Title: Plastics recycling via plasma-based depolymerization utilizing aqueous and gaseous discharge exposure

Statement of work-summary

The proliferation of plastics has contributed to significant environmental damage, not only damaging animal habitats but also entering the food chain and thus becoming a public health risk through the release of toxins (e.g. dyes and modifiers) contained in the plastics. Disposal of plastics via landfill and energy recovery are not practical solutions owing to long half-lives and greenhouse gas emissions, respectively. Mechanical recycling is a solution, but is limited by polymer type and produces lower quality plastics. Currently, plastics upcycling, the conversion of plastics to higher value products, is energy intensive due to high heat requirements (for thermolysis). Plasma offers a greener approach to the depolymerization of plastics and also offers the possibility of upcycling to make higher value products such as higher grade plastics and fuels. Nonthermal plasmas in particular are energy efficient and operation on air means implementation does not require exotic feed gases for operation. Here, the plasma is used to essentially deconstruct the polymer to its precursor monomers via scission. The key to realizing this plasma vision is optimizing gas phase and surface chemistry. Surface chemistry related to polymer depolymerization in liquids is compelling in that the environment is a natural heat sink and a reservoir of reactive species input by the plasma itself. Additionally, self-organization processes can locally greatly enhance the electric field and density locally of reactive species. The self-organization effects have yet to be fully explored. The goal of this effort is to study and characterize the decomposition products derived from the interaction of polymeric powder, liquid suspension of particles, and solid target with plasma generated by a low frequency plasma jet and a DC 1 atm glow. Here we aim to elucidate how plasma parameters including surface self-organization, induced fluid flow, and droplet emission effect decomposition processes as inferred using emission spectra and FTIR.

Vision and Goals

The amount of plastic produced in the world is growing exponentially. While this production supports societal needs, most of the plastics produced at the end of life becomes waste. Only 10% of this waste globally is recycled—which means that this waste is accumulating, unsustainably in the environment.[i] This accumulation is giving rise to a whole host of environmental problems ranging from destruction of marine habitats to the release of chemicals of emerging concern, particularly those related to additives used to make plastics more durable. This exponential growth in plastics production is also not sustainable as it is derived from a limited resource—petroleum.[ii] The production of plastics is a thermal process and, in this regard, its production has a large carbon footprint. The ultimate solution is simply to cease the production of new plastics and harvest the waste plastic.[iii] By depolymerization of the recovered plastics, one can produce monomers and precursors necessary to make new plastics thus closing the cycle. *Imagine a chemical process that takes in pristine as well as mixed waste and then depolymerizes the aggregate to form precursors using only green energy. Imagine that this process is completely nonthermal with the bulk of the reactants and solvent solution residing at room temperature, so that energy loss is minimal.* The interaction of plasmas with liquid water drives locally nonequilibrium conditions. Local temperature, species concentrations, photon deposition, kinetic energy of ions and electrons, pH, and ionic strength can all exist in states far from equilibrium.[iv] **It is this very aspect that makes plasmas an interesting, transformative approach to the chemical recycling of plastics waste. Here the activation energy is provided by the plasma itself, produced by renewable electricity**. In this work, we leverage ongoing, in-house plasma depolyermerization and polymer modification research as shown in Fig. 1.

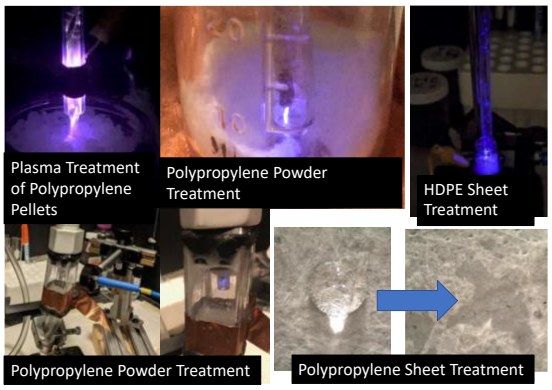

Figure 1. In-house plasma polymer studies

Plasmas, a unique opportunity: Plasmas offer an intriguing transformative opportunity for chemical-based plastics recycling. A gas phase plasma is a source of energetic electrons, ions, excited molecules, reactive species and UV light. When brought into contact with liquid water, a boundary layer forms on both sides of the interface where prevailing conditions are far from equilibrium. This region is a source of highly reactive, short-lived species as well as longer lived reactive species such as ozone and hydrogen peroxide that diffuse into the bulk solution. At the contact point, high temperatures can prevail even though the bulk solution is at room temperature. One particular discharge of interest is the glow discharge with a liquid cathode or anode. In this case, a discharge in air or an inert gas is struck between an external electrode and the liquid solution.[iv] An immersed electrode in the solution completes the circuit. Charge is carried by ions in solution for current continuity. Electrolytic processes such as oxidation or reduction occur at this immersed electrode depending on the polarity. In this case, the solution is made chemically active. Here, the plasma is the source of activation energy. pH in the boundary region can be made acidic or basic depending on discharge polarity. The plasma column temperature is hot, ~2000K and so locally at the surface, the liquid is hot and thus significant volatilization occurs there.[v] Reactions not possible in equilibrium, thermal systems are therefore possible. Typical electrolytic yields are >10x that of a conventional electrolytic cell. Since the

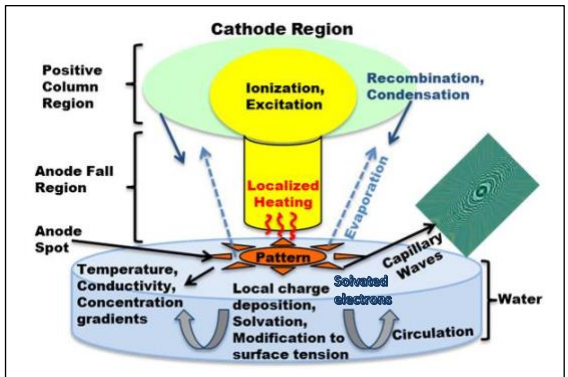

Figure 2. Complex chemistry driven by plasma contact with liquid water

plasma attachment destabilizes the interface, surface tension gradients exist, giving rise to self-organized convection cells that transport liquid to the plasma point of contact. In this respect understanding and controlling self organization processes are critical. Another key aspect of plastics recycling is high value product recovery during processing. In the presence of self organization, both droplet emission can be observed. The droplets contain particles and molecules synthesized in the solution. In this respect the droplets can be a means of sequestering monomers and fragments derived from the plasma and activated liquid treatment. Because these droplets appear to be charged, they can be controlled thereby providing a basis for collection.

The complex interplay between plasma and liquid water is shown in Fig. 2, making such a system an **ideal activated medium to carry out nonequilibrium chemistry.**[iv] These physical processes, such as localized heat, solvated electrons and reactive oxygen species, each have relative contributions that are controllable in dose and each has the capacity to depolymerize plastics. *These conditions afford us with unique reaction pathways that we aim to quantify and explore.* We stand on the precipice of a new and transformative method to carry out chemical reactions purely driven by electrical energy used to form the plasma. *Herein lies the opportunity: Using just plasma and liquid water ambient air, one can generate conditions with sufficient free energy to depolymerize plastics in solution.* The concentration of reactive species and solvated electrons can be tailored by varying plasma conditions. Locally one can replicate conditions for depolymerization but at pH and temperatures not assessable by conventional processing methods. It is our goal to fundamentally characterize these conditions and tailor them for the purpose of depolymerization. We will also explore the prospect of using plasma as a polymer pretreatment to convert the surface polymeric particles from hydrophobic to hydrophilic. This change improves water uptake and thus giving rise to higher liquid phase reaction rates for processes such as hydrolysis. **The vision is therefore to exploit nonequilibrium plasmas for the purpose of achieving high reaction rates using green electrical energy.** To get to this point however requires obtaining a better understanding of the plasma induced chemical kinetics, a chief goal of this work. While addressing science questions is a key goal of this work, our approach will involve experimentally demonstrating these principles at the bench scale and using this insight to infer efficiency and opportunities for scale up. This approach affords us the opportunity to demonstrate these concepts with great effect by augmenting the performance of a conventional system.

Proposed work: The proposed approach two-tiered. First, we aim to understand the mechanisms of plasma interaction with polymeric powders (mixed and homogenous) and solid substrates with the goal of controlling relative depolymerization rates and effects such as plasma-induced precipitation to facilitate separation. The plasma treated samples will then then examined using advanced diagnostics such as Ramen and FTIR spectroscopy along with surface analysis using SEM and XPS. These advanced diagnostics will be applied at PPPL.

Science and Technology Question: Is there a plasma-based, physio-chemical architecture that could facilitate the reuse of mixed plastics waste, converting the waste stream to precursors of value that could be used as feedstock for the production of new plastics ,thus closing the loop?

Conventionally, plastics can be converted into precursors via processes such as pyrolysis or hydrolysis.[iii] For example, PET is converted into dimethyl terephthalate and ethylene glycol by hydrolysis.[vi] These products can be used to synthesize new plastics. The hydrolysis process occurs at elevated temperatures in typically acidic and basic solutions of relatively high molarity. In this respect, it is a thermal process that creates additional waste streams. Pyrolysis features thermal processes as well with high temperature catalysis operating at 700-800 K, as shown in Fig. 3.[vii] In this treatment architecture, the media to be processed along with the catalyst and containers have to be raised to high temperature which results in significant loss of energy associated with waste heat.

We aim to show that nonthermal plasmas offer, in the near term, an improvement in efficiency of conventional plastic recycling processes and, in the longer term, an environmentally friendly potential solution to plastic recycling. A nonthermal plasma can be thought of as chemically active gas sustained by electrons. Here the input electrical energy goes into electrons which drive excitation, ionization and bond breaking of gas feedstocks. The heavy particles remain at or near room temperature. Since one can manipulate the electron energy distribution, one can selectively drive specific chemical reactions, thereby providing some means of tunability. The general approach taken in this work, schematically shown in Fig. 4, addresses two possible architectures: 1) augment conventional methods and 2) replace conventional methods. Nonthermal plasmas can be utilized in the processing of waste plastics in 3 key ways:

1) *Surface energy modification*. The interaction of oxygen containing plasmas with polymer surfaces modifies the surface energy making the surface hydrophilic. Increased hydrophilicity improves solubility in water for conversion as well as improves the surface uptake of water, thereby greatly enhancing the hydrolysis reaction rate or any liquid phase reaction rate.[viii] Therefore, a plasma can be used to pretreat polymeric powders before they are processed in a hydrolysis reactor, for example. The key science challenge is control of atmospheric pressure plasmas in a fluidized bed configuration – feedstock gas and polymeric powder – to selectively pretreat surfaces to improve hydrolysis efficiency.
2) *Separation*. The interaction of plasma with polymeric powders not only modifies the surface but it also affects the charge state of individual particles. When such particles are deposited in water, they can agglomerate forming macro-sized particles or floc. The conditions of the floc formation vary with polymer type. Plasma pretreatment of particles in the presence of water may provide a unique means to separate different plastics types and thus facilitate the harvest of pristine plastics waste streams- essentially a re-imaging of conventional froth flotation.[vi] The key science question is – how can a combination of plasma induced liquid phase chemistry which determines solution conductivity and plasma driven surface chemistry be used to facilitate selective agglomeration?

Overarching objective. The proposed effort aims to integrate plasma processes into proven, but inefficient, plastics recycling architectures for the purpose of not only improving energy efficiency and recovery yield of precursors but also to provide a method for polymer specific mass separation so that mixed wastes can be credibly processed. The research roadmap of this approach, shown in Fig. 4, demonstrates augmenting upcycling as well as the pathway to transform the process by making it purely plasma based. The bottom portion of the figure shows the conventional treatment train, which for the most part is purely thermal. Pulverized waste, either mixed or homogenous, enters the plasma treatment stage. Here the powder is aerated in an atmospheric pressure plasma where the surface of the plastics particles are modified, making them hydrophilic. The functionalized powder is then transferred to the next process step, which consists of one of two possibilities: 1) Direct injection into a conventional hydrolysis reactor (or catalytic bed, depending on plastic type).[ix] Here treatment and process efficiency are enhanced owing to prior plasma pre-treatment. 2) For mixed waste, the plasma treated particles are transported to a reactor that facilitates polymeric separation thereby creating multiple streams of waste to hydrolyze or pyrolyze either conventionally or via plasma assistance. High value precursors are then separated to convert to higher value plastics. Plasma augments the conversion process, allowing for higher efficiency and recovery of precursors. Throughout the process, plasmas enhance treatment and add value to conventional methods. This approach allows for plasma enhancements to improve the process, allowing the architecture to ultimately evolve to a fully

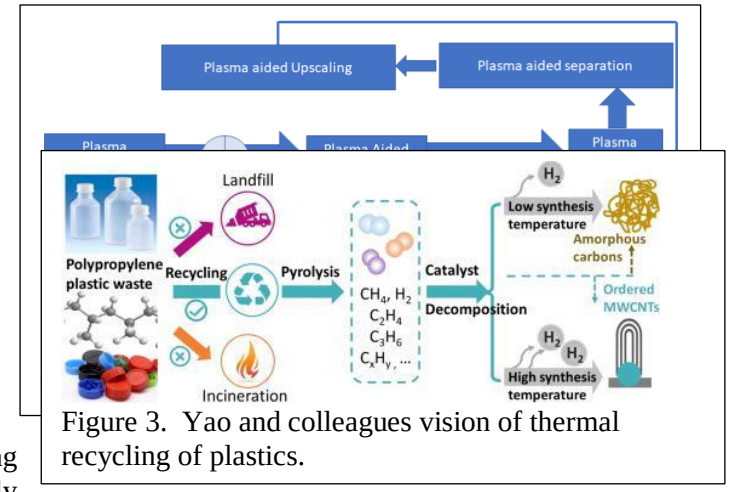

Figure 3. Yao and colleagues vision of thermal recycling of plastics.

plasma-based approach as shown in Fig. 5.

Proposed experiment plan. In this proposed activity, plastics in the form of powder or solid substrate will be treated in an aqueous salt-water solution. The discharge to be used in this case is a 1 Atm dc glow. A DC glow with a liquid anode is formed at atmospheric pressure when voltage is applied between a rod cathode, typically with gas flow such as helium, and a liquid electrolyte such as salt-water. The DC plasma formed between these two electrodes has the form of glow discharge as shown in figure 1a, where the cathode fall region (CF), the positive column (PC), the Faraday Dark Space (FDS), and the anode dark space (ADS) are apparent in discharges for example from Bruggeman[x] and our group (UM PSTL) as illustrated in Figure 1b. The atmospheric pressure glow discharge with liquid anode is a remarkable physical system, displaying an array of not well understood phenomena. For example, why does the plasma attachment at a liquid anode transition from a spot attachment to an intricate, symmetrical pattern above some threshold current as shown in figure 1b? What drives this self-organization? While these patterns appear to be relatively static, a host of secondary phenomena is made apparent when the discharge is imaged with a fast frame rate camera. For example, these images revealed upward traveling droplets emerging from the pattern attachment at speeds exceeding 30 m/s. What is the interaction between the self-organized pattern and the liquid surface that gives rise to the emission of these high-speed droplets into the gas phase? What forces are at play that facilitate their emission? And what is the fate of the droplets when they enter the gas phase? Why do some of these droplets maintain shape despite traversing a gap at a blistering gas temperature of ~1000 K at 1 atm while others seem to vaporize only to reveal emission from the electrolyte or trapped nanoparticles? The droplets no doubt charge when exposed to the plasma and thus have the capacity to interact with each other electrostatically; not unlike dust in a dusty plasma. The discharge is therefore ***complex like a dusty plasma*** but rather than solid particles, this discharge contains an aerosol of droplets of liquid electrolyte—thus creating **a foggy plasma**.[xi] The physical processes surrounding such droplets in a background plasma offers up a cornucopia of rich physics as identified by Stancampiano and colleagues. These particles are likely surrounded in their own atmosphere of vapor, clusters and ions that evaporate from the surface—and thus would be a source of depolymerization products in the gas phase. The very motion of the particles can be expected to be a complex combination of neutral drag, electric field, and convection. Their presence offers an excellent opportunity for understanding the interaction of droplets with a uniform plasma —a prospect that has proven challenging in atmospheric pressure plasmas owing to streamer formation.[xii] Figure 3 depicts a fast camera image of an observed, upwardly propagating 0.35 mm diameter droplet emitted from the surface. Such large droplets can serve as a macroscopic platform to understand charging and mass transport. Droplet dynamics are important not just from a basic science

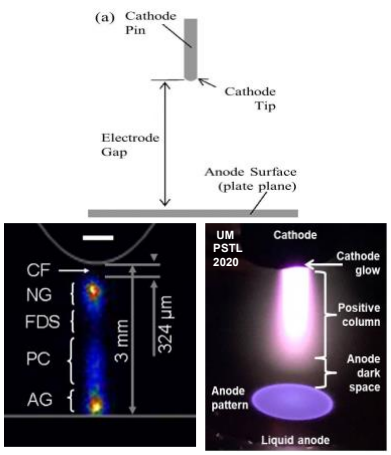

Figure 1a. An 1 atm DC Glow with liquid anode. Note features similar to typical glow discharge

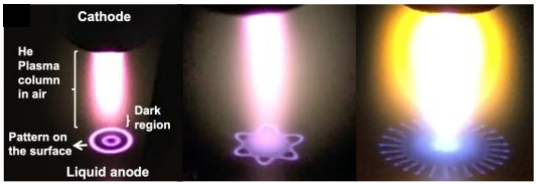

Figure 1b.Diversity of self-organized patterns observed

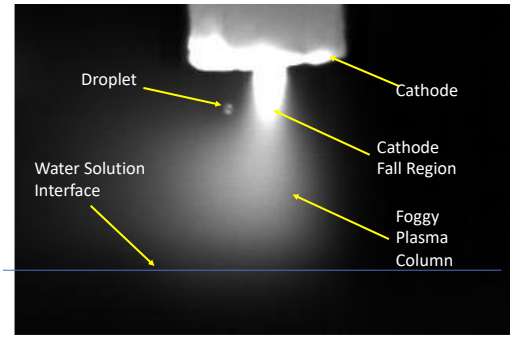

Figure 3. Droplet emission from self organized patterns in DC glow with liquid anode

point of view, but also aerosol-plasma applications ranging from plasma medicine to plasma assisted deposition of, for example, nanoparticles as observed in this work. This larger droplet must interact in some way with the multitude of smaller mist particles present in the vapor cloud—either —physically through drag or electrostatically via charge.

Here a basic understanding of plasma-aided chemistry and reaction pathways are studied for the purpose of determining control and projecting the capacity of scale up and yielding a rough estimate of conversion and energy efficiency. These experiments will feature basic plasma cells with a dispersion of polymers in the form of powders. We will also characterize the effect of plasma on the synthesis of new compounds derived from gas phase monomers generated in the reactor. By varying plasma conditions such as plasma temperature and density, we will investigate how the distribution of masses in the gas phase vary, thereby providing a control knob not only for the synthesis of new plastics but also for fuels. Table 1 describes the basic experiments and modeling activities. The key science questions addressed include:

- Plasmas can functionalize the surface of plastics particles, thereby affecting surface energy. Can this ability be used to enhance clumping of similar plastics types and thus provide a mechanism for mixed waste separation before introduction into the treatment train?
- Plasma treatment of polymer surfaces makes surfaces hydrophilic. Hydrophilic surfaces enhance water uptake. Can such an aqueous or gas phase plasma pretreatment be used to enhance conventional hydrolysis of plastics such as PET?

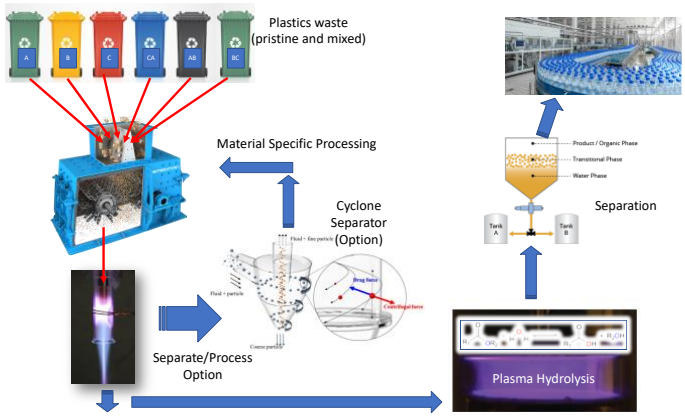

Figure 5. The transformative vision of plasma based depolymerization and upcycling

- Plasma in contact with liquids gives rise to extremely nonequilibrium conditions, including temperature and chemical properties such as pH. Can these nonequilibrium zones in this plasma liquid interface be used to drive plasma induced hydrolysis without the needs of strong acids and bases, thereby reducing the need for consumables? Here nonequilibrium pyrolysis can be tuned as well as the local pH for maximal effect? How can these processes be used to optimize the overall process?
- At the endpoint of the hydrolysis process, separation of high value components from solution is required. Can plasma exposure be used to control selectivity in the precipitation of the precursors?
- Monomers produced in the reaction stage can be upcycled using a variety of catalyst methods. What is the effect of the presence of plasma on gas phase up-conversion? What novel products are possible? Can plasmas be used as a source of activation energy and reactive species to facilitate to tailor the production of higher value polymer-based products or fuels?
- Plasmas can drive advanced oxidation processes that can eliminate via mineralization a range of organic contaminants and via advanced reduction eliminate fluorinated compounds. Can a plasma ”muffler” be used to purify exhaust streams to lessen the impact of processing on the environment?

Tasks

1. It has been observed that the emergence of the pattern is accompanied by the equally self-organized flow field patterns in the liquid below.

a. We hypothesized that the subsurface flow occurs due to the spatially nonuniform pattern attachment where thermal energy and charge are introduced. The flows therefore should indeed mirror the pattern morphology in *space and in time*. We further hypothesize that the function of the complex flows is to bring in fresh electrolyte into the attachment regions to support the discharge current. The flows are therefore likely to be self-consistent with the discharge current demand. These flows are important in that they transport suspended plastics particles to the plasma source and thus provides a mechanism for the enhancement of treatment rates. Preliminary work indicates that when the plasma self organizes, the flow patterns are complex but ordered, suggesting that it could potentially improve treatment rates even further. These flows will be characterized and then used to treat PET powder both with and without self organization. Changes to surface conditions such as the breaking of C-C, C-H, C-O bonds via interaction with plasma derived processes will be characterized using FTIR, Ramen, and mass spectroscopy.

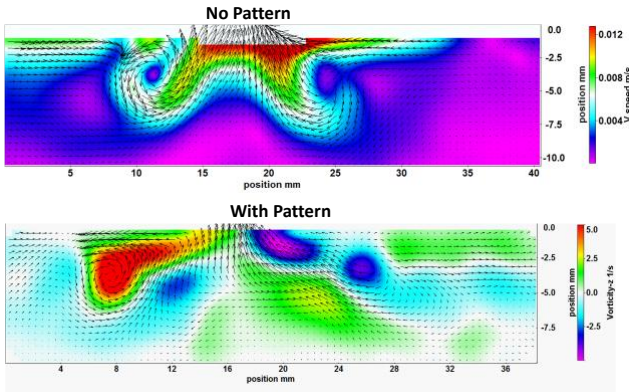

Figure 6. Dramatic difference in liquid convection velocity flow field with and without plasma pattern determined using PIV.

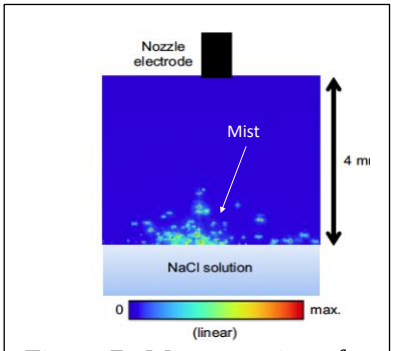

Figure 7. Mie scattering of vapor derived from a liquid cathode experiment. (Sasaki, 2014)

2. To date, a number of studies including our own work have (e.g. Shirai and Sasaki (fig. 7)) have used simple scattering experiments to detect and image droplet phenomena derived from the plasma liquid interaction. In this work, we intend to go further by quantifying the size and velocity distribution as well as well as explore any particle to particle and particle to pattern coupling. Droplets are observed to emerge from the plasma discharge contact point. The presence of the plasma which occurs during pattern formation is a direct indication that droplets are correlated with pattern formation. Why? We also notice that the discharge changes color as the current increases and the pattern becomes more complex. We hypothesize that droplets are emitted into the liquid, are subsequently charged, and then form clusters which contain solution ions that may play an important role in sustaining the discharge. Upon evaporation, these droplets introduce electrolyte salts along with polymer products into the gas phase.
    a. We tested the hypothesis by characterizing the density of droplets as a function of discharge current using light scattering. Mie scattering, can be used to detect particles and determine the particle density and size distribution. Estimating the size, density and circulation velocity is critical to understanding the dynamics of the foggy plasma as well as providing a basis for theoretical analysis. We will use an in-situ droplet analysis tool to make detailed measurement of size distribution and velocity. The tool uses a diffuse light source to avoid specular scattering effects. Additionally, by tracking the particles we can also assess forces on particles. A band pass filter at probe wavelength will be used to minimize effects of plasma light emission. A clear goal of this task will be to determine what relationship if any exists between the droplet cloud and the pattern below. The particle motions will also provide some insight into the importance of Coulombic

interactions and the degree to which the droplet component of the plasma is strongly coupled. Using biased plates, if the droplets are negatively charged, then perturbation to natural droplet convection should be observable. This task is important in that droplets likely are rich in polymer molecules since they are emitted from the region of the self organized plasmas. This provides an opportunity to capture treated polymers (as particles in droplets) or polymer molecules trapped in the droplet. We will also place witness plates near the cathode to collect positively charged droplets to be examined later for monomer content. The collected liquid will be examined using FTIR and Ramen spectroscopy. The key goal here is to understand the effect of the treatments on surface structure and provide evidence if any of true depolymerization.

3. Fast camera imaging of droplets can yield insight into the dynamics of the droplets. Solitary droplets such as the one shown in Figure 3 have been observed. Presumably these droplets are charged. Mapping the droplet motion in the vicinity of a biased plate gives insight into the charge carried by the particle. It is then possible to understand the forces acting on the particle such as drag and convection effects in addition to the electric field at the probe plate. With the spectroscopically determined electric field in the positive column, one can completely model the behavior of droplets interacting in this background plasma.

Advanced Diagnostics at PPPL PCRF

This project will be supported with critical advanced diagnostics at the PPPL PCRF. The diagnostics task supporting this effort is entitled: "Measurement of Decomposition Products derived from the interaction of an atmospheric pressure nonthermal plasma and a polymer substrate." This diagnostics campaign was approved by the PPPL PCRF. The measurements will be carried out by two graduate students with the assistance of PPPL PCRF staff. The two students are currently studying processes in reactors applicable for depolymerization. One student is carrying our plasma jet -polymer powder and low frequency plasma jet-polymer powder in liquid studies. The second student is specifically studying plasma self-organization on the liquid surface. These plasmas activate the water and provide not only high temperature for pyrolysis but also a reservoir of reactive species to facilitate depolymerization. The duration of actual testing is not expected to exceed one month but the tests will be spread out over the course of a year depending on facility availability as well as post processing which will occur at Michigan. The post processing involves more detailed chemical analysis of the treated samples (mass spec) as well as in-house optimization of the source based on initial tests which includes critical steps such as sample extraction, drying and preparation for analysis at the PPPL PCRF. Here further tests of plasma treated samples will be carried out assess the impacts of the pretreatment carried out at Michigan and to clearly identify fragments.

i) The experimental apparatus that will be brought to PPPL includes a plasma source reactor, the power supply, the Faraday cage, and the polymer target. The apparatus is relatively compact, with a footprint of approximately 7.5 cm and a height of approximately 15 cm. The mass of the apparatus is roughly 450 grams. The input power is ns pulsed power supply (brought up with reactor). The device operates at atmospheric pressure and uses air or argon as the feedstock gas.

In situ diagnostics at PPPL

Two measurements are of interest. We will be carrying out resolved, optical emission spectroscopy sweep to obtain spectra that will allow for post processing to yield insight on 1) plasma density via Stark broadening of hydrogen lines, 2) gas temperature via either Raleigh scattering or from nitrogen rotational spectra and 3) gas phase species emitting in the visible obtained via a broadband OES survey. We would like to study the mass spectra associated with the decomposition products in the gas outflow using the FTIR spectrograph (JASCO-FTIR 660+).

We will use HRS 750 SpectraPro spectrometer coupled with PIMAX 3 iCCD camera for OES diagnostics. The spectrometer is equipped with 3 different gratings to measure broadband and high-resolution spectra.

The apparatus itself is relatively portable. We will bring the apparatus and power supply. At Michigan we will prepare suitable shielding and optimize the pin to polymer discharge before coming to PPPL. Optical

emission spectroscopy and FTIR will be carried out at PPPL. Post processing of OES can be carried out at the university.

The proposed project is of one year duration. The project will be carried out in two phases. In phase one preliminary data will be obtained to study the effect of plasma liquid processes such as self organization, induced fluid flow and droplet emission on depolymerization as inferred from mass spectrum analysis and SEM here at Michigan. During this time the apparatus will also be optimized to support the second phase of activity which involves making in situ depolymerization measurements at PPPL with pulsed discharge.

Technical Accomplishments

The self-organized plasma discharge with liquid anode was tested with various plastic powders. This approach while providing required temperature and densities. It was found however that this discharge type compatible with the diagnostics at PPPL so in situ testing would not be possible with FTIR system. Instead, the interaction of the pattern plasma with low density plastics was investigated. One issue with the discharge was the limited circulation of the powders into the active reaction zone. The self organized flows kept surface powders away from the plasma zone. While surfactants aided into the mixing, the chemical constituents associated with the surfactants were problematic in that plasma activity with them yielded products unrelated to plasma depolymerization. The experiments however did identify the droplet formation –a critical mass transport mechanism. Here droplets are formed by gases breaking the interface leading to mass from the liquid phase entering the hot plasma. Via this vehicle, microplastics can also be introduced into the plasma. The accomplishment of this work included 1) verification of droplet formation 2) verification of mass transport of liquid phase species into the gas phase as inferred by emission spectra and 3) droplet size distribution matched very well model of gas breaking through the interface as can be seen in figure 8. This observation was exciting in that it yielded another mechanism for the introduction of plastics into the hot plasma. Details of droplet formation and implications for discharge dynamics has been published.[xiii] This mechanism is clearly promising. The next step is to engineer a better way to get the plastic into the surface plasma. An alternative method was devised during this work however. Here via forced bubbling, one could induce droplets that would then enter the gas phase and thus be treated by the plasma. This method worked well—future work will involve coupling the gas phase products to a gas chromatograph.

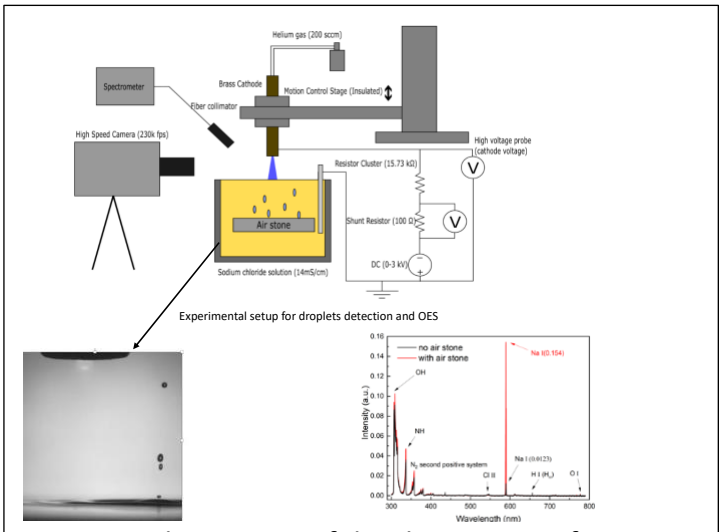

Figure 8. Observation of droplet emission from discharge with liquid anode. Droplet distribution and observed emission of vaporizing droplets verified new transport mechanism.

As proposed, to study plasma polymer interactions in the gas phase a fluidized plastics particle bed was utilized. In this manner the fluidized bed provided a vehicle to disperse the plastic powder into the self-organizing spark discharges. Here the plasma source was essentially a pulsed corona jet as proposed for the PPPL experiments. The fluid-like circulation recirculated the powder through the active plasma zones This set up was compatible with the PPPL FTIR diagnostic in that the water signal could be eliminated so that depolymerization phenomena could be observed.

Accomplishments: Summary of PPPL fluidized bed experiments:

The goal of the PPPL experiments was to identify depolymerization products and to understand how plasma conditions including feed gas mixtures impact monomer formation. Figure 9 illustrates discharge operation and measured depolymerization products. An observational study of a nonthermal plasma reactor used for decomposing polymer powders into light hydrocarbon species was been carried out. While nonthermal plasma hydrogenolysis has been accomplished in the past, this was the first study to concurrently measure plasma discharge properties along with gaseous products and the modifications apparent in the solid remnants. Important observations of this work include 1) the need for a thermal component of the plasma to produce gaseous products, which included measurable amounts of methane, acetylene, and ethylene, other impurities, and likely hydrogen. 2) It was also observed that hydrogenolysis plays an important role for polymer decomposition. LDPE had the largest gas production and a significant breakup of polymer chains (as observed in the residual solid product), likely owing to its low melting point and ease of vaporization, though all polymers tested produced some hydrocarbons. 3) The rotational, vibrational, and electron temperature, as well as the electron density, of the atmospheric pressure spark discharge were similar to those found in the literature, and did not change substantially with either gas composition or polymer composition thus exposing each plastic type to the statistically similar plasma conditions. The research paints a coherent conceptual picture of the active plasma processes including the decomposition of hydrogen molecules, currents and heating of the surface, and the resulting gas products and the related changes in polymer structure and composition.

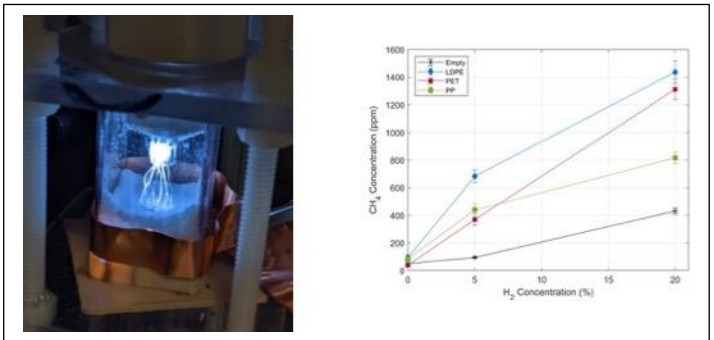

Figure 9. Depiction of fluidized bed pulsed discharge along with depolymerization driven by plasma as a function of hydrogen concentration.

The data suggest that localized flash heating is critical for depolymerization. In this respect either in situ FTIR capabilities or a power supply capable of higher power density should be used to fully understand the role of the thermal discharge mechanism and improve heat transfer around the powder. The frequency parameter-space should also be explored to understand the role of metastable species and gas composition in promoting the discharge location and attachment. Metastables may play a key role in achieving branching which suggests better contact area with plastic aggregate. A sensitivity study of the role of hydrogen in conjunction with localized heating is suggested in this work. These two effects are synergistic in regards to depolymerization. Overall this work suggests nonthermal plasma may be useful to up-convert plastics into useful end products, but there is still significantly more parameter space to explore to find the right combination of plasma characteristics, residence time, and selectivity of end products. A key consideration however is managing the stochastic nature of the sparks both spatially and in time as well as increasing overall streamer density for larger treatment mass.

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