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Fused Filament Fabrication of Polymer Blends with *in situ* Layerwise Chemical Modifications

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Abstract

The layerwise paradigm of additive manufacturing advertises voxel level control over both geometry and material properties of parts but the latter is difficult to achieve. Recently the Savannah River National Laboratory has demonstrated a new technique for voxel level material property control via layerwise surface chemical modification of polycarbonate homopolymer by UV ozone during manufacturing. This technique can be utilized to modify each respective phase of a polymer blend feedstock to become more similar in preparation for potential *in situ* co-polymer formation by a further modification. Successful creation of co-polymers during manufacturing could allow for further voxel level material property control than modification of a homopolymer could allow. Test feedstock comprised of melt mixed polycarbonate and polystyrene homopolymers, an immiscible polymer blend, were printed in an atmosphere containing ozone. FTIR measurements indicate both phases of the blend may be modified simultaneously to form new oxygen functional groups, increasing chemical similarity. Calorimetric and thermomechanical analysis show no indication of increased mixing, crosslinking or co-polymer formation due to the treatment. Uniaxial tension to failure experiments demonstrate minimal loss of mechanical properties as the blend incompatibility dominates. Future work will focus on understanding the complex relationships between configurable processing parameters (layer height, print speed, temperature, etc), reaction site creation density, and blend degradation prior to further modification.

Introduction

Additive manufacturing (AM) promises voxel level control over both geometry and material properties; however, the latter is difficult to achieve. Recently, the Savannah River National laboratory (SRNL) has demonstrated a new, uniquely AM approach to voxel level material property control via *in situ* layer by layer surface chemical modifications during manufacture by a reactive atmosphere. The surfaces of deposited bisphenol(A) polycarbonate (BPA-PC) layers during Fused Filament Fabrication (FFF) AM were continuously modified by UV/ozone treatments. Mechanical property changes were observed as a result of the treatment during uniaxial tension to failure testing as UV/ozone modified BPA-PC dog bone samples' elastic modulus increased ~26% on average while the elongation at failure decreased by ~21% on average relative to pristine, unmodified BPA-PC dog bones. A density functional theory simulation of the reaction between UV/ozone and BPA-PC in the melt state predicted aromatic epoxides and methoxyls would be added to the BPA-PC backbone as the dominant reactions while also causing chain cleavage. Predicted chemical modifications were confirmed by UV/Vis and FTIR characterization of the printed samples, validating the addition of oxygen functional groups to the BPA-PC backbone during manufacturing. This technique could be extended to immiscible blended polymer feedstocks such that each phase of the blend could be modified *in situ* to increase chemical similarity and affect further material property control than *in situ* modified homopolymer feedstock alone could allow.

Blended polymer feedstocks have been successfully processed by multiple AM modalities such as FFF or laser powder bed fusion (L-PBF) to produce parts[1-4]. Traditionally, blended polymer feedstocks have enabled parts to have tunable mechanical, thermal and chemical properties that are difficult or impossible to achieve with commercially available homopolymer feedstock and could bring the same advantages to AM parts. However, a multi-step process is generally required for blended feedstocks to achieve the desired performance as many blends are thermodynamically immiscible and exhibit high interfacial tension which results in poor mechanical performance. Often, compatibilizers, which include block or graft co-polymers, or other chemical modifiers must be produced and then added during melt processing of the blend to decrease the polymer A-polymer B interfacial tension and improve polymer dispersion prior to manufacturing[5].

The creation of co-polymers during additive manufacturing could increase part design flexibility and improve property control at the voxel level. As a strategy, polymer blends may be additively manufactured inside an atmosphere containing reactive process gas such as ozone or ammonia to populate each respective phase of the blend with similar or identical functional groups which could then be utilized as common reactive sites for further modification. Conceivably, a third component could then be introduced either as a liquid phase reactant or as a second gas phase reactant to crosslink the new functional groups added to each phase of the blend to form co-polymers. This strategy, if successful, could be a cost effective, one step method to create co-polymers that is applicable to many polymer blend formulas as ozone and ammonia are known to react with many types of polymers[6].

In this manuscript, the authors describe the first test case of a blended polymer feedstock additively manufactured in a reactive atmosphere which contains ozone. The test case feedstock is a filament comprised of a 50/50 weight percent ratio of melt mixed Bisphenol(A)-polycarbonate and polystyrene (BPA-PC/PS), an immiscible polymeric blend[7]. The modification of both BPA-PC and PS homopolymer surfaces by ozone treatment has been extensively studied. Each respective polymer backbone forms new oxygen functional groups at similar treatment conditions and timescales. The new oxygen functional groups created are attributed to include carbonyls, hydroxyls, peroxides, carboxylic acids, etc[8-10].

For the remainder of this manuscript, we will first discuss our sample production and characterization methodologies and then the results. An *ex vivo* polymer- process gas reaction study setup in a FTIR spectrometer was used to understand both the chemical modifications of the (BPA-PC/PS) blend and respective homopolymers and timescales of the reactions at manufacturing conditions. Dynamic mechanical analysis (DMA) and differential scanning calorimetry (DSC) were used to study thermomechanical and calorimetric changes between the modified and unmodified blended samples. Finally, uniaxial tension to failure experiments were performed to characterize the mechanical performance of both the modified and unmodified blended samples.

Methods

Filament Preparation

3DX max polycarbonate and polystyrene pellets were purchased from 3DXTech and Sigma Aldrich respectively. Pellets were first dried at 80 °C in a vacuum prior to processing. The dried pellets were mixed as a 50/50 weight fraction and extruded by Leistritz ZSE 18. The cooled melt mixed extrusion was pelletized for re-extrusion by a Filabot EX2 configured with a 3.0 mm 3X extended melt nozzle. Melt mixed pellets were re-extruded into 2.85 mm filament at 245 °C and 85% extrusion speed.

Printer Modifications

Printing of all samples was performed by a stock Ultimaker 2+ Connect configured with an enclosure kit provided by Matter Hackers. Two VMUS-4 ozone generators injected ozone at the point of deposition and was measured to be .9 wt% by a UV-106H ozone analyzer at a flow rate of 2.6-2.8 slpm. Dry air was supplied to the ozone generator via in-line desiccant. Ozone flow was initiated at the start of each print.

Printed Sample Preparation

All samples were printed with the following parameters:

Print Speed	7 $mm.sec^{-1}$
Bed Temperature	90 °C
Nozzle Temperature	260 °C
Layer Height	200 µm
Ozone Concentration (Modified Only)	.9 wt%
Ozone flow (Modified Only)	6.0-6.4 slpm

Table 1: Printed Sample Manufacturing Parameters

FTIR

FTIR intensity measurements of the reaction between filament samples of BPA-PC, PS, and BPA-PC and ozone in time were performed in a Harrick Praying Mantis Diffuse Reflectance Infrared Spectroscopy (DRIFTS) FTIR accessory outfit with the high temperature reaction chamber was setup in a Jasco 6300 series FTIR spectrometer. A 6.35 mm x 6 mm cylinder of steel was placed inside of the reaction cup and covered with aluminum foil for filament placement, heat transfer, and ease of sample cleanup. The high temperature reaction chamber dome was outfit with

100μm thick CVD diamond windows supplied by Applied Diamond in the IR transmission slots. A time series of measurements were made every ~37 s. Configurable parameters of the spectrometer were set according to Table 2. All other parameters were set as default/auto. Filament samples were manually roughed by 80 grit sandpaper prior to placement in the high temperature reaction chamber to encourage diffuse reflectance as opposed to specular reflectance.

Scan Speed	.25 mm.sec^{-1}
Scans	3
Interval Time	40 s
Wavenumber Resolution	4 cm^{-1}
Aperture	7.1 mm

Table 2 Jasco 6300 FTIR Configurable Parameters for DRIFTS FTIR

FTIR measurements of DMA printed samples were performed in ATR-IR mode with all settings set to default/auto apart from setting the number of scans to 16.

DSC

Calorimetric characterization by differential scanning calorimetry of printed modified and unmodified BPA-PC/PS cylindrical samples of target dimensions 10 mm x 3.2 mm were performed on a Mettler Toledo DSC 3+ differential scanning calorimeter (DSC). Samples were heated at a ramp rate of 10 °C /min from 0 to 250 °C "as printed". The glass transition temperature for all samples was calculated by using the midpoint method in the Mettler Toledo STARe evaluation software.

DMA

Thermomechanical characterization by dynamic mechanical analysis of printed modified and unmodified BPA-PC/PS blend samples was performed on a Mettler Toledo DMA/SDTA 1+ in shear mode. Cylindrical samples of target dimensions 10 mm x 3.2 mm were clamped with 6 in.-lbf of torque and were sheared in oscillation at 1, 10, 100, and 200 Hz. Samples were heated from 70 to 170 °C at a ramp rate of 1 °C min^{-1}. The Mettler Toledo DMA/SDTA 1+ operates in hybrid force/displacement control where one oscillatory cycle is completed either by reaching 20N of force or .1 μm of displacement.

Tensile Testing

ASTM D638-14 Type V specification dog bone specimens with grips modified to 12mm in length were prepared for tensile testing. The specimens were printed in both the XY and Z planes. Samples were printed both in air and in an atmosphere containing ozone. A MTS Deben Microtest set to a crosshead speed of 0.5 mm.sec^{-1} was used to perform uniaxial tension to failure testing.

Results

BPA-PC, PS, and BPA-PC/PS filament were monitored for IR spectral changes over time while at expected processing temperature (90 °C) both with and without ozone exposure, Figure 1. All three filament types exhibit no measurable spectral changes after 10 minutes without ozone exposure as expected. Ozone treatment causes changes for all 3 sample types in oxygen containing regions of the spectrum. PS, which contains no oxygen atoms inherently in its backbone, exhibits new, strong peak growth at 1745 cm^{-1} indicating the addition of C=O bonds which is suggestive of carbonyl or carboxylic acid formation as well as small peak growth at 1670 cm^{-1} which could indicate aromatic epoxidation in a similar manner to BPA-PC ozone modification reported by Baker, et al. The growth of these peaks is measurable after 40 s of exposure and likely begins as soon as ozone exposure begins, but changes subside after 80 s of exposure. The formation of C=O bonds on the PS backbone increases chemical similarity with BPA-PC which inherently possesses C=O bonds owed to carbonate groups on the backbone. The addition of carboxylic acids and/or carbonyls would be expected to interfere with normal chain alignment to affect an increase in free volume leading to a reduction in the glass transition temperature. BPA-PC exhibits minimal but measurable spectral changes after ozone exposure. A small peak growth at 1670 cm^{-1} as well as a decrease in peak intensity at 3050 cm^{-1}, is observed. It is interesting to note that FTIR spectra reported by Baker, et al. in ATR-IR mode showed no peak growth at 1670 cm^{-1} but instead showed asymmetric broadening of the 1770 cm^{-1} peak towards lower wavenumbers. The changes in BPA-PC spectra observed after ozone modification during DRIFTS FTIR measurements vs ATR-IR mode track even stronger with simulated IR spectra expectations of aromatic epoxide formation discussed by Baker, et al. Changes in BPA-PC spectra subside after 80 s of ozone exposure as well. Improved temporal resolution is needed to precisely understand the kinetics of the oxygen functional group formation on each respective polymer. However, the timescale of reaction propagation observed is well within typical additive manufacturing layer durations.

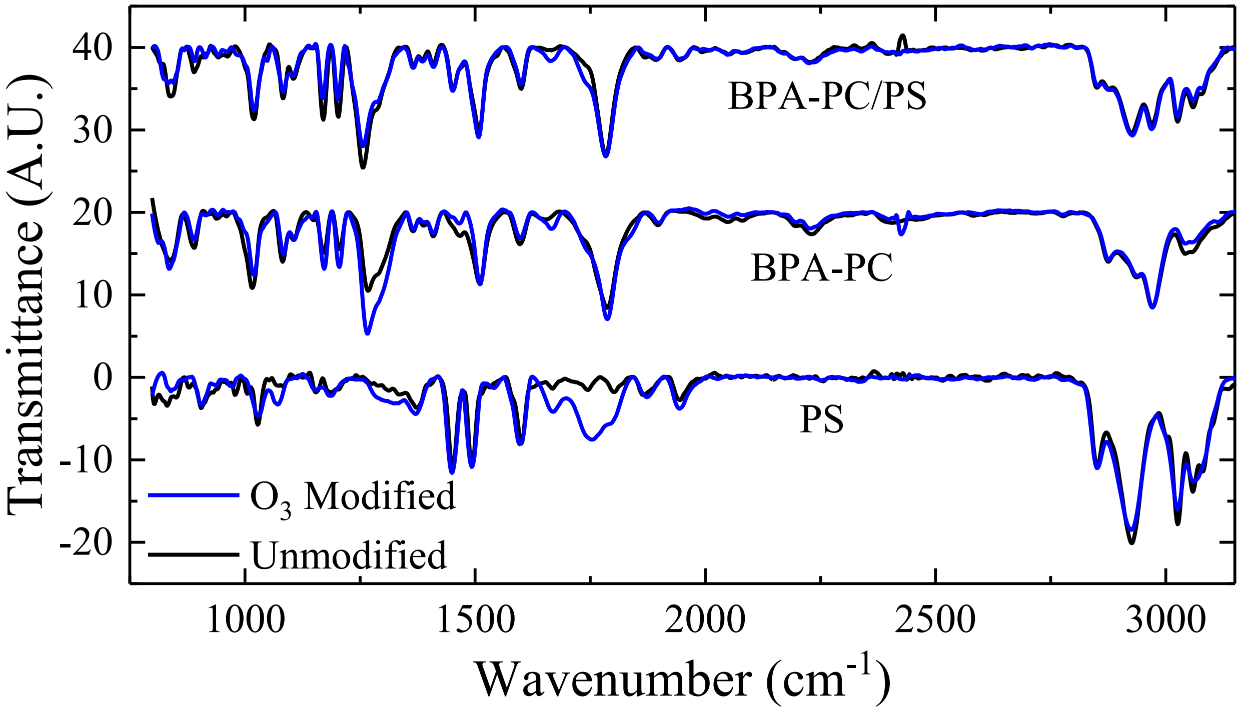

FIGURE 1: IR spectra of filament samples of Polystyrene (PS), Bisphenol(A)-Polycarbonate (BPA-PC) and BPA-PC/PS melt mixed blends at 90 °C modified by ozone in a Harrick Praying Mantis DRIFTS Accessory

IR spectra of the unmodified melt mixed BPA-PC/PS blended samples exhibit characteristic peaks uncommon to both homopolymers at wavenumbers 1452 cm^{-1} and 1787 cm^{-1} attributed respectively to aromatic C=C stretching in PS and C=O stretching from carbonate ester in BPA-PC indicating chains of both polymer phases are present at the surface and available for modification[10, 11]. Spectral changes of BPA-PC/PS after ozone treatment indicate each respective phase of the blend is modified simultaneously. Asymmetric broadening at the lower wavenumber side the 1787 cm^{-1} peak is observed in BPA-PC/PS blended samples but not observed in BPA-PC homopolymer samples. This broadening is attributed to the new C=O bond formation observed in PS homopolymers at 1745 cm^{-1}. Peak growth at 1670 cm^{-1} which was observed for both BPA-PC and PS samples alike was also observed in BPA-PC/PS blended samples, while a slight decrease at 3050 cm^{-1} is observed similarly for BPA-PC homopolymer modification.

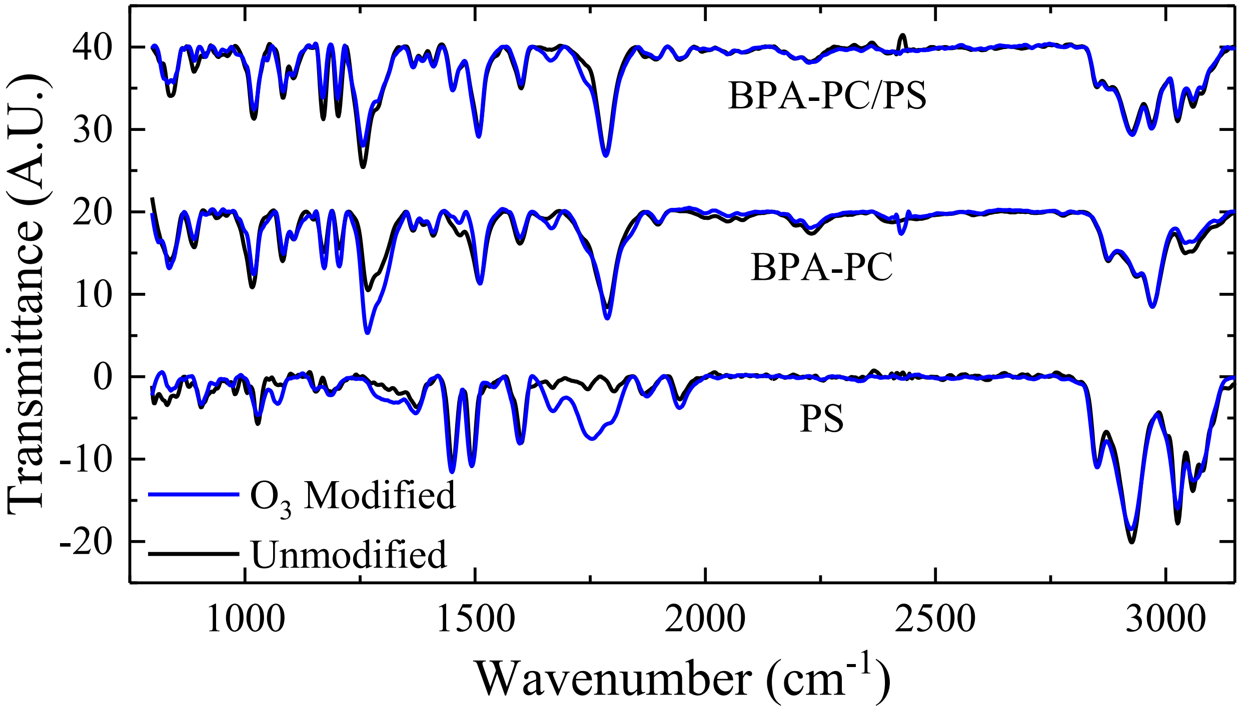

Figure 2 Placeholder Figure IR Spectra of printed and filament feedstock BPA-PC/PS ozone modified and unmodified samples

Printed samples IR spectra were characterized in ATR-IR mode due to poor data quality collected by the Praying Mantis DRIFTS accessory as the relatively smooth surface finish increases specular reflectance that dominates the signal, Figure 2. Modified and unmodified printed samples were compared to samples modified in the reaction chamber of the Praying Mantis DRIFTS accessory and exhibit similar spectral features. Similar to the filament samples of BPA-PC/PS unmodified BPA-PC/PS printed samples exhibit peaks uncommon to both polymers at wavenumbers 1452 cm^{-1} and 1770 cm^{-1} indicating both phases of the blend are present at the surface and available for modification alleviating concerns of possible skinning affects. Printed modified BPA-PC/PS spectra are very similar to modified BPA-PC/PS filament spectra in the regions 1650 cm^{-1} to 1800 cm^{-1} confirming both polymer phases have oxygen functional groups populated during manufacturing.

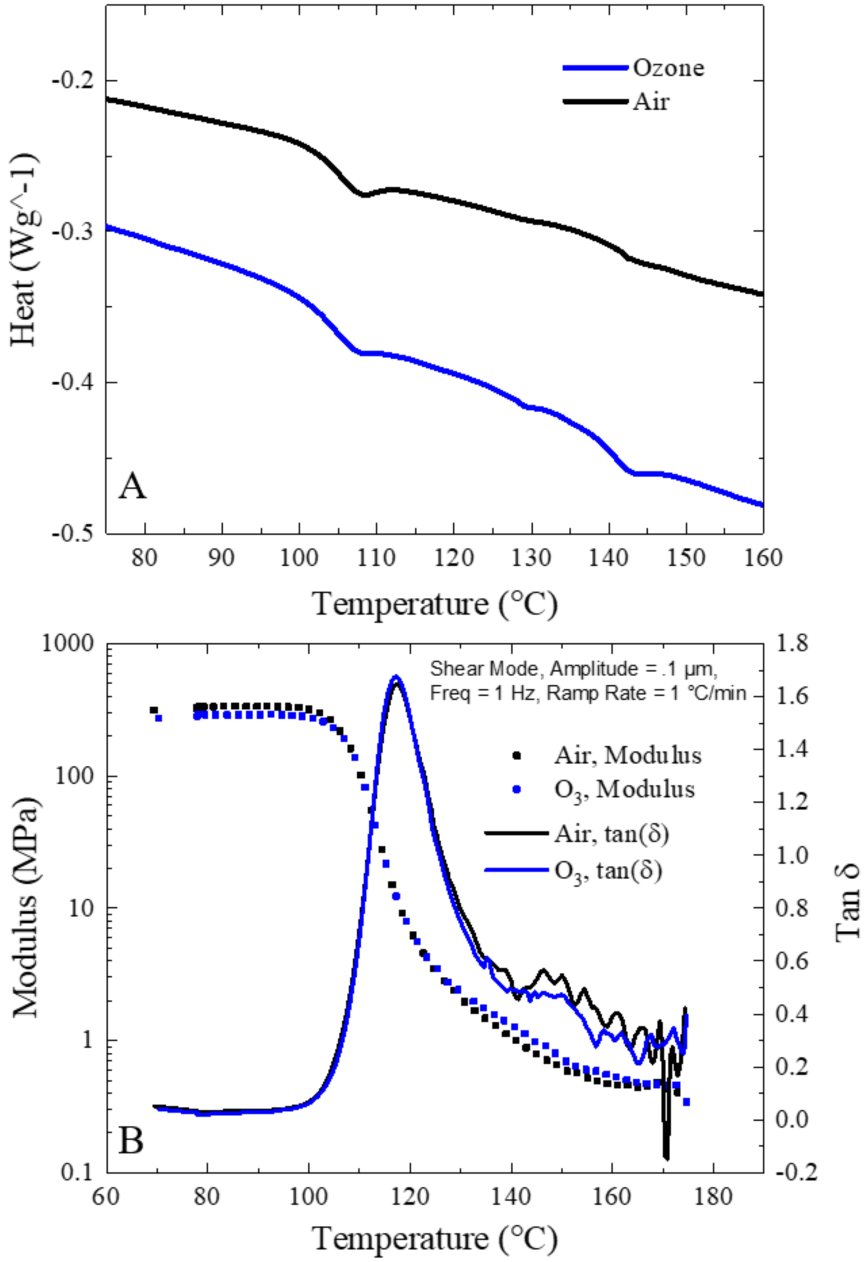

Figure 3 A) Calorimetric and B) Thermomechanical analysis of both unmodified and ozone modified printed samples

	Ta (°C)		Tb (°C)	
Method	Modified	Unmodified	Modified	Unmodified
DSC	108	109	143	143
DMA	117.24	117.48	N/A	N/A

TABLE 3 Summary of calorimetric and thermomechanical testing results

Despite chemical modification to each phase of the blend, minimal changes are observed in both calorimetric and thermomechanical analysis between ozone modified and unmodified BPA-PC/PS printed samples, Figure 3. Calorimetric characterization of unmodified printed samples shows two endotherms at 108 °C and 145 °C corresponding to the glass transition temperature (Tg) of the PS and BPA-PC phases respectively. However, thermomechanical characterization of the unmodified printed samples displays a single peak at 117 °C corresponding to the polystyrene phase Tg. Mechanical rigidity is lost after heating past the Tg of polystyrene and therefore masks the polycarbonate phase resulting in thermal behavior similar to a homopolymer. No significant changes in Tg or the onset of Tg are observed for either phase regardless of the characterization method employed due to ozone modification. This suggests that minimal if any chain cleavage has occurred in either phase which would otherwise be expected to shift the Tg or the onset of Tg towards cooler temperatures. No significant changes in morphology of the blend are observed as a result of ozone modification as the percent crystallinity of each phase is unchanged and there is no evidence of either intra or interphase crosslinks being formed. Considering both calorimetric and thermomechanical characterization of modified BPA-PC/PS, there are no strong indicators of increased compatibilization or co-polymer formation occurring due to the treatment. If this was the case, new peaks which are an average of the thermal properties of both phases or shifting of endotherms closer together would be expected to occur.

Ozone is well known to rapidly accelerate polymer degradation by chain cleavage and other oxidative processes which leads to a significant loss of mechanical properties[6]. In simulations of BPA-PC and ozone reactions performed by Baker, et al, chain cleavage is expected to occur at site 6:7 C-O bond though it is less probable than methoxylation and aromatic epoxidation. This reaction can account for the decrease in strain at failure observed in ozone modified BPA-PC printed samples and a similar mechanism of action is likely to occur in PS as well. Therefore, a careful balance must be struck when increasing the density of potential reaction sites as polymer degradation may be commensurately increased. Too much polymer degradation prior to phase-to-phase crosslinking through further modification could mitigate the benefits of *in situ* co-polymer formation.

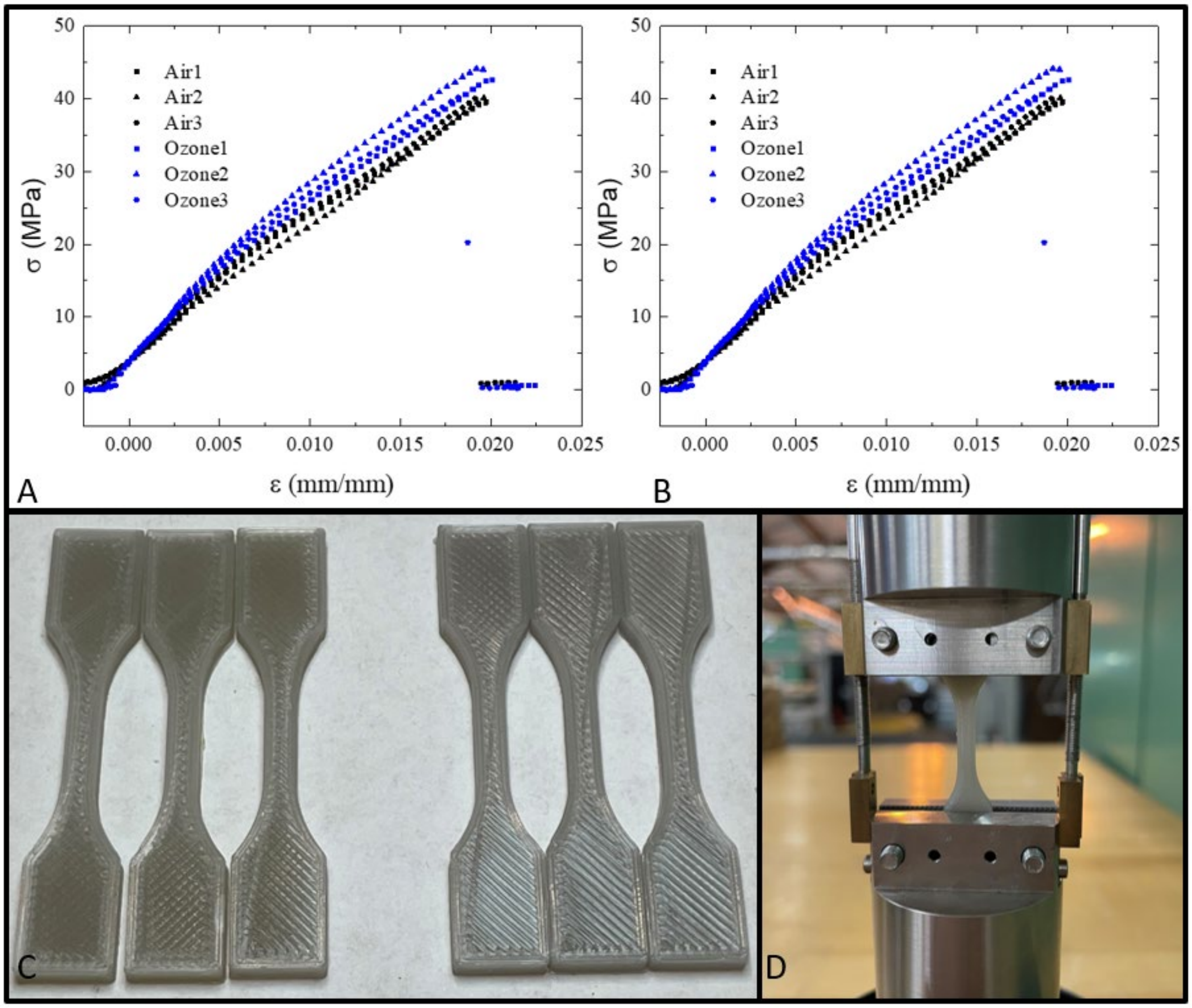

Figure 4 Tensile testing of unmodified and ozone modified BPA-PC/PS printed dog bone blends blends in the A) XY and B) (Placeholder) Z directions. Photographs of C) ozone modified (left) and unmodified (right) xy tensile bars and D) Xy tensile bars loaded into the MTS Deben Microtest

To begin understanding the effects of ozone pretreatment on the BPA-PCPS blend mechanical properties, ozone modified and unmodified BPA-PC/PS ASTM D638-14 type V tensile specimens were printed in both the XY and Z orientations. Specimens were then elongated to failure in uniaxial tension. Both modified and unmodified specimens exhibit brittle failure modes in both the XY and Z orientations with minimal material yield prior to failure as is typical in uncompatibilized BPA-PC/PS blends (Cite). XY orientation dog bone specimens' ultimate tensile strength is slightly increased from **38.84** MPa +/- **1.55** to **42.35** MPa +/- **1.48** while strain at failure is decreased from **.0238** +/- **.003** to **.0221** +/- **.001.** This suggests that the phase to phase interfacial properties of the blend continue to dominate the performance after this level of chemical modification. This is not surprising when considering the calorimetric and thermomechanical characterization indicated no changes in blend morphology or compatibility. Significant changes in the blend performance will likely not be observed until phase to phase crosslinks are intentionally created by a second chemical modifier is introduced.

Specimen Type	Print Orientation	Ultimate Tensile Strength (MPa)	Strain at Failure(mm/mm)
Ozone	XY	**42.35** +/- **1.48**	**.0221** +/- **.001**
Air	XY	**38.84** +/- **1.55**	**.0242** +/- **.003**

TABLE 4: Summary of Tensile Testing Results

Summary and Future Work

As this work demonstrates, oxygen functional groups may be simultaneously populated onto each respective phase of BPA-PC/PS blends by ozone surface treatments during additive manufacturing. *Ex vivo* reaction studies of the interaction of ozone with BPA-PC and PS homopolymers as well as the BPA-PC/PS blend show changes in oxygen regions of IR spectra which conclude after 80 s of treatment. PS forms a new, strong peak at 1745 cm^{-1} indicating new C=O bond formation, an increase in chemical similarity to BPA-PC. Calorimetric characterization of samples by DSC and thermomechanical testing by dynamic mechanical analysis show no strong indicators of increased interphase mixing or interphase crosslinking occur as a result of the modification. Mechanical testing to failure shows that the treatment does not have a significant impact on mechanical properties as ultimate tensile strength and strain at failure are largely unchanged in ozone treated dog bone specimens. In consideration of the thermomechanical data collected by DMA, tensile properties uniaxial tensile testing to failure and calorimetric analysis by DSC together, there are no indicators of increased blend compatibilization. However, the preparation of additively manufactured polymer blend surfaces by ozone to create oxygen functional groups on each respective phase of the blend could allow for further modification that leads to co-polymer formation. The newly formed functional groups represent potential common reaction sites populated on each respective phase of the blend. It will be critical to further understand the affects of the gaseous pretreatment on the blend as there will be complex relationships between configurable processing parameters (layer height, print speed, temperature, etc), reaction site creation density, and blend degradation. A balance must be considered between reaction site density and commensurate polymer degradation.

A second gas phase reactant or a liquid phase reactant that could crosslink the new oxygen functional groups on each polymer phase will be identified such that co-polymers could be formed *in situ.* Further DFT simulations of PS and ozone will be performed to understand the most probable reaction pathways and precisely identify the functional groups added to the backbone. As it is likely this second reactant will contain nitrogen groups and be in the liquid phase. A hybrid FFF/Inkjet system will be used to further this work such that gaseous and liquid reagents may be used simultaneously to crosslink dissimilar polymers *in situ*. Additional fundamental studies will focus on characterizing the interaction of liquid reagents with the process gas pretreated surface.

Critical phenomena to understand will include surface wettability, length scale of liquid reagent penetration and rheological characteristics of the liquid reagent for jetting control.

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