due to the extra 20 seconds of treatment time. There is still 7.7 at% spread between the most and least oxygenated points. As the benefit for pretreatment did not seem

Measurement	Oxygen at%	Carbon at%	[C]/[O]
Control	**5.0** (6.6, 3.7, 4.6)	**93.9** (91.1, 96.3, 94.2)	**0.053**
Stationary	**7.3** (3.7, 4.4, 13.7)	**92.0** (95.6, 94.8, 85.5)	**0.079**
Rotate	**10.5** (9.3, 7.2, 14.9)	**88.5** (89.8, 91.5, 84.2)	**0.12**

Table 5: XPS analysis of control TPO (Control), stationary TPO samples exposed to oxidative plasma for 60 s (Stationary), and rotated TPO samples exposed to oxidative plasma for 4 periods of 20 seconds (Rotate). Visual representation of this data is shown in Appendix Figure 20

significant, sample rotation for peel tested samples in the following sections was only applied during the plasma polymer deposition step.

8.4 Sample Analysis with Qualitative Peel Tests

The first method of evaluating sample adhesion quality followed the procedure outlined in 4.7.

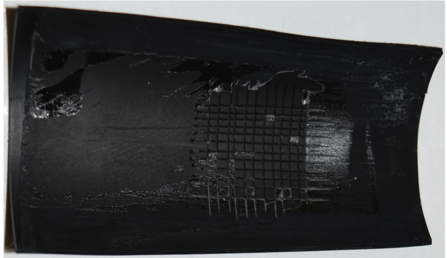
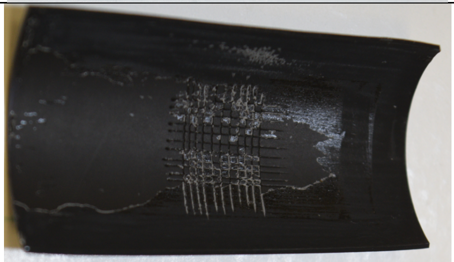
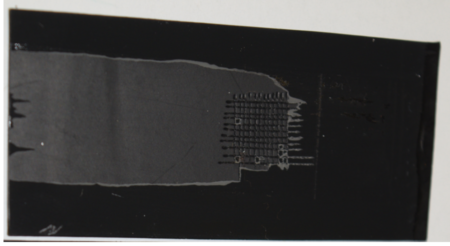
Sample	Peel Test Result
30s PPE:N	
60 s PPB:N	
60s Carbon Rich PPB:N	
Rotated o-PPE:N	

Table 7 outlines peel test results for select samples. 3 samples (30s PPE:N, 60 s PPB:N, and 60s Carbon Rich PPB:N) were produced with continuous plasma and without sample rotation or oxidative pretreatment, for the purpose of determining effective deposition times and flow ratios. The last sample (8/7 S2) was alternatively produced with pretreatment, pulsed plasma, and sample rotation, representing the theoretically ideal sample production process.

All samples tested showed near complete delamination of the polyurethane layer upon peel testing, indicating poor adhesion between the TPO substrate and the PU coating. According to the classification chart for characterizing samples tested by the ASTM D3359-09 standard, all samples fall under 0B will well over 65% of the coating within the crosshatched area removed[34]. Changing the carbon source required for plasma polymer deposition from Ethylene to Butadiene had no clear effect on adhesion quality. Further attempts to improve top finish adhesion were made by systematically adjusting the deposition time, power (through input voltage), and feed ratios, with no produced samples showing improved top finish adhesion. The "theoretically ideal" sample, based on increased surface energy before deposition and improved deposition homogeneity, had the least remaining top finish after peeling. The peel test results shown here summarize the insufficient adhesion quality characteristic of all produced samples. Tests with differing operating voltage, frequency, feed composition or pulsing showed similar delaminating profiles and are omitted for brevity.

In a number of tests, the adhesive strip of the used 3M 600 transparent scotch tape delaminated as opposed to the sample polyurethane coating delaminating. Samples 5/3 S2 and especially 4/24 S4 show signs of this, with strips of the adhesive adhered to the sample surface where the top finish remains. Figure 11 shows a sample with complete tape delamination over the whole surface. The failure

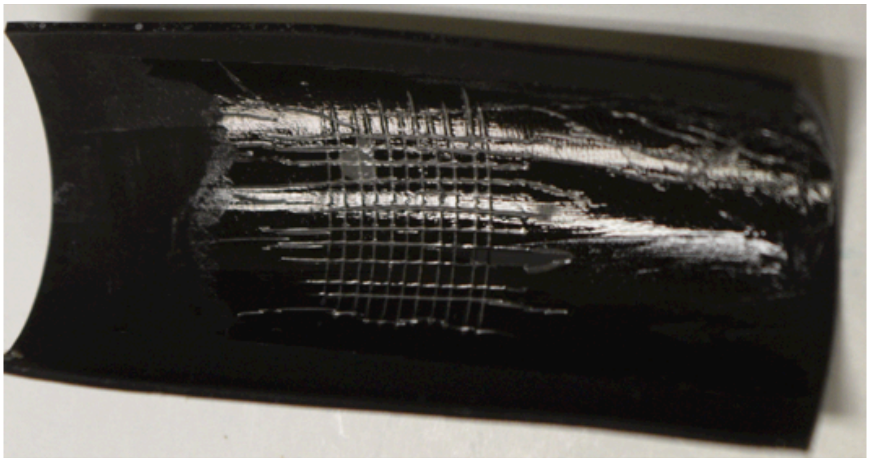


Figure 11: Failed qualitative peel test showing adhesive delamination from scotch tape

mechanism was found to be dependent on peel speed, with retested samples showing complete delamination with slower removal of reapplied tape. Peel tests across sample replicates confirmed this. Heavy tape delamination was therefore considered a failed test rather than a significant result potentially indicating high sample adhesion.

According to basic polymer theory, mechanical failure is highly dependent on strain rate. This presents an issue with interpreting results, as peel speeds have an apparent effect on the mode of failure. Past samples produced at lower pressure, that showed good adhesion, never resulted in scotch tape delamination. It is therefore most likely that peel tests resulting in scotch tape delamination were performed incorrectly, emphasizing that qualitative peel testing is quite user dependent. An automated, and quantified, peel test was consequently pursued.

8.5 Quantitative Peel Tests

8.5.1 Analysis of Samples Produced without Plasma Polymer Deposition

Despite high standard deviations across sample sets, it is clear that all samples produced with plasma pretreatment followed by deposition of plasma polymer outperform control samples in terms of adhesion. Samples produced with only air or nitrogen plasma treatment, without any deposition step, reinforced the efficacy of the two-step, pretreatment and deposition, plasma process. This can be seen in Figure 12 below, with sample production details outlined in Table 7. The sample labeled “Rotated o-PPE:N” analyzed here is equivalent to “Rotated o-PPE:N” in Table 8.

Sample	Pretreatment	Deposition
Control	None	None
Air	4x30 seconds 2 SLM Nitrogen / 500 SCCM Oxygen t_{on} = 100ms, t_{off} = 400 ms 10 kV_{pp} and 18.7 kHz d=45%	None
Nitrogen	4x30 seconds 5 SLM Nitrogen t_{on} = 100ms, t_{off} = 400 ms 10 kV_{pp} and 18.7 kHz d=45%	None
Rotated o-PPE:N	1 minute 2 SLM Nitrogen / 500 SCCM Oxygen t_{on} = 100ms, t_{off} = 400 ms 10 kV_{pp} and 18.5 kHz	4x2 minutes, sample rotation 5 SLM Nitrogen / 30 SCCM Ethylene t_{on} = 100ms, t_{off} = 400 ms 10 kV_{pp} and 18.5 kHz
Rotated o-PPB:N (Upper and Lower)	60 seconds 2 SLM Nitrogen / 500 SCCM Oxygen t_{on} = 100ms, t_{off} = 400 ms 10 kV_{pp} and 18.7 kHz d=45%	4x120 seconds 5 SLM Nitrogen / 30 SCCM Butadiene t_{on} = 100ms, t_{off} = 400 ms 10 kV_{pp} and 18.5 kHz d=45%

Table 7: Sample preparation conditions for data sets in Figure 14

Two different peel tests results are shown for samples produced with Butadiene as the carbon source, to represent the large range in adhesion values obtained across individual sample sets. These samples are labeled “Upper” and “Lower”. Despite this large deviation in values, the improvement over alternative methods is apparent. Samples treated in air had similar adhesion values to control samples, and showed no improvements in adhesion, while nitrogen treated samples had some adhesion enhancement. Despite the significantly lower adhesion values of the Ethylene sample compared to the Butadiene samples, adhesion values show significant improvements over control and alternative production method samples.

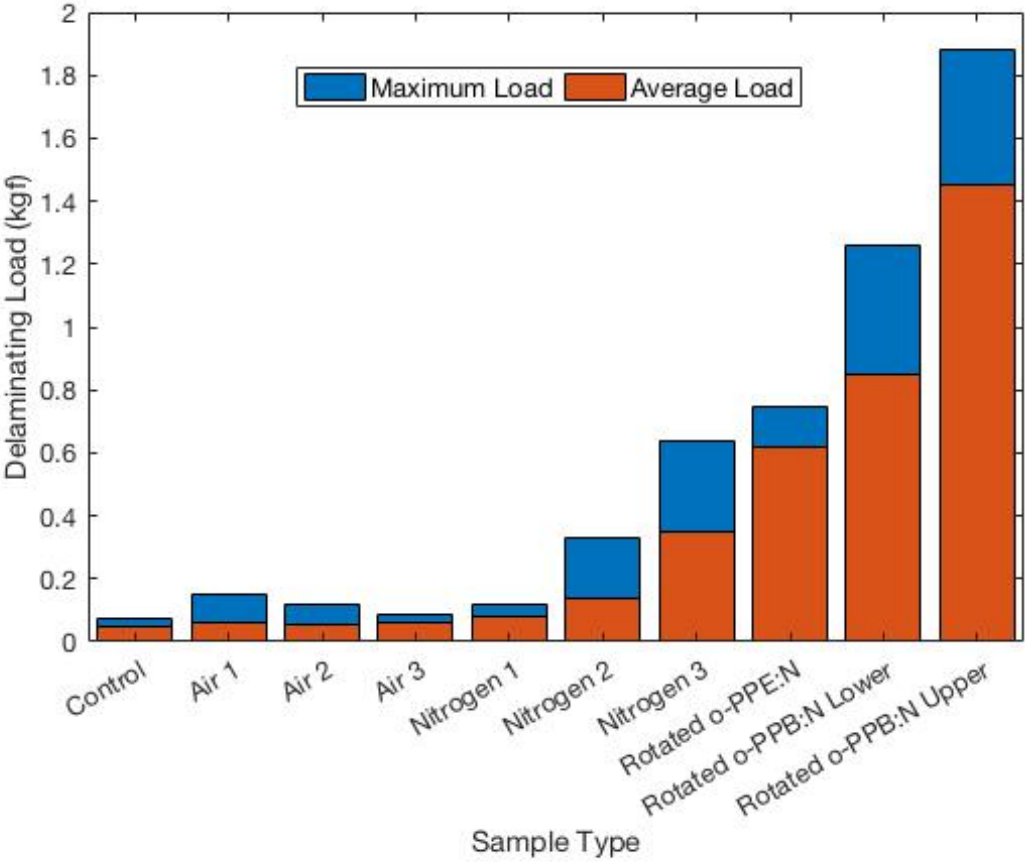


Figure 12: Automated peel test results for samples outlined in

8.6 Analysis of Samples Produced with Plasma Polymer Deposition

Quantitative peel tests, following 4.7, completed by CGT confirmed results from Section 5.4 indicating that samples had insufficient adhesion strength. Table 8 outlines production conditions for a series of peel tested sample sets, corresponding to the results shown in Figure 13. Each bar represents an average of two samples tested, other than S5 which is a single sample.

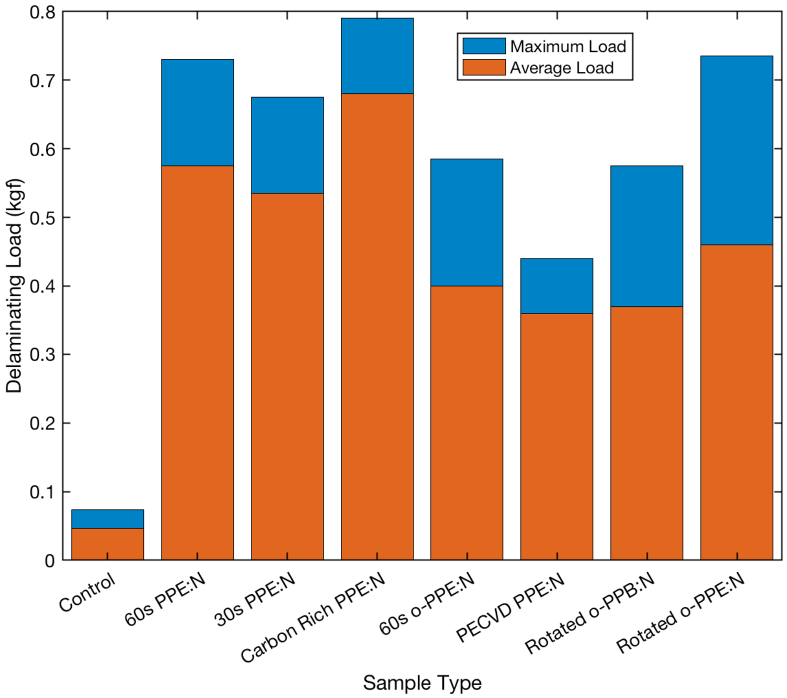


Figure 13: Comparison of Quantitative Peel Test results for samples outlined in Table 7. S5 is a single data point while all other bars represent averaged pairs

	13.56 MHz	13.56 MHz
Rotated o-PPB:N	1 minute 2 SLM Nitrogen / 500 SCCM Oxygen t_{on} = 100ms, t_{off} = 400 ms 10 kV_{pp} and 18.5 kHz d=45%	4x2 minutes, sample rotation 5 SLM Nitrogen / 30 SCCM Butadiene t_{on} = 100ms, t_{off} = 400 ms 10 kV_{pp} and 18.5 kHz
Rotated o-PPE:N	1 minute 2 SLM Nitrogen / 500 SCCM Oxygen t_{on} = 100ms, t_{off} = 400 ms 10 kV_{pp} and 18.5 kHz d=45%	4x2 minutes, sample rotation 5 SLM Nitrogen / 30 SCCM Ethylene t_{on} = 100ms, t_{off} = 400 ms 10 kV_{pp} and 18.5 kHz

Table 8: Sample preparation conditions for CGT quantitative peel tests, shown in Figure 13

Despite the improvement in deposition homogeneity resulting from samples produced with rotation throughout treatment under pulsed plasma, this did not translate to increased adhesion values as can be seen from ‘Rotated o-PPB:N’ and ‘Rotated o-PPB:E’. It is likely that the pretreatment process was the cause, as a non-rotated sample produced under continuous plasma but with a similar pretreatment process, ‘60s o-PPE:N’, had comparably low adhesion values.

Across all samples tested, the highest adhesion value was recorded over sample ‘Carbon Rich PPE:N’, with was produced with increased ratios of Ethylene present in the feed to reactor. This prompted a shift to increased carbon content fed to the reactor.

The automated, quantitative, peel test method using the Shimanzo uniaxial tensile tester was designed to record the delaminating load of polyurethane top finish across the whole sample surface, which was then reduced to an average and maximum value for each tested sample. The delaminating load curves for select samples are shown in Figure 14, above the corresponding maximum and average values displayed in bar chart form. Table 2 outlines the relevant sample production conditions. The DBD sample was produced with increased carbon content relative to previously produced samples, following past insights.

The PECVD, or low pressure deposition, produced sample had comparable adhesion values to samples produced with DBD treatment. Results across sample sets had high standard deviations, and adhesion values varied along a single sample surface. The 3 control samples shown had smaller standard deviations. DBD samples exhibit significantly higher delaminating loads than control, and this was accomplished using Ethylene rather than Butadiene. However, sample adhesion values fall well short of the desired 1.3 kg_f stipulated by CGT.

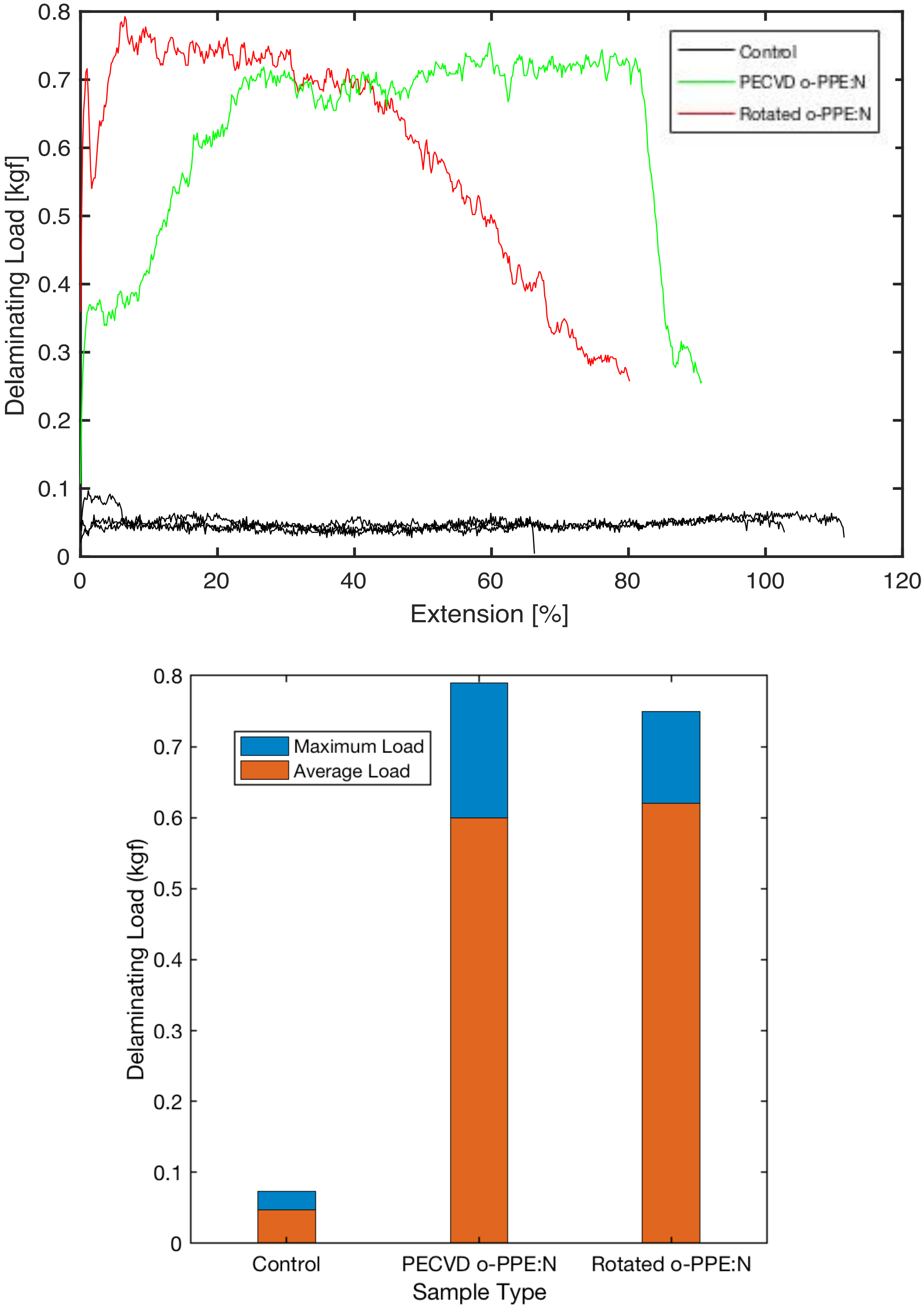


Figure 14: Automated peel test results for Rotated o-PPE:N, PECVD o-PPE:N, and untreated Control samples. Production conditions are outlined in Table 2

Figure 15 Table 2

8.6.1 Critique of Automated Peel Test Procedure

A noted issue with the quantitative automated peel test is that the delaminating load recorded is dependent on the area of polyurethane top finish removed. For samples with very poor adhesion, this is the whole area covered by the adhesive tape. For most samples, adhesive failure of the top finish tends to begin at a single point, with a thin strip delaminating, and then spreads to the whole surface covered by tape as peeling progresses (seen in Figure 16, and better seen in Figure 17). The PECVD (red) curve in Figure 14 represents the profile resulting from increasing delaminating area. While the plateau value of each curve characterized sample production conditions, the delaminating profile seemed unrelated. It is likely explained by substrate surface characteristics that were not properly controlled for: oil residue, surface roughness, or LMWOM concentrations resulting from pretreatment. Comparing the resulting delaminating curves, rather than maximum adhesion values and values averaged over plateau regions, therefore provides little insight to the sample production conditions under study.

Peel test analysis is additionally complicated by two distinct delaminating mechanisms: cohesive and adhesive failure. Samples with low top finish adhesion exhibit adhesive failure between TPO and PU top finish. This results in an area with complete removal of the applied PU layer, leaving the substrate exposed. Samples with high adhesion will fail cohesively, with failure occurring within the applied layer of polyurethane. This results in partial delamination of PU top finish, with the remaining PU still coating the whole substrate surface. A visual comparison between samples exhibiting these two failure mechanisms is shown in Figure 16. It was repeatedly observed, that once delamination transitioned from the cohesive to adhesive failure mechanism, the adhesive mechanism would be sustained.

Figure 16: Samples showing adhesive (top) and cohesive (bottom) failure during peel tests. Adhesive failure results in areas with the bare substrate exposed, while cohesive failure maintains PU coverage over whole sample surface.

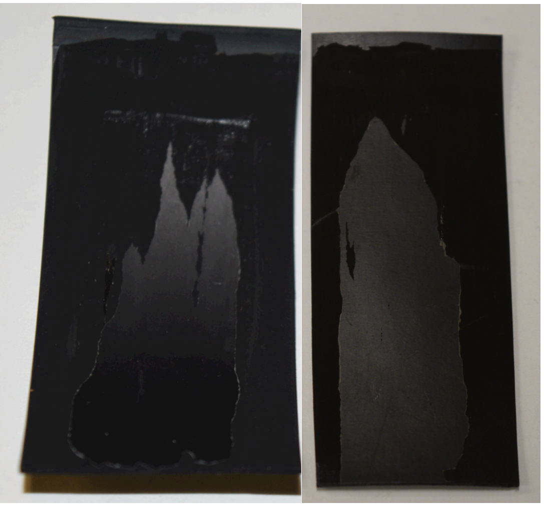


Figure 17: Samples showing the progression in top finish delamination. As the peel test continues, the delaminating area steadily increases, limited by the full width of the adhesion test tape.

To illustrate the difference in cohesive and adhesive adhesion values, an additional test was introduced. Two samples, which had shown cohesive failure and good adhesion, were retested after a cut had been made to the polyurethane top finish. The initially tested and retested samples are shown in Figure 18 below, where

Figure 18: Samples after automated peel test (Left) Sample 1 after initial peel test, without cut applied and (Right) Sample 1 after second peel test, after cut was applied perpendicular to orientation of peel test. Sample was produced following the conditions outlined in Table 10 for Butadiene sample.

It seems that to evaluate sample top finish adhesion quality under reproducible conditions, ensuring full coating delamination across the entire sample by inducing damage may be required. A constant delaminating area allows for direct comparison between different samples, to avoid the effect of sample surface defects and the resulting delaminating profile of inconsistent area. The measured delaminating load will not necessarily be the adhesion strength of an otherwise undamaged sample, but it will be more representative of relevant production conditions (feed composition, flow rates, power) than the current method.

Past results, with a PECVD system, showed no delamination upon qualitative peel testing (following Section 4.7) which requires similar but more extensive damage to the top finish. This indicates that despite some high adhesion values measured by quantitative peel testing, past coatings are still not fully reproduced here using the atmospheric pressure setup. The initial qualitative peel tests, showing near complete top finish delamination with each test, support this.

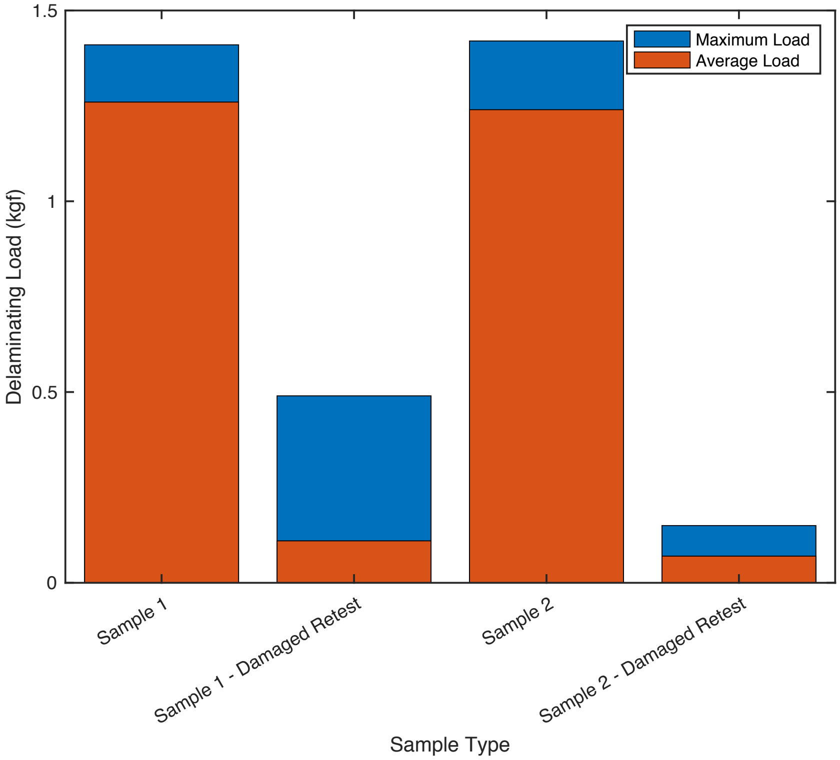


Figure 19: 11/22 Automated peel test results for retested, damaged, DBD samples (production conditions outlined in Table 2). Full data set shown in appendix Figure 23.

Samples	Pretreatment	Deposition
Figure 26	60 seconds 2 SLM Nitrogen / 500 SCCM Oxygen t_{on} = 100ms, t_{off} = 400 ms	4x60 seconds 5 SLM Nitrogen / 30 SCCM Butadiene t_{on} = 100ms, t_{off} = 400 ms

9 Conclusions

Thin films of nitrogen rich plasma polymer were successfully deposited onto silicon wafers and TPO. XPS characterization confirmed over 20 at% nitrogen incorporated throughout deposited films. Further chemical analysis of pretreated samples showed inconsistent surface oxygenation, which could provide an explanation for poor adhesion results. Extended pretreatment procedures, requiring pulsed plasma treatment and repeated sample rotation, still showed inconsistent oxygen content across the sample surface. However, plasma polymer deposition under pulsed plasma, with sample rotation in between deposition periods, produced coatings with visibly higher homogeneity than with continuous plasma or without sample rotation. This did not translate to improved peel tests. In fact, results showed that early samples produced using continuous plasma, without pretreatment or any sample rotation, resulted in the strongest top finish adhesion.

Damage to the top finish layer, in the form of a cut, significantly reduced adhesion results and forced full top finish delamination upon another peel test. Past samples produced with PECVD consistently passed qualitative peel tests that required more extensive damage. This indicates that samples produced using atmospheric plasma processes do not reproduce the adhesion quality of samples produced at low pressure.

As attempts to improve treatment homogeneity failed to increase adhesion, it is likely that poor sample performance was the result of more than just the filamentary nature of DBD. There is some unknown factor in sample production that has still not properly been controlled for, likely relevant to the fresh substrate surface. Focus on TPO characterization before any plasma treatment could provide insight.

Of the outlined project objectives, the first 2 were accomplished while the last 2 require significant improvements. Plasma polymer deposition was accomplished using an atmospheric pressure process, and the use of non-toxic precursors allowed for open atmosphere operation in a potential industrial setup. Peel tests were used to demonstrate the significant adhesion enhancement between TPO and PU resulting from deposition of a nitrogen rich thin film. While some samples produced using Butadiene as a carbon source were found to exceed CGT's production standard of 1.3 kg_f adhesion, this could not be repeatedly achieved or accomplished using non-toxic Ethylene. Lastly, plasma treatment procedures requiring pulsed plasma, and therefore extended treatment times for similar extents of treatment, and sample rotation increase sample production time. Significant improvements including additional steps for initial substrate quality control are required at lab scale to meet industrial standards. Nevertheless, the demonstrated adhesion enhancement, using an atmospheric pressure DBD plasma system, is a promising concept for polymer production. The work presented in this thesis demonstrates the potential of atmospheric pressure plasma polymer deposition for top finish adherence or general multilayer laminate production.

10 References

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11 Appendix

This section contains various figures that were deemed unnecessary or superfluous for the main body text. All following figures have been referenced somewhere in the main text, above.

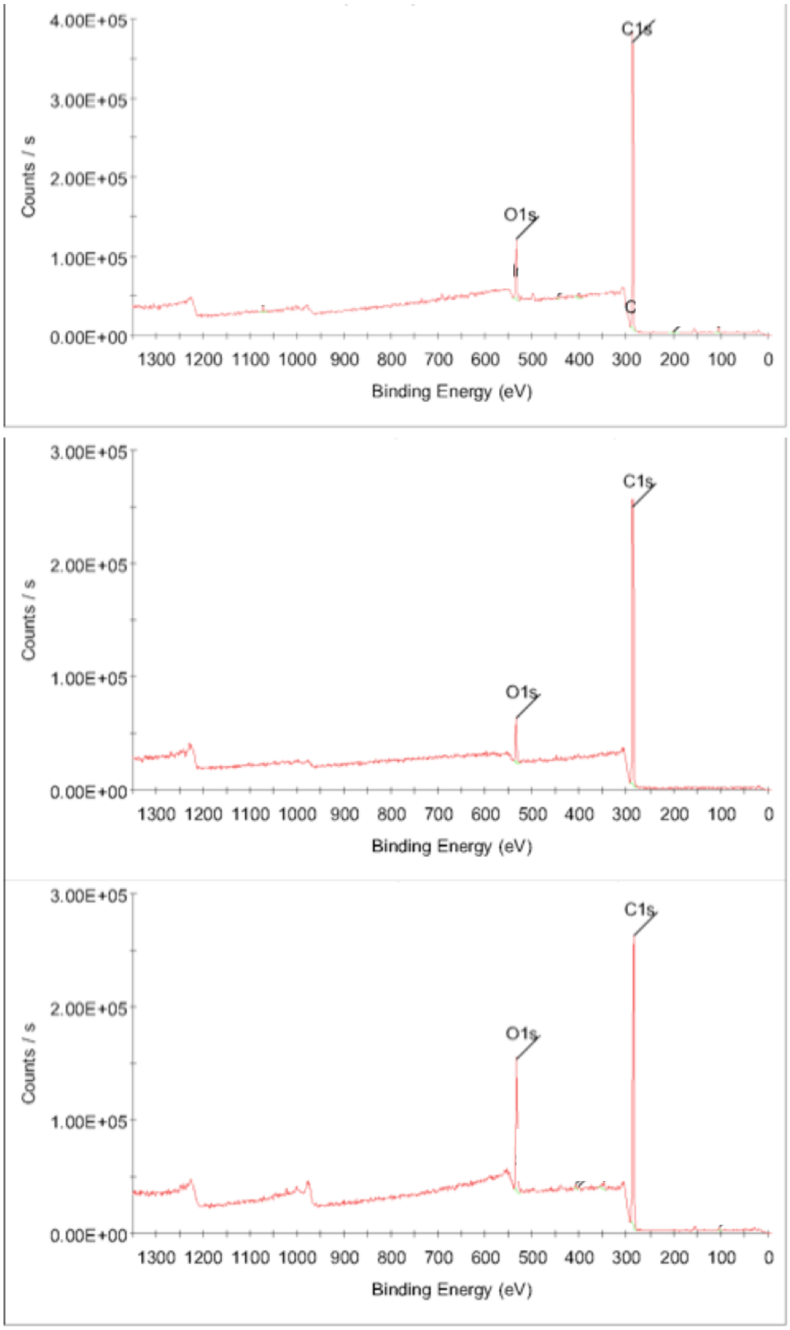

Figure 19: C1s and O1s peaks for control TPO (Top), TPO treated for 30 seconds (middle), and TPO treated for 60 seconds (bottom). Operating conditions of 8 kV_{pp} and 16.9 kHz. Sorry for these garbage images… I did not export all data properly, and only have word document reports containing these auto generated images, rather than raw data in excel

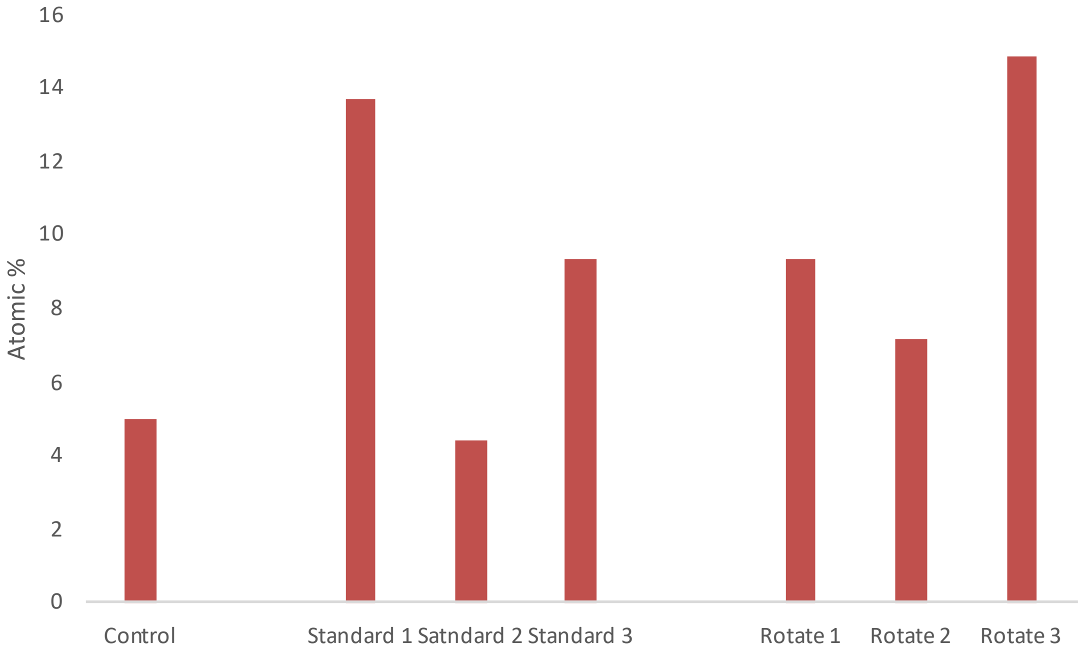

Figure 20: XPS results for oxygen atomic% of control (3 average samples), standard (TPO treated for 60 seconds under 2 SLM Nitrogen and 500 SCCM Oxygen, pulsed at t_{on}=100 ms and t_{off}=400 ms, 9.9 kV_{pp} and 18.8 kHz), and Rotate (same operating conditions but 4 20-second treatment periods with 90° sample rotation in between

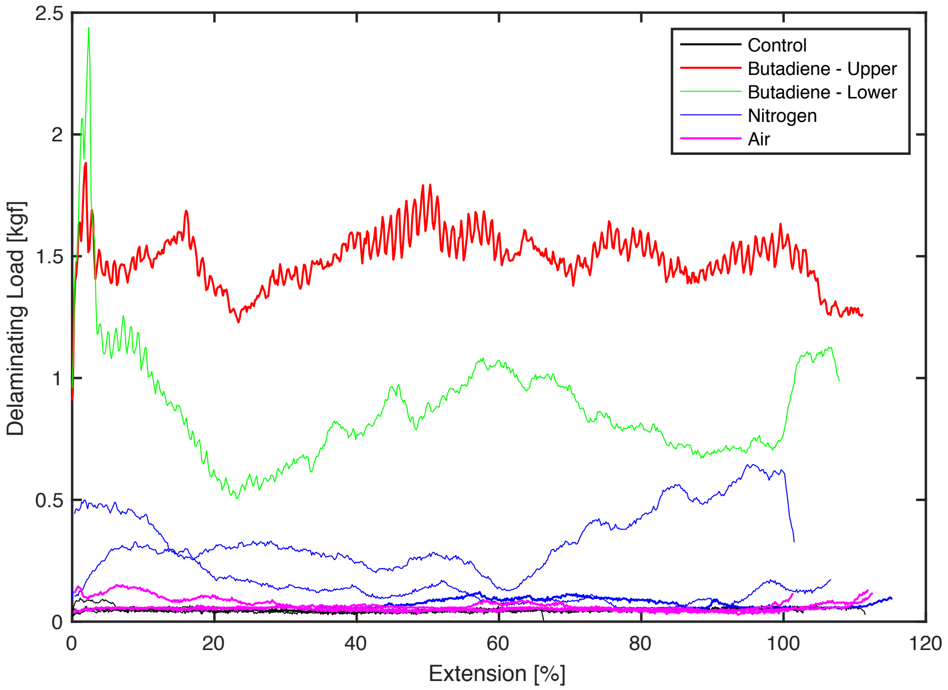

Figure 21: Automated peel test results for samples outlined in

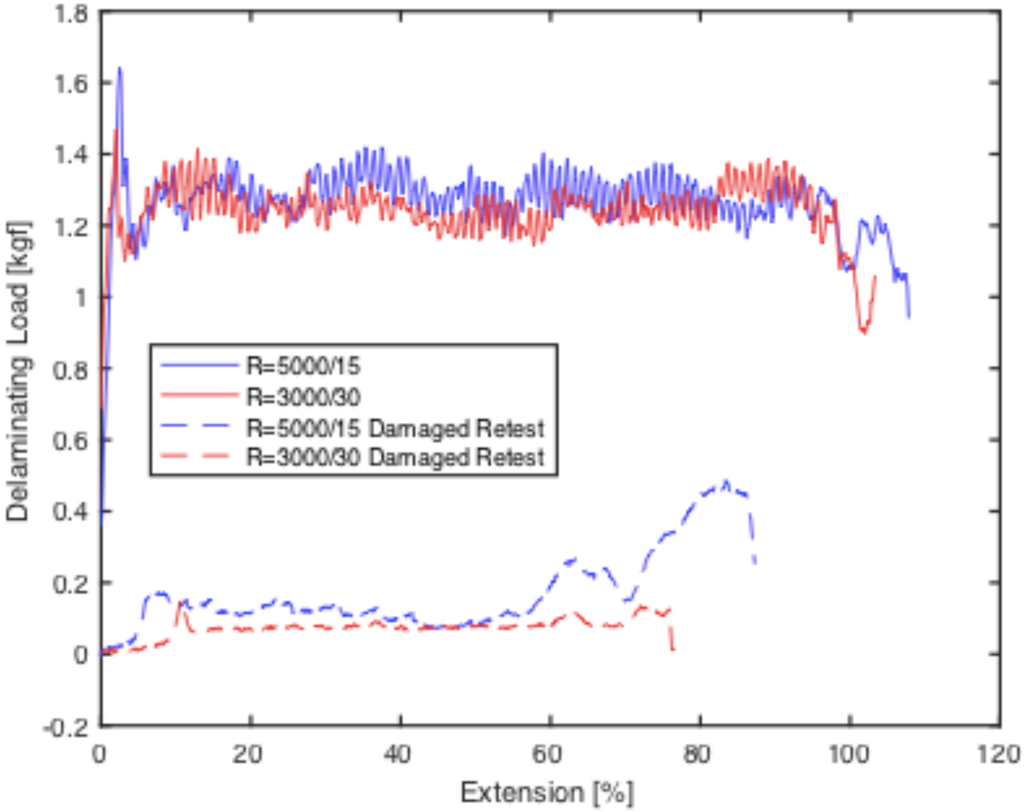

Figure 22: 11/22 Automated peel test results for retested, damaged, DBD samples (conditions outlined in Table 10). Samples were produced using standard pretreatment and deposition using differing flow rations of Nitrogen to Butadiene (either 5000/15 for a carbon lean feed or 3000/30 for a relatively carbon heavy feed)