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Effect of Plasma Treatment on Soil Degradation of a Biodegradable Mulch Film

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Master Thesis

EFFECT OF PLASMA TREATMENT ON SOIL DEGRADATION OF A BIODEGRADABLE MULCH FILM

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Abstract

Biodegradable Mulch Films (BMFs) offer a sustainable alternative to traditional non-degradable PE mulch films. However, their slow rate of biodegradation can lead to plastics accumulation in the soil. In this study, a commercially available BMF based on polybutylene adipate co-terephthalate (PBAT) and polylactic acid (PLA) is examined. Here the effects of gliding arc plasma treatment on the bulk and surface properties, as well as its soil degradation behavior, is studied. An increase in surface oxygen containing species and hydrophilicity was observed following plasma treatment. Only a small hydrophobic recovery was noted over 30 days. No changes in the bulk polymer molecular weight or thermal properties following treatment were noted. However, a decrease in mechanical strength was observed following gliding arc plasma treatment. The onset of soil biodegradation occurred earlier for a plasma treated film and we attribute this to an improvement in the initial adhesion of bacteria on the surface.

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PROBLEM INTRODUCTION

Plastic usage is common in agriculture and can be seen everywhere from mulch films, storage silos and greenhouse covering. [1–3] Mulch films consist of 51%[4] of the entire plastic usage in agricultural applications. Mulch films are used to create a more suitable environment for crop growth by providing a physical barrier thus aiding in soil moisture retention, preventing weed growth, and maintaining a desirable soil temperature. Previous studies have reported a significant improvement in crop yield after using plastic mulch films: For example, a 45-47% improvement in musk melon outputs and up to 369% increment in bell pepper yields have been reported[5]. In addition, there are reported savings of 12-35% of water on farms resulting from the use of mulch films[6]. All of this provides a strong argument for the use of plastic mulch in agricultural applications and why it is needed to keep up with increasing food demands.

Traditional polyethylene (PE) mulch films are cheap, flexible and tend to do well in harsh outdoor conditions.[3,7] However, due to their non-biodegradable nature, traditional films must be removed from the field and this gives rise to added labor costs. From an environmental point of view, this also poses a potential problem of microplastic accumulation in the fields. Likewise, films must be disposed of following removal which might include landfill tipping fees. Also, there have been reports of farmers burning the plastic[8,9] which is not a desirable end of life outcome for these materials from an environmental point of view.

THE RESEARCH QUESTION

Does plasma treatment of the biodegradable mulch film enhance cellular adhesion and soil degradation?

This question has been answered in this study, the smaller answer is yes, the plasma treatment of the films affects and enhances the degradation of such films whereas there are many more questions that need to be answered to see the full picture presented in this study:

- ***How does it impact the properties of the films?***
  Plasma treatment of the commercially available mulch films does not affect the chemical and physical properties of the films. Whereas it does impact the mechanical properties of the films due to high output power and heating effect. This does result in pin holes but can be mitigated using lower power plasma treatment such as dielectric barrier discharge.
- ***Stability in commercial point of view?***
  The stability of the treatment has been a topic of discussion but prior to treatment it was found that the hydrophobic recovery of the films was pretty low. A mere reduction of around 5° in contact angle is considered negligible. Hence making this treatment viable for especially for transportation and storage. Thus, we can confidently comment on the commercial viability of the treatment. ***Bulk and surface properties modification.***

    As discussed, there were major changes in the surface property of the films such as introduction of Oxygen rich groups which caused a significant reduction of contact angle. As for bulk properties, the chemical and thermal properties do not change post plasma treatment. As this treatment produces a lot of heat there are some reduction of mechanical properties was significant but we believe that using a much milder treatment can produce samples that are just as strong.

3.0 LITERATURE REVIEW

Biodegradable mulch films (BMF's) provide alternative end of life strategies over non-biodegradable mulches. BMF's are either soil degradable, wherein they could be tilled with the

soil or compostable so they can be thrown into a composter, which are common in farms. Some commercially available mulch films are listed in Table *1* and these are generally composed of polysaccharides and aliphatic or aromatic polyesters which are prone to hydrolysis.[9,10] In particular, the usage of PHA (polyhydroxyalkanoates), PBAT (polybutylene adipate co-terephthalate), PLA (poly-lactic acid) and starch is fairly common in these biodegradable/compostable films.[11] Blends of PBAT and PLA are quite popular in the literature[12,13]. Blending PLA/PBAT results in better modulus of elasticity and tensile strength as compared to PLA which is brittle and PBAT which has a low modulus.

Table 1 Some commercially available mulch films.

Name	**Composition**
Mater-Bi®	PBAT, Corn TPS, vegetable oils
Ecovio®	PBAT, PLA (~7%)
BioFlex®	PBAT, PLA (~30%)
Mirel®	PBAT, PHB
MIMgreen®	Cellulose fiber

Soil degradation of BMFs are estimated to take as many as six years or more to full degrade.[14,15] Not surprisingly, the geographic location where the mulch film is used influences the degradation rate, where cooler climates generally reduce the rate of degradation.[16] Lamparelli et al.[17] express concerns with low temperatures affecting the rate of degradation of PBAT/PLA blends. They

further report that the presence of microbes in soil makes it the faster method of degradation over hydrolytic degradation under these conditions.

The biodegradation of polymers in soil is described as a three-step process consisting of film surface colonization by soil microorganisms, followed by enzymatic depolymerization of the polymer into small molecules (monomers/oligomers) that are subsequently utilized for energy production and biomass formation.[3,18] The initial degradation phase of polymers is dominated by surface colonization of soil microbes [3,19]. Thus, bacteria attachment on the film surface can be an important determining factor in dictating the rate of degradation. Bacterial attachment on plastics has been studied in detail and results suggest that polymer surfaces can serve as a substrate for microbe environment.[20–22] This has been further strengthened by research in biofilm formation on plastic surfaces.[23–25]

Generally, polymers have relatively hydrophobic surface properties and this limits their rate of biodegradation[26]. Engineering of the polymer surface to enhance favorable microbial interactions may be a means to increase biodegradation of polymers. This was shown by Lea et al.[27] who demonstrated an increase in the wettability of PLLA films following alkaline etching and this resulted in favorable enzymatic degradation. The authors reported this happens due to the ability of the surface to permit water, enzymes, and aqueous solutions to easily colonize and access the surface of the polymer. In the c current study, a plasma surface treatment technique will be utilized to alter the surface hydrophobicity of a polymer film to understand its influence on soil microbial attachment and degradation.

Surface treatment of polymers is a commonly applied industrial practice to improve adhesion, printability, and dye uptake of polymer surfaces.[5,28] Plasma treatment is one of the most versatile

methods of surface modification when compared to other techniques such as physical modification, flame and chemical surface etching. [29] Plasma treatment can result in a variety of surface changes including functionalization, deposition, etching and crosslinking.[5] Unlike other methods, plasma surface treatment does not involve the use of harsh chemicals or release toxins, which makes it an environmentally friendly method of polymer surface modification. [29,30] Atmospheric plasma specifically can be used to incorporate a variety of nitrogen and oxygen containing species on polymeric surfaces.[31] In this study we utilize a gliding arc plasma treatment to modify the surface of a BMF. Gliding arc plasma is generated between diverging electrodes at high voltages and is quenched by gas flow. It achieves high reactivity and efficient productivity (high energy density) and is an environmentally clean process.[32]

Here we test the hypothesis that surface treatment of a biodegradable mulch film can aid in colonization of a BMF and reduce soil degradation times. In this work we investigate the effects of atmospheric pressure gliding arc plasma on microbial attachment and soil degradation performance of a commercially available mulch film based on a blend of PBAT and PLA. The surface of a treated and untreated film is characterized using X-ray Photoelectron Spectroscopy (XPS) and contact angle measurements to assess the efficacy of the plasma treatment to modify the film surface. Moreover, Differential Scanning Calorimetry (DSC) and Gel Permeation Chromatography (GPC) was used to characterize the influence of plasma treatment on the bulk condition of the film. Additionally, tensile testing was performed to assess the impact of the plasma treatment on the mechanical properties of the treated film. The study has been limited to aerobic soil and aerated compost degradation to ensure that the study is most relevant to application at a farm. Soil degradation under anaerobic conditions was carried out in static aerated pile for 248 days and resulting films were characterized via GPC, DSC, and Scanning Electron Microscopy

(SEM). Finally, microbial adhesion was evaluated by comparing cellular adhesion of *Pseudomonas Guariconesis* on the surfaces of plasma treated and untreated samples and differences in cellular adhesion is viewed in the context of biodegradation results.

Experimental work

Materials

Organix™ A.G. film was sourced from Berry Hill Irrigation Specialists and used as purchased. The film is described to be "OK biodegradable" as per TUV-certification and is based on BASF's EcoVio (a blend of PBAT and PLA, as described in Table *1*). The thickness of the film is ~20µm and one side of the film is black while the other side is white.

Figure 1 Experimental set-up for plasma treatment of biodegradable mulch films. Films were wrapped around a rotating cylinder (100mm diameter, 130RPM) and placed ¼" from the plasma head.

Plasma Treatment

A gliding arc plasma treater PJ-2 from Corotec was used for the treatment of the films (Figure 1). The plasma head inputs at 8A and 20V with the output being at 0.06A and 12kV. The films were wrapped around a rotating cylinder (130 RPM) measuring ~76mm in width and 100mm in

diameter. The low thermal mass of the films meant that they had to be treated through multiple passes of plasma allowing the surface to cool down after each pass. The treatment was carried out for 20 seconds with the sample placed ¼" from the plasma head. For this study only the black side of the film was treated which allowed better visualization of the treatment thus making quality control much easier for the experiments.

Film Characterization

Contact Angle measurements for the films were made using a Ramé-hart goniometer combined with DROPimage advanced image analysis software. A 1µL water droplet was placed on the film at three different sections of the surface and the angle measured (10 measurements per drop). The angle reported is the average of 30 measurements.

X-ray photon spectroscopy (XPS) was performed using an XPS - K-Alpha spectrometer (ThermoFisher Scientific, UK). XPS data was collected (analysis chamber pressure=4.5×10^{-6} Pa) using a micro-focused, monochromatic Al Kα X- ray source (1,486.6 eV) with a lateral resolution of 30 µm. The atomic concentrations of all the elements were calculated by determining the relevant integral peak intensities using Shirley background.

Thermal Characterization of the materials was carried out using a TA Instruments Q250 DSC in a nitrogenated environment. ~ 9mg of the sample was packed in a hermetically sealed pan and was heated to 200ºC at 15ºC/min to get rid of the thermal history, cooled to -50ºC at 10ºC/min and then heated back again to 200ºC. The melting, glass and crystallization transitions were observed, and the enthalpies were calculated using TA Instruments TRIOS software.

Gel Permeation Chromatography (GPC) was performed using a Shimadzu LC 2030 plus detector system containing two Agilent ResiPore, 300 x 7.5mm columns. In this experiment a refractive index detector (RI) was used. HPLC grade Chloroform (Chloroform, HPLC Grade, 99.5+% min, stab. with amylene, Thermo Scientific™) was used as the mobile phase and calibration was carried out using polystyrene (PS) standards (Sigma Aldrich, range of 500-1,000,000 g/mol). Sample concentration was 2.5mg/ml and the solutions were filtered using a 0.2-micron PTFE filter. Experiments were carried out at 1 ml/min and at a temperature of 30°C.

Degradation

Soil degradation of 3" x 3" samples was carried out in a 50-gallon forced aerated static pile compost. It consisted of 15 % spent coffee grounds (SCG) and 15 % coffee chaff (CC) with 70% manure compost mix as the inoculum. Using standard substrate like SCG and CC helps establish a good baseline scenario as the nutrients in the substrate will remain constant over time and not get affected by the place of procurement. In this experiment, films were buried in soil and periodically removed for visual inspection to assess degradation. To accomplish this, three films were placed in custom mesh bags (made by sealing Saint-Gobain ADFORS screens on three sides) and taken out during the time of measurement (~15-30 days) without disrupting the rest of the pile.

Surface Morphology of the films were observed using a TESCAN SEM at 10keV at 20mm working distance at 500x magnification. Samples were sputter coated with Palladium at 2Mbar using a SPI-module sputter coater in an argon environment.

Cell adhesion can be measured on the surface by various methods as described by Salánki et al. [33]. In this study cell attachment was assessed using a modified "centrifugal assay" method.[34–36] Cultures of *Pseudomonas guariconensis* which were identified using enrichment of cultures

method from field trials of the films were maintained on PCA plates and stored in the refrigerator before use. Cells were transferred monthly to fresh plates. For cell adhesion each cell type was grown in 20ml of tryptic soy broth (TSB) broth at 28-30°C overnight. The samples were stuck inside a 6-well plate using a double-sided 3M tape. 9ml of TSB media is transferred to the plate. 1 ml of 10^8 CFU/ml of bacteria cells were incubated into each well. The plate is statically incubated at 30°C for 48 hours. After the growth cycle, the plate is taken out and centrifuged at 800G.The plate is then inverted and centrifuged again to remove any lightly attached cells on the surface. Finally, films were allowed to dry in an incubator for 20 minutes before sputter coating with gold palladium prior to imaging via SEM. Cell adhesion before and after treatment was observed using a TESCAN SEM using a 10 KeV electron beam, at 2000x magnification at 12mm working distance. Image post-processing was performed using ImageJ.

RESULTS AND DISCUSSION

Film Characterization

Surface Properties: XPS, contact angle, hydrophobic recovery

XPS is a highly sensitive analysis technique commonly used to characterize the surfaces of plasma treated films. XPS survey results are presented in Figure *2* and Table *2*. For the untreated film, peaks attributed to the O1s (535.08eV), Ca2p (350.08eV), C1s (287.08eV) and S12p (101.08eV) were observed in the survey scan. For plasma treated films, an increase in both oxygen and nitrogen containing species were observed on the surface with increasing plasma treatment time. For example, the O/C atomic ratio of an untreated film was found to be 0.225. For plasma treatment times of 10 seconds, the O/C atomic ratio increased by about 95% and for treatment times of 15 and 20 seconds the O/C ratio increased to 124 and 107% respectively. Likewise, an increase in the N/C atomic ratio was observed following plasma treatment: Whereas an untreated film exhibited no N1s peak (401eV), one was observed for plasma treated films and the N/C ratio of these films was found to be in the range of 0.054-0.055. Similar trends have been observed for plasma treated conventional polymers such as PTFE, acetylene and PE. [37–40] As for biodegradable plastics, Laput et al. noted an increase in O/C atomic ratio from 0.515 to 1.326 for PLA following atmospheric pressure low temperature glow discharge argon plasma with pulse durations of 5μs. Likewise, under these same conditions they observed an increase in O/C atomic ratio from 0.696 to 1.560 for a PLA polymer matrix composite containing 30wt% hydroxyapatite.[41] Jorda Vilaplana et al found a similar result for PLA with both O/C and N/C ratio increasing following atmospheric plasma treatment.[42] Slepicˇka et al found that the O/C increased for poly-4-methyl-1-pentene (PMP) following diode plasma discharge using DC Ar plasma treatment from 0.003 for untreated

to 0.401 following treatment at 8W for 240 seconds.[43] An increase in O/C and N/C ratio was also observed for oxygen and nitrogen, low pressure, non-thermal plasma treated PLA films[44].

Table 2 Elemental composition and C1s regional analysis

Sample	Plasma Treatment time (s)	Elemental Composition(%)						C1s(%)		
		C	O	F	N	Si	Ca	C-C,C-H	C-O-C,C-OH	C=O
EV00	0	78.2	17.6	0	0	3	1.1	96	0	4
EV14100	10	66.2	29	0	3.6	1.3	0	70	14	16
EV14150	15	63.4	32	0	3.5	0.5	0.6	63	18	19
EV14200	20	63.1	29.4	3.9	3.4	0	0.3	65	17	18

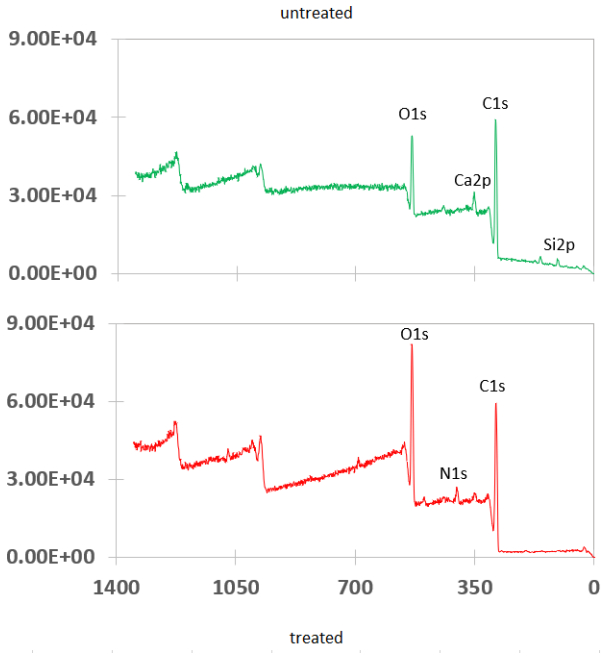


Figure 2 XPS survey spectra of treated and untreated films

High resolution XPS results (C1s) are presented in **Figure 3**a. As shown, C1s core-level spectra were curve-fitted to the two most prominent peaks corresponding to C-C/C-H (285eV) and C=O peaks (288.7 eV) for untreated films. After plasma treatment (**Figure 3**b.) peaks at 285.6 eV and 288.7 eV are observed and indicate an increase in the presence of oxygen containing species regions attributed to C-O (e.g., C-O/C-O-C) and C=O respectively. The concentration of these

oxygen containing species increases with increasing plasma treatment time as summarized in Table SI1. As shown, an initial increase in relative oxygen containing species to 14% is observed following a 10 second treatment and this increases further to a maximum of approximately 18% with increased treatment time. In the remainder of this paper, we will limit the discussion to the 20 second plasma treated sample, referring to it simply as the plasma treated sample.

Polymers usually are hydrophobic in nature and generally have a contact angles >80°.[45] Increasing the hydrophilicity for drug delivery or increased rate of reaction have been pointed out in the biomedical field.[46] A contact angle reduction from 94º to 54º was observed after plasma treatment of the films (**Figure *4***) and this correlates with the increased concentration of oxygen containing species on the surface (Figure 5). A reduction in the contact angle of PLA from 84° to 75° and for PBAT from 74° to 55° was observed following plasma coating with acetylene.[47] A reduction of contact angle is also accompanied by an increase in the oxygen containing species on the surface.[47–49] This could be attributed to oxidation of the surface polymer post treatment when the sample is exposed to the atmosphere.

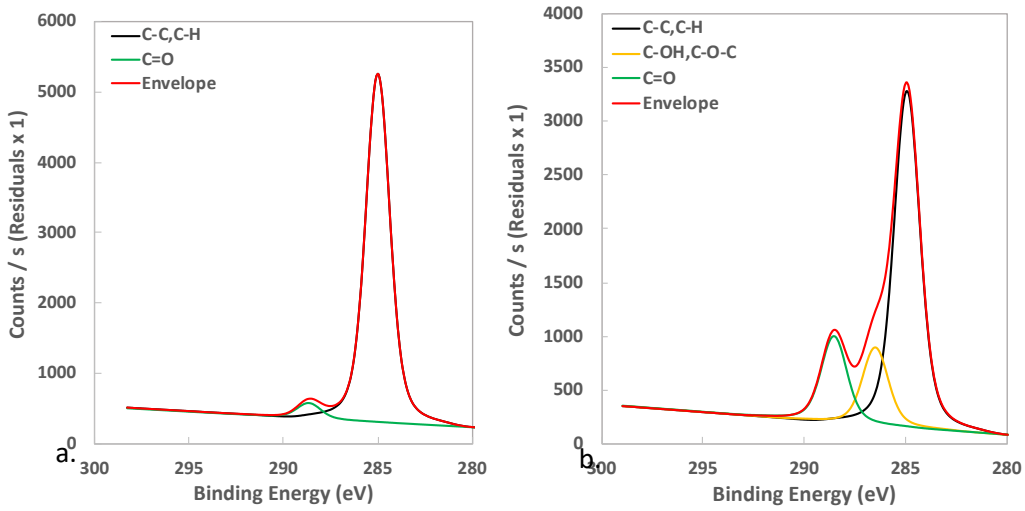


Figure 3 Counts / s vs binding energy plot for a. untreated and b. plasma treated film shows additional peak at 286eV.

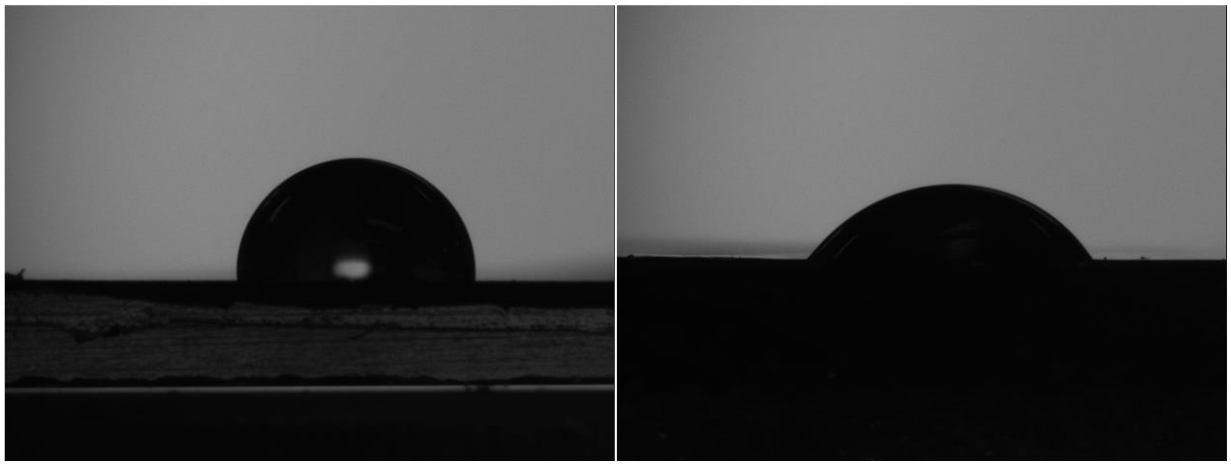


Figure 4 Reduction of contact angle was followed the surface plasma treatment, the contact angle of (a) untreated BMF was measured to be 94° whereas (b) treated mulch measured at 54°

It is well established that the surface properties change with post-plasma treatment aging time, can return back to their original, untreated state.[50] Several mechanisms have been advanced to explain

this so-called hydrophobic recovery process and include surface recontamination, the diffusion of polar groups on the surface into the bulk and the diffusion of un-modified molecules to the surface.[51,52] As shown in **Figure 3**b, the treated film shows only an ~18% hydrophobic recovery over the first 15 days that remains stable for the remainder of the 30-day observation time. This stability is desirable from an applications point of view in that it allows the pre-treating of mulch films well in advance of field application. A similar observation has been made for Dielectric Barrier Discharge (DBD) plasma treated PLA; for example, following a 30 second DBD plasma treatment the water contact angle increased from about 53° to 63°over the first five days whereupon it remained stable for the remainder of the 90 day observation period.[51]

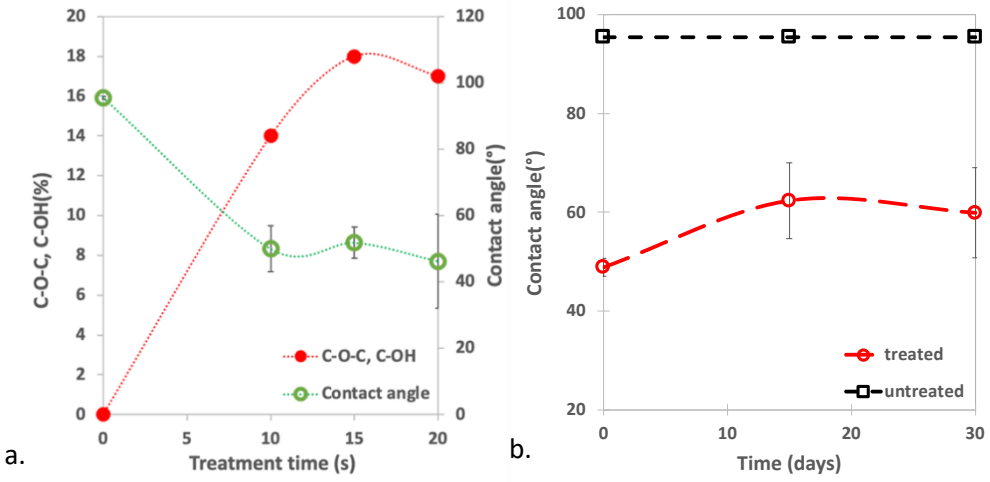


Figure 5 Surface properties of biodegradable mulch film is affected by plasma treatment. a. Contact angle and oxygen containing species change with treatment time. b. Hydrophobic recovery of the plasma treated sample is limited, thus enabling pre-treatment of mulch.

Bulk Properties

The thermal properties of a treated and untreated film is presented in the DSC second heat thermograms presented in Figure 6b; here two melting transitions corresponding to the PBAT (~127ºC) and the PLA (~150ºC) components are observed. This agrees with that reported in the literature[53,54] and the presence of two melting peaks results from the immiscibility of the two polymers. No significant changes in the DSC scans suggests that plasma treatment does not significantly alter the bulk material of the polymer film (see also Table 3). The M_n of the treated film was determined to be 50,400 g/mol (PDI=1.7) and showed only a small difference as compared to an untreated film (M_n=51,000g/mol; PDI=1.78). This observation, combined with the DSC results provide a strong argument to suggest that the gliding arc plasma treatment has little to no effect on the constituent polymers of the films and does not change any bulk properties of the plastic. That plasma treatment influences only the surface of a polymer while leaving the bulk properties unaffected is not an uncommon observation. For example, no change in the thermal characteristics of PHA and starch based films have also been noted post plasma treatment.[49,55]

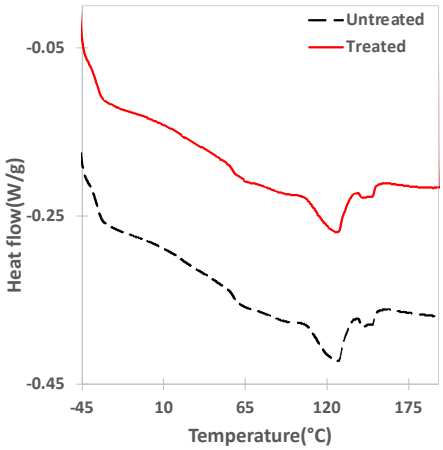


Figure 6 Second heat DSC thermograms following treatment show no differences in the thermal transitions of the constituent polymers.

Table 3 Consolidated DSC values compares the DSC transitions.

Sample	Component	T_m (°C)	T_g (°C)	ΔH_m (J/g)	T_c (°C)	ΔH_c (J/g)
Untreated	PBAT	127.6	-34.8	4.9	93.7	7.3
	PLA	150.7	57.3	0.5	123.9	0.2
Treated	PBAT	126.6	-35.1	4.8	93.8	5.8
	PLA	150.7	58.2	0.4	122.3	0.2

Mechanical properties

Mechanical properties for BMF are an important factor to consider as they provide a physical barrier from the external environment. Moreover, BMFs are subject to stress during their application onto the field and therefore their mechanical properties are of primary concern. To assess this, the tensile behavior of an untreated and plasma treated BMF were evaluated in the machine direction. As shown in **Figure 8**, the untreated BMF displays a tensile yield strength of approximately 8MPa, an ultimate tensile strength of approximately 15MPa and an elongation at break of about 400%. This generally agrees with that reported in the literature. Xin Wang et al. report an elongation of break of 357-480% for blends of PBAT/PLA.[56] Similarly, Guocheng Han et al. report a tensile strength of 18-20MPa and an initial elongation of break of 600%.[57]

A reduction in mechanical properties was observed following plasma treatment (**Figure 8**). Here a reduction in both strain at break (44% decrease) and ultimate strength (56% decrease) was

observed. The observed reduction in the mechanical properties is not due to changes in the chemical composition of the bulk film material as confirmed by the DSC and GPC results presented earlier; rather the reduction in properties appears to result from localized damage to the surface of the film that initiated failure following the application of stress. Interestingly, the elongation at break of the treated films showed higher variability as compared to untreated films (**Table *4*** The variation of length at break increases from an acceptable 8% for untreated BMF to a higher value of 30%).

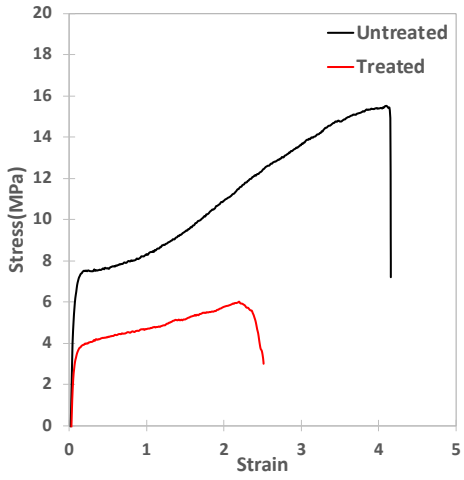


Figure 7 Stress vs strain curve for treated and untreated mulch

Table 4 The variation of length at break increases from an acceptable 8% for untreated BMF to a higher value of 30%

S. No	Untreated *mm elongation @ break*	Treated *mm elongation @ break*
1	162.49	*60.53*
2	142.49	*125.77*
3	151.06	*61.68*
4	166.57	*76.09*
5	184.71	*112.19*
6	167.71	*106.30*
Std. dev	14.62	27.93
Average	162.50	90.43
Variance	8.00%	30.00%

Surface plasma treatment of polymers previously have reported to show relatively small effects on the bulk properties of plastics by researchers[58–61]. For example, Mintra Meemusaw et al.[58] report only a slight reduction in the elongation of break post surface treatment but increase in mechanical properties when the pellets were treated before producing films. This is due to increased crosslinking providing improved yield strength. In contrast, Bussey at al. report a reduction in the young's modulus of films based on tetravinylsilane post plasma treatment at higher powers due to an increase in oxygen ratio that replaces stronger Si-C bonds with weaker Si-O-C bonds[62]. Some others have reported a more significant reduction of mechanical properties post plasma treatment of materials. [63–65] A. Bieder at al. reported increased crack on onset strain post plasma treatment of silicon oxide barrier films. They also discuss a likelihood of reduced young's modulus with decreasing gas flow rate of the plasma source, this is due to higher carbon content in the polymer.[64]

We postulate that the loss in mechanical property is due to the high intensities of the plasma treatment as also has been stated in previous studies. [58,62,63,66] Given that the bulk properties of the

materials are unaffected by the plasma treatment and the sporadic nature of the defects observed here may indicate that optimizing the plasma treatment process may help to reduce the effect that treatment has on mechanical properties. In fact, previous studies report there might also be an increase in the mechanical properties post treatment following process optimization.[65,67] As an alternative, milder treatments such as dielectric barrier discharge (DBD) plasma treatment may result in better mechanical properties of these thin films. Furthermore, for applications where the plastic is not the major stress bearing member (e.g. paper coated with such materials) or in cases where material thickness is >20µm, optimizing the gliding arc plasma treatment process may not be necessary.

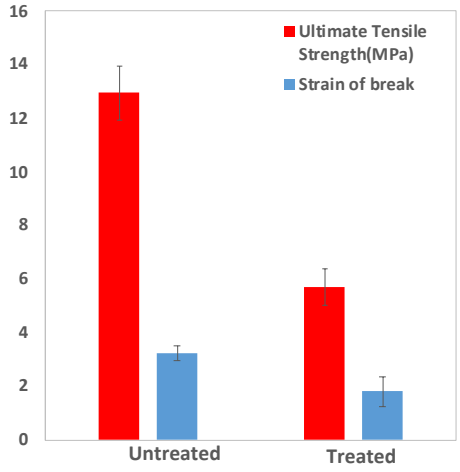


Figure 8 A reduction in mechanical properties was observed in the films following plasma treatment. This is due to the higher power of the plasma source used in the study which introduces small defects on the films. Milder forms of plasma treatment (e.g. Dielectric barrier discharge) may be more appropriate for thin films such as the BMFs examined in this study.

Degradation

Soil degradation of the BMFs was carried out in static pile soil bins for three months. Images of treated and untreated films in soil are presented in Figure SI.5. Here significant difference in the surfaces of the films is noted even after this short time period. Untreated mulch film shows little to no signs of damage with some amount of organic media that could be seen on the surface. In contrast, plasma treated mulch after two months in soil shows cracks about 2-3µm in width. This confirms the claim that surface modification of these plastic mulches positively affects the rate of degradation. It was also noted that the process of degradation in soil is a slow process.

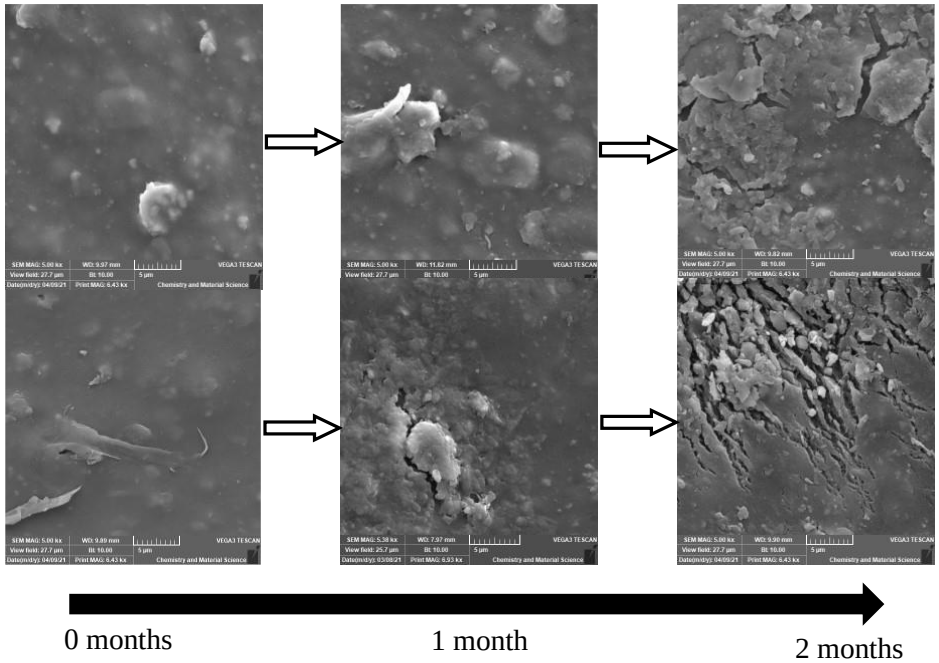


Figure 9 SEM images of untreated(top) and treated(bottom) films. 2 months after soil burial, no surface damage is observed on the untreated film apart from soil/dirt adhered on it whereas clear signs of damage can be observed on the treated films in the form of surface tears.

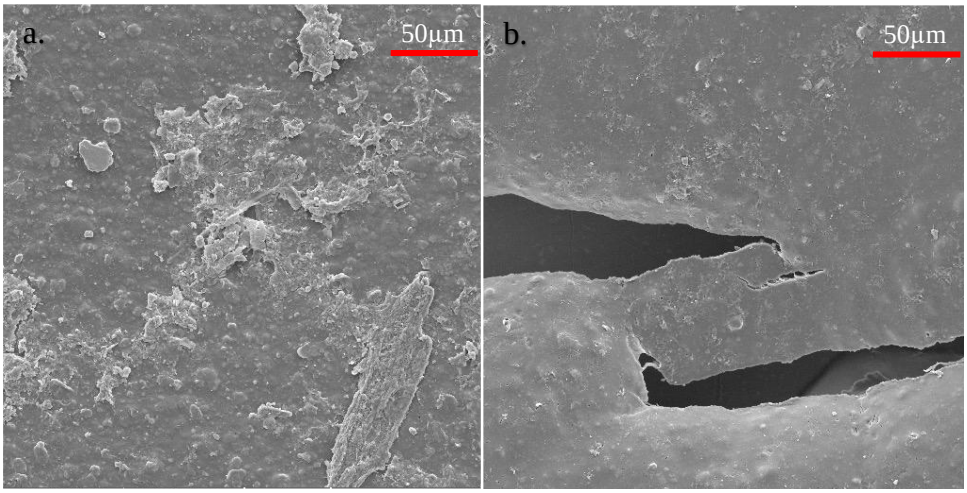
Figure 10 Experimental setup for compost

Composting was chosen as the preferred method of testing the effects of plasma on degradation. As Broadhagen et al.[9] in their work pointed out that there is a lack of in-soil composting/biodegradation standards currently being used in research. They go on to point out that most products labelled as biodegradable are not truly soil biodegradable but rather degradation results from external activities such as erosion, photooxidation and fragmentation. Jiao Jian et al.[68] in their work make comments about the viability of composting of PBAT and have reported complete degradation of the polymer in 90 days in compost. Setting up an in-house aerated compost bin let us have more control over the test environment and to ensure that the degradation is a result of microbes present in soil and have minimal impact due to the outside environment (Apparatus shown in **Figure *10***).

Polymer degradation in soil can be divided into different phases, the first being the attachment of soil microbes on the surface of the polymer, followed by enzymatic depolymerization by hydrolysis and further breakdown and utilization of the hydrolysis products to release CO_2. The latter two being a bulk phenomenon whereas the first step is a surface change and no changes in weight or chemical composition is observed.[3] Surface morphology of untreated and plasma films before and after soil degradation are presented in

Figure **11**. As shown in

Figure 11a. an untreated film is free from cracks on the surface whereas a plasma treated film (20 seconds, ¼" distance) exhibits cracks after only 65 days in compost. A clear distinction can be made between the two with the amount of physical damage on the surface. The treated sample shows large holes measuring ~120µm in length and 25µm in width following the same exposure time. This accompanied by no change in the molecular weight of the constituent polymers (presented in Table 5) (51,280 g/mol (PDI=1.68) for untreated film and 51,350 g/mol (PDI=1.68) for treated film.



c. d.

Figure 11 Plasma treated films exhibit enhanced biodegradation under composting conditions as compared to an untreated film. SEM images following 65 days of exposure to composting for (a) untreated film and (b) treated film. After 248 days, the difference in the extent of degradation is evident without the need for magnification. For example, an untreated film (c) shows some minor signs of degradation such as a few small cracks whereas the plasma treated film (d) exhibits large cracks and is easily fragmented.

Figure 12 Films pictured at 12x magnification after 15, 90 and 180 days in aerated static-compost. Plasma treated BMF (top) shows signs of fragmentation whereas untreated films (bottom) show lower degree of degradation over this same time.

Some physical damage can be observed on the untreated films after 180 days of composting of the untreated film; at this point the treated films are heavily damaged and have holes and tears (**Figure 12**). This is also followed by a significant reduction of the average molecular weight, which was measured to be 40,000 g/mol, (PDI=1.87) (). Significant changes are observed 248 days after composting, as presented in

Figure **11**c and 11d. Whereas only small cracks are observed on an untreated film the surface of the plasma treated film is covered with cracks and the films are fragile and easily fragmented. No

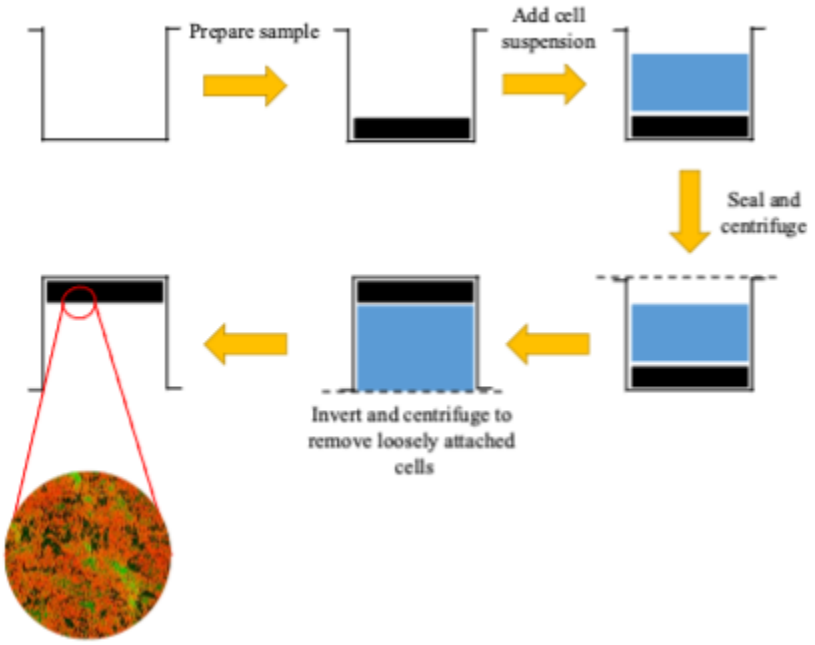
visible changes can be observed on the untreated film otherwise. Hence it could be concluded that the surface plasma treatment of the films can result in enhanced degradation of this BMF.

Cell Adhesion

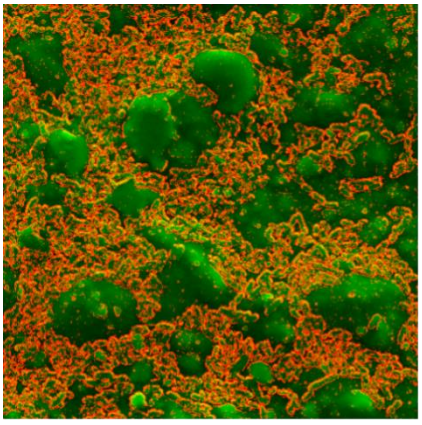
Cellular adhesion to non-polar BMFs is a key factor in determining the rate of soil degradation. The procedure we used to study microbial attachment on surface of a treated and untreated film is shown in Figure 7. Here films were adhered on a 6 well plate (**Figure 3**) and then filled with a cell suspension. Following 48 hours of incubation the plate was centrifuged, first in a right side up configuration to promote cellular attachment and then subsequently in an inverted configuration to remove any loosely attached cells. The cell culture was poured out and the surface was allowed to dry in an incubator set at 30°C for 15 minutes. *Pseudomonas guariconesis*[69] were isolated from soil in farms where the films were used. Figure 13 shows bacteria attachment on untreated samples whereas Figure 13c shows the state of bacteria attachment on plasma treated surface and was post processed using imageJ software. For reference Figure SI.4 presents unprocessed images. As shown in Figure 7a, about 2/3 of the untreated film surface is covered whereas nearly the entire surface of the treated film is covered. We attribute this to an increased hydrophilicity of the film making it easier for the bacteria to attached to the surface.

Cell attachment and biocompatibility of plastics and films have shown to improve following plasma treatment[37,44,61,70]. Chen et al.[37] who studied the effect of ammonia and oxygen plasma on cell attachment on PTFE surfaces and report an increase in the number of Pseudomonas Guariconesis count due to a reduction of contact angle following plasma treatment. Luigi Canullo et al.[70] also discussed higher hydrophilicity related to higher adhesion of cells on surface. Sundriyal et al.[48] in their study on adhesion report reduction of contact angle post plasma treatment; this

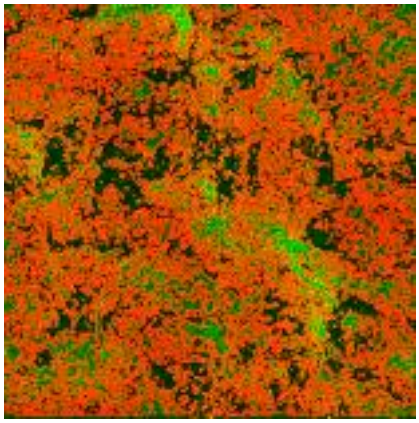
resulted in significant increase in the cell count on the surface of PLLA. We hypothesize that this initial colonization of cells is a major contributing factor of improved degradation and translates to lower lag phase in plastic degradation.



a.



b.



c.

Figure 13 Cellular adhesion is enhanced following plasma treatment. A) Schematic shown steps involved in the study of cell attachment on surface of the films. i) Films adhered to a 6 well plate

(black) and ii) filled with cell suspension (blue) where they remain for 48 hours in an incubator. iii) plate is sealed, and centrifuged right side up (to promote adhesion) followed by iv) centrifugation in an inverted orientation to remove loosely attached cells. The resulting surface was dried, sputter coated and observed under the SEM right. SEM images (enhanced using ImageJ) of (b). untreated film as compared to (c) treated film demonstrates the improved cellular adhesion.

CONCLUSION

In this work gliding arc plasma treatment was used to accelerate soil biodegradation for a commercially available mulch film based on PBAT and PLA. These films showed increased hydrophilicity following treatment and this was accompanied by an increase in the oxygen containing functional groups observed on the surface as confirmed using XPS. It is envisioned that mulch films can be pretreated before laying in the fields with only minimal loss in surface activation as indicated by lack of hydrophobic recovery. There was no modification made to the bulk properties of the polymer such as the melting, crystallization, and glass transition temperatures. In addition, no changes in molecular weight were observed following plasma treatment. A reduction in mechanical strength of the films was observed following treatment and this could be attributed to the presence of pin holes due to the aggressive gliding arc plasma treatment utilized in this study. We hypothesize that optimization of the gliding arc plasma treatment or the use of a milder surface treatment (e.g., dielectric barrier discharge (DBD)) may help to mitigate mechanical property losses.

Plasma treated films show early signs of degradation such as cracking and fragmentation of the film that became more severe as time progressed. While this was also true for untreated films the differences between the two differed greatly. During composting, surface degradation dominated over the first 65 days, as no change in molecular weight (GPC results) or thermal characteristics (DSC results) was observed whereas at longer times (180 days), a reduction in the molecular weight of the constituent polymers is observed. This can be attributed to better microbial adhesion following surface treatment. This was demonstrated by showing that bacteria exhibited improved adhesion to plasma treated films using a modified “centrifugal assay” method.

Plasma treatment is a cheap and environmentally friendly method of plastic film surface modification, and these results indicate that it can improved biodegradation of a BMF. In addition to BMFs, single-use products such as plastic-coated paper cups, plastic silverware and take-out food containers may also benefit from this approach. Future work with these activated films includes studying their degradation in soil over longer time periods and examining the effects of weathering of plasma treated films.

Provide a summary of how your proposed research is related to the pressing needs and global issues of today within a societal context. The statement should be sufficient to convince the thesis committee about your knowledge of the contemporary issues in your chosen research field. The summary should answer how your research topic is important in solving a need for the global community.

FUTURE WORK

Although the current films degrade well in compost but due to their poor mechanical properties, they cannot be used the fields yet as they play an important role in the mulch's use. To better understand this and optimize plasma treatment. Hence the following can be suggester:

- Using a much milder surface plasma treatment such as Dielectric Barrier Discharge (DBD), this reduces the amount of physical and thermal damage observed on the films and overall, a lack of pinholes observed. This kind of treatment can increase the hydrophilicity of the surface with less damage.
- Optimizing the current plasma treatment conditions, with using different voltages and current and gasses to reduce the amount of energy (especially thermal)
- Understanding better the mechanical damage done by gliding arc plasma treatment by the virtue of more mechanical testing.
- Studying the effects of plasma treated film in full scale field trials. This would allow us to compare surface treated films with untreated films in real life conditions.

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