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 although 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 with UV and ozone during manufacturing. This technique can be utilized to modify each respective phase of a blended polymer feedstock to increase chemical similarity in preparation for potential *in situ* interphase crosslinking. Successful crosslinking of dissimilar 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 and UV light. FTIR measurements indicate both phases of the blend may be modified simultaneously *in situ* to form new oxygen functional groups, increasing chemical similarity. Calorimetric and thermomechanical characterization show no indicators of increased compatibilization due to the treatment. Uniaxial tension to failure experiments demonstrates minimal loss of mechanical properties as the blend phase to phase interfacial properties dominates the behavior despite the chemical modifications. 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 while identifying a suitable crosslinker to improve mechanical and thermal properties of the blend.

Introduction

Additive manufacturing (AM) advertises voxel level control over both geometry and material properties although, 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* layerwise surface chemical modifications during manufacture by a reactive atmosphere which is detailed in the authors' previous work. Surfaces of deposited bisphenol(A) polycarbonate (BPA-PC) layers during Fused Filament Fabrication (FFF) AM were

continuously modified by UV/ozone treatment. Mechanical property changes were observed as a result of the treatment during uniaxial tension to failure testing as UV/ozone modified BPA-PC dogbone samples' elastic modulus increased ~26% on average while the strain at failure decreased by ~21% on average relative to pristine, unmodified BPA-PC dogbones. A series of density functional theory (DFT) simulations of 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 with chain cleavage predicted to be a less probable but additional reaction. 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[1]. 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 allow 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[2-5]. 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 to prepare blended feedstocks prior to manufacturing 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 manufactured and then added during melt processing of the blend to decrease the polymer A-polymer B interfacial tension and improve polymer dispersion to achieve the desired performance [6].

In situ crosslinking of dissimilar polymers during additive manufacturing could increase immiscible polymer blend compatibility and potentially improve material property control at the voxel level allowing for further design flexibility. As a strategy, immiscible 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 oxygen functional groups such as carbonyls, hydroxyls, and epoxies which could be utilized as common reactive sites for further modification. Conceivably, a second chemical modifier 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. Perryman and Dadmun employed a similar strategy to minimize the mechanical anisotropy of additively manufactured homopolymer feedstock. An FFF machine was adapted to spray multi-amines on the surfaces of deposited ABS which readily oxidizes in air above 100 °C. The multi-amines react with the oxidized functional groups to form new covalent bonds which crosslinks the polymer chains located at process induced interfaces resulting in improved fracture energy in the Z-direction [7]. If successful, the strategy outlined above for *in situ* polymer blend crosslinking could be a cost effective, one step method to create compatibilized polymer blend parts that is applicable to many feedstock formulas as ozone and ammonia are known to react with many types of polymers [8].

In this manuscript, the authors describe the first test case of a blended polymer feedstock additively manufactured in a reactive atmosphere which contains ozone and UV light. 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 [9]. The modification of both BPA-PC and PS homopolymer surfaces in the solid state by ozone and UV light treatment has been extensively studied. Each respective polymer forms new oxygen functional groups at similar treatment conditions and timescales. The new oxygen functional groups created are attributed to include carbonyls, hydroxyls, etc. [10-12].

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 was setup in an 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 oven prior to processing. The dried pellets were mixed as a 50/50 weight fraction and extruded by a 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 Ultimaker 2+ Connect configured with an enclosure kit purchased from Matter Hackers. Two VMUS-4 ozone generators supplied ozone at the point of deposition and was measured to be a concentration of 0.9 wt% with a UV-106H ozone analyzer at a flow rate of 6-6.4 SLPM total. Dry air was supplied to the ozone generators via in-line desiccant. Ozone flow was initiated at the start of each print. Two 100 W Everbeam UV lights with a center wavelength of 370 nm illuminated the print bed with a power density of 5 mW/cm^2.

Printed Sample Preparation

All samples were printed with the following parameters in Table 1:

Print Speed	7 mm s^{-1}
Bed Temperature	90 °C
Nozzle Temperature	260 °C
Layer Height	200 μm
Ozone Concentration (Modified Only)	0.9 wt%
Ozone flow (Modified Only)	6.0-6.4 slpm

Table 1: Printed Sample Manufacturing Parameters

Fourier-transform infrared (FTIR) spectroscopy

      FTIR intensity measurements of the reaction between filament samples of BPA-PC, PS, and BPA-PC/PS 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 and setup in a Jasco 6300 series FTIR spectrometer. A 6.35 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 100 μm thick CVD diamond windows purchased from Applied Diamond in the IR transmission slots. A time series of measurements were made every 40 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	0.25 mm s^{-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

ATR-IR FTIR measurements of printed and filament samples were performed with all settings set to default/auto apart from setting the number of scans to 16 in the same Jasco 6300 series FTIR spectrometer.

Differential scanning calorimetry (DSC)

      Calorimetric characterization by differential scanning calorimetry of sections cut from 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.

Dynamic mechanical analysis (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 20 N of force or 0.1 μm of displacement.

Tensile testing

ASTM D638-14 Type V specification dogbone specimens with grips modified to 12 mm in length were prepared for tensile testing[13]. The specimens were printed in the XY orientation. Samples were printed both in air and in an atmosphere containing ozone and UV light. A MTS Deben Microtest set to a crosshead speed of 0.5 mm s^{-1} was used to perform uniaxial tension to failure testing.

Results and Discussion

Spectroscopic confirmation of in situ chemical modification

BPA-PC, PS, and BPA-PC/PS filaments were monitored for chemical modification by DRIFTS IR over time while at expected processing temperature (90 °C) both with and without ozone exposure, Figure 1,2. 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 regions of the IR 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 aldehyde formation. A small peak growth at 1670 cm^{-1}, a
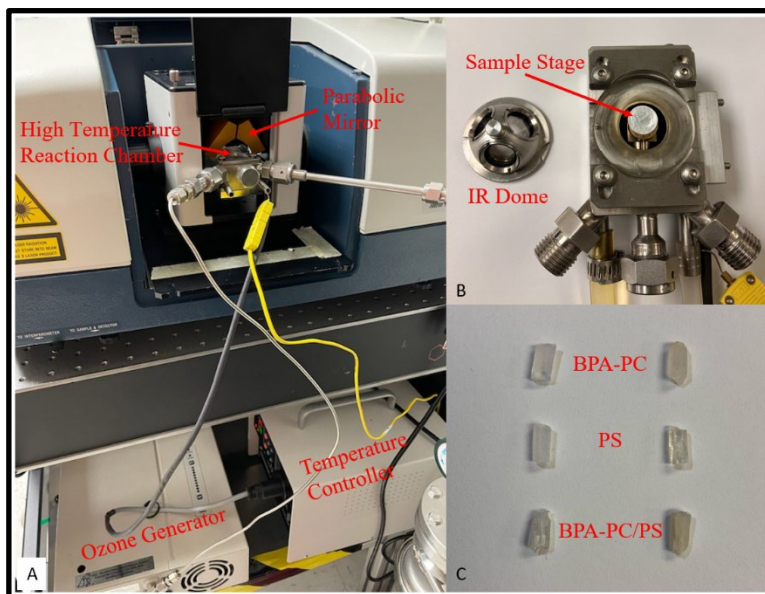

Figure 1 Photographs of A) Praying Mantis DRIFTS IR setup B) Praying Mantis high temperature Reaction Chamber and C) Unmodified(left) and ozone modified(right) filaments

change in C=C stretching, and flattening of peaks at 3058 cm^{-1} and 3080 cm^{-1} in the C-H regions are also observed. 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. BPA-PC exhibits minimal but

measurable spectral changes after ozone exposure as a small peak growth at 1670 cm^{-1} as well as a decrease in peak intensity at 3050 cm^{-1}, is observed. 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.
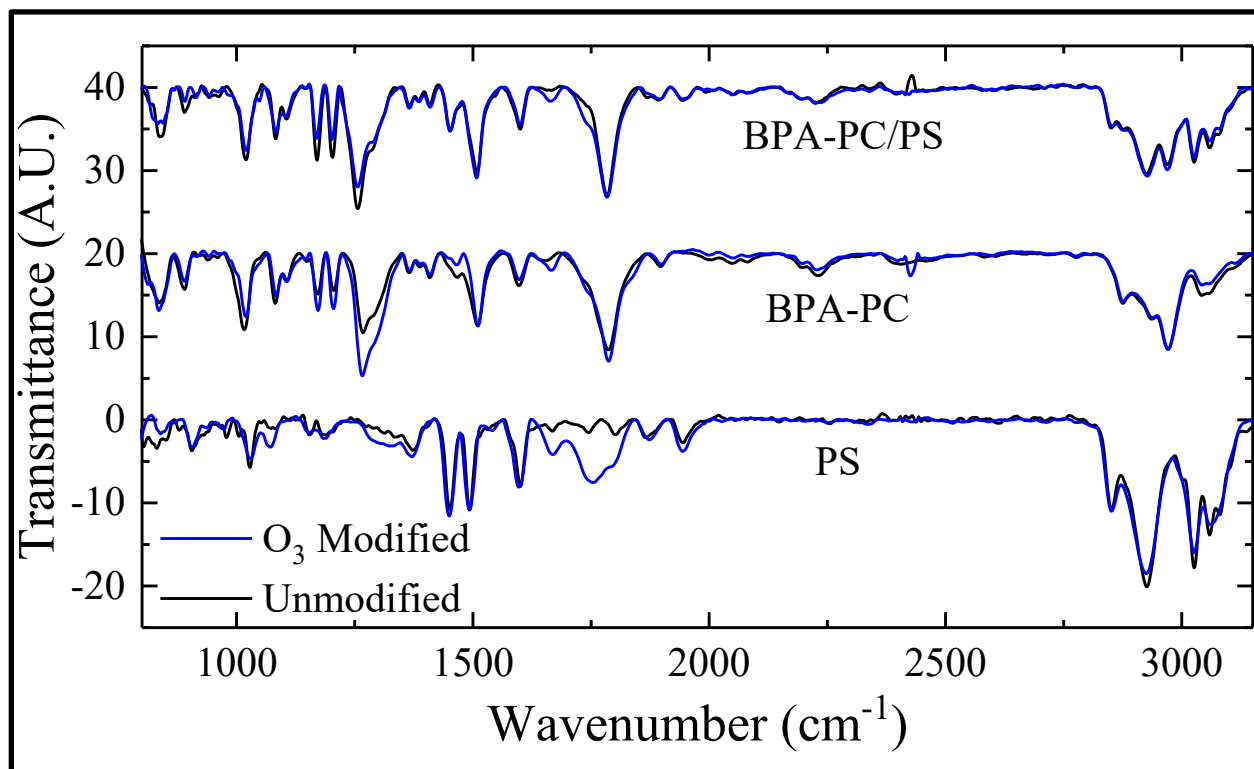

Figure 2: DRIFTS IR spectra of PS, BPA-PC and BPA-PC/PS filament both unmodified and ozone modified for 10 minutes in a Harrick Praying Mantis DRIFTS accessory at 90 °C

DRIFTS IR spectra of the unmodified melt mixed BPA-PC/PS blended samples exhibit characteristic peaks uncommon to both homopolymers at wavenumbers 1171, 1205, 1257, 1452, and 1787 cm^{-1}. These peaks are attributed respectively to C-O stretching of carbonate on BPA-PC (1171, 1205 and 1257 cm^{-1}), aromatic C=C stretching in PS (1452 cm^{-1}) and C=O stretching from carbonate ester in BPA-PC (1787 cm^{-1}) indicating chains of both polymer phases are present at the surface and available for modification [12, 14]. Strong asymmetric broadening at the lower wavenumber side of 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 homopolymer at 1745 cm^{-1}. Peak growth at 1670 cm^{-1} and peak flattening at 3058 cm^{-1} and 3080 cm^{-1}, which was observed for both BPA-PC and PS homopolymer samples alike was also observed in BPA-PC/PS blended samples. It is likely modified chains from both phases of the blend are contributing to the changes at 1670, 3058, and 3080 cm^{-1}.
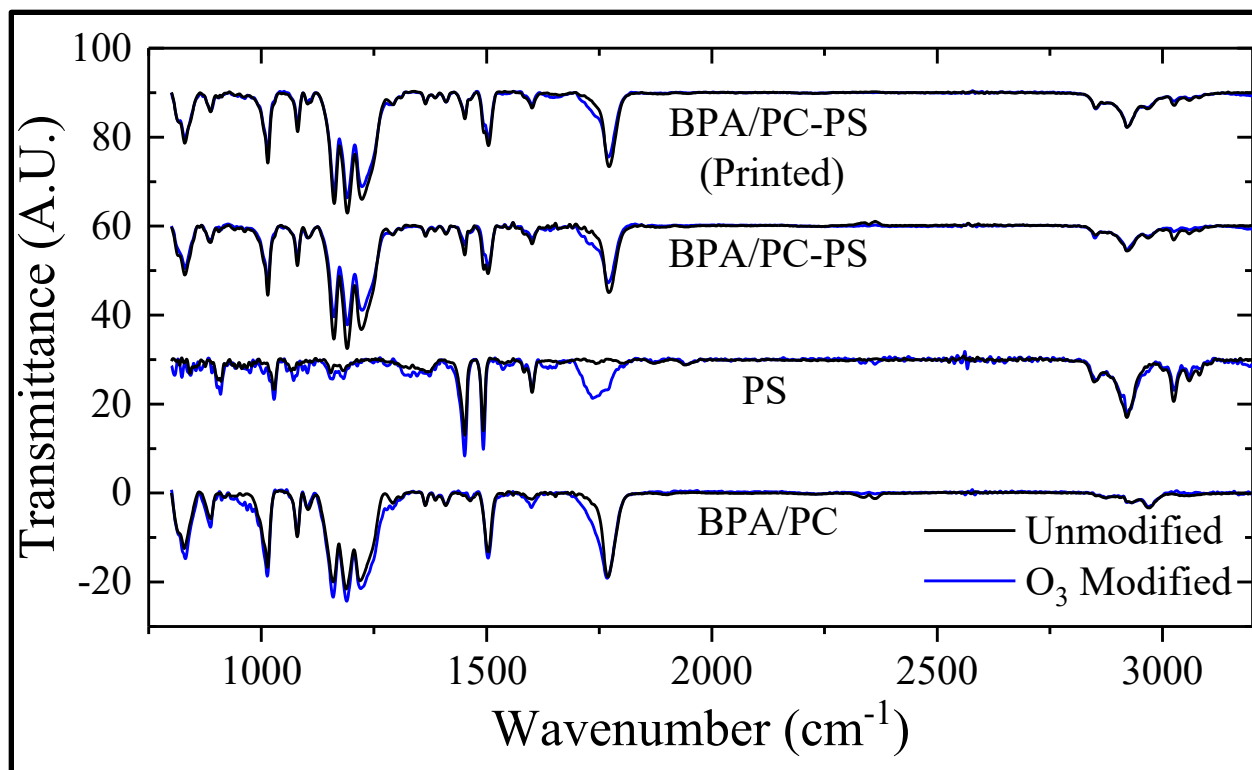
Figure 3 ATR-IR spectra of unmodified and ozone modified BPA-PC, PS, and BPA-PC/PS filaments and unmodified and ozone modified printed BPA-PC/PS dogbone specimens

Both filament samples modified in the Praying Mantis high temperature reaction chamber and printed samples' IR spectra were characterized in ATR-IR mode, Figure 3. Printed samples could not be characterized by DRIFTS IR due to poor data quality resulting from the relatively smooth surface finish increasing specular reflectance and dominating the signal. Ozone modified and unmodified PS filament samples' ATR-IR spectra are similar to DRIFTS IR spectra, but BPA-PC filament exhibits new changes in ATR-IR after ozone modification that were not observed during DRIFTS IR, notably broadening of the 1770 cm^{-1} peak towards lower wavenumbers which was noted by Baker, et al. to indicate aromatic epoxidation. This peak is shifted slightly from 1787 cm^{-1} in the DRIFTS IR experiments due to the lack of heat. A similar shift is noted for the 1745 cm^{-1} peak observed in ozone modified PS as this peak shifts to 1735 cm^{-1} without heat. The dissimilar ozone modified BPA-PC spectra between DRIFTS IR and ATR-IR combined with similar spectra for ozone modified PS spectra between the techniques points to an increased diffusion coefficient of ozone in PS relative to BPA-PC as ATR-IR imaging depth is limited to the surface while DRFITS IR can "see" deeper into the bulk[15]. ATR-IR spectra of ozone modified BPA-PC/PS blended filament shows asymmetric broadening towards lower wavenumbers of the 1770 cm^{-1} peak. Given that both PS and BPA-PC are present at the surface and each modified homopolymer displays change in this region, it is likely modified chains from each phase are contributing to this signal.

Like filament samples of BPA-PC/PS, unmodified BPA-PC/PS printed samples exhibit peaks uncommon to both polymers at wavenumbers 1171, 1205, 1257, 1452, and 1770 cm^{-1}

indicating both phases of the blend are present at the surface and available for modification during printing. Printed ozone 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} as asymmetric broadening at 1770 cm^{-1} is observed thus confirming both phases of the blend may be chemically modified simultaneously *in situ.*
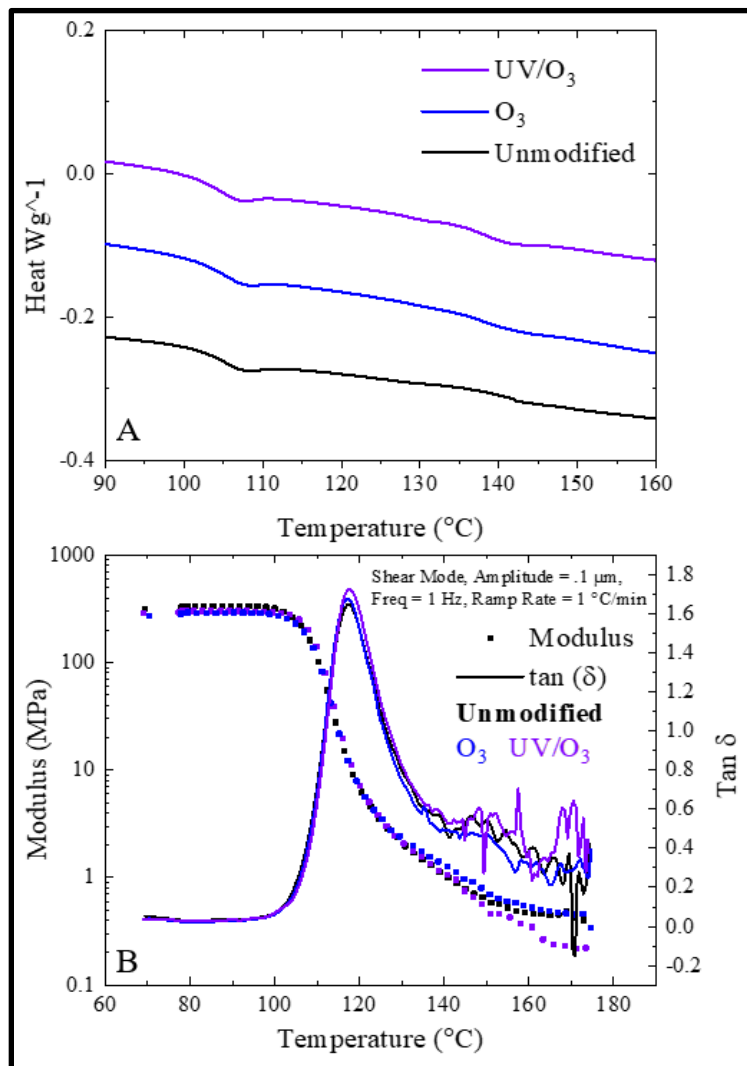

Figure 4 A) Calorimetric (10 °C min^{-1}, exo up) and B) Thermomechanical analysis of unmodified, O$_3$ modified, and UV/O$_3$ modified printed samples

Chemical modification impact on blend thermal transitions

Given that chemical modifications are made to both phases of the BPA-PC/PS blend, calorimetric and thermomechanical characterization of modified and unmodified BPA-PC/PS printed samples were performed to determine changes in the blend behavior, Figure 4, Table 3. Calorimetric characterization of unmodified printed samples shows two baseline shifts, one at 103.2 °C and a second at 143.4 °C corresponding to the glass transition temperature (T_g) of the PS and BPA-PC phases respectively. However, thermomechanical characterization of the unmodified printed samples displays a single peak at 117.34 °C in the loss tangent corresponding to the polystyrene phase T_g. Mechanical rigidity of the sample is lost after heating past the T_g of the polystyrene phase and therefore masks the polycarbonate phase's ordinary thermal behavior. Ozone and UV/ozone modification of the blend decreases the T_g of the polycarbonate phase by 5.0 °C and 6.3 °C respectively while the polystyrene phase remains unchanged in calorimetric characterization. This suggests one of three scenarios may be occurring. This could indicate dissimilar chain cleave kinetics/energetics between the two phases as chain cleave can explain a decrease in the T_g and chain cleave is a well-known result of ozone modification [8]. This could also indicate that while both phases of the blend are present at the surface and available for modification, the volumetric percentage each phase of the blend is contributing to the surface is dissimilar and thus more BPA-PC chains are modified than PS chains. Lastly, this could also

indicate PS thermal transitions are unaffected by ozone modification. Minimal changes are observed in thermomechanical analysis between modified and unmodified samples regardless of the treatment condition, however, the onset of modulus loss increases from 101.8 °C in the unmodified blend to 104.4 °C in UV/ozone modified samples. Considering both calorimetric and thermomechanical characterization of modified BPA-PC/PS, there are no strong indicators of increased compatibilization 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 thermal transitions of each phase closer together would be expected.

	$T_{g,a}$ (°C)			$T_{g,b}$ (°C)		
	Air	O₃	UV/O₃	Air	O₃	UV/O₃
DSC	103.2	103.7	102.8	143.4	138.4	137.1
DMA	117.3	117.2	117.6	N/A		

TABLE 3 Summary of calorimetric and thermomechanical testing results

Determination of mechanical property changes due to ozone degradation

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 [8]. In simulations of molten state BPA-PC and UV/ozone reactions performed by Baker, et al., ozone induced chain cleavage of BPA-PC is expected to occur at C-O bonds along the backbone under HOMO-LUMO excitation though it is less probable than methoxylation and aromatic epoxidation. This reaction can account for the decrease in strain at failure observed in UV/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 creating potential reaction sites as polymer degradation may also occur. There may be a tipping point in which too much polymer degradation prior to phase-to-phase crosslinking through further modification could mitigate the benefits to be gained.

To begin understanding the effects of UV/ozone pretreatment on the BPA-PC/PS blend mechanical properties, modified and unmodified BPA-PC/PS ASTM D638-14 Type V tensile specimens were printed in the XY orientation (i.e., tensile load applied parallel to deposited roads). Specimens were then elongated to failure in uniaxial tension. Both modified and unmodified specimens exhibit brittle failure modes with minimal material yield prior to failure as is typical in uncompatibilized BPA-PC/PS blends, Figure 5, Table 4 [9]. In unmodified printed dogbone specimens of BPA-PC/PS ultimate tensile strength (UTS) is decreased relative to BPA-PC homopolymer specimens reported by Baker, et al. with an UTS of 40.3 MPa +/- 0.62 which is expected behavior of uncompatibilized polymer blends. UV/ozone and ozone modified specimens exhibit slightly increased UTS of 42.5 MPa +/- 0.99 and 42.5 MPa +/- 1.48 respectively. The strain at failure is slightly decreased from 0.0198 +/- .001 in unmodified specimens to .0194 +/- .001 in ozone only modified specimens while UV/ozone modified specimens exhibit slightly increased strain at failure, 0.0206 +/- 0.002. The minor changes in mechanical performance between modified and unmodified dogbones suggests that the phase to phase interfacial properties of the blend continue to dominate the performance despite the chemical modifications. This is not surprising when considering the calorimetric and thermomechanical characterization indicated no

changes in blend morphology or compatibility. Significant changes in the blend mechanical performance will likely not be observed until phase to phase crosslinks are intentionally created by a second chemical modifier which would be expected to improve stiffness, toughness and ultimate tensile strength.
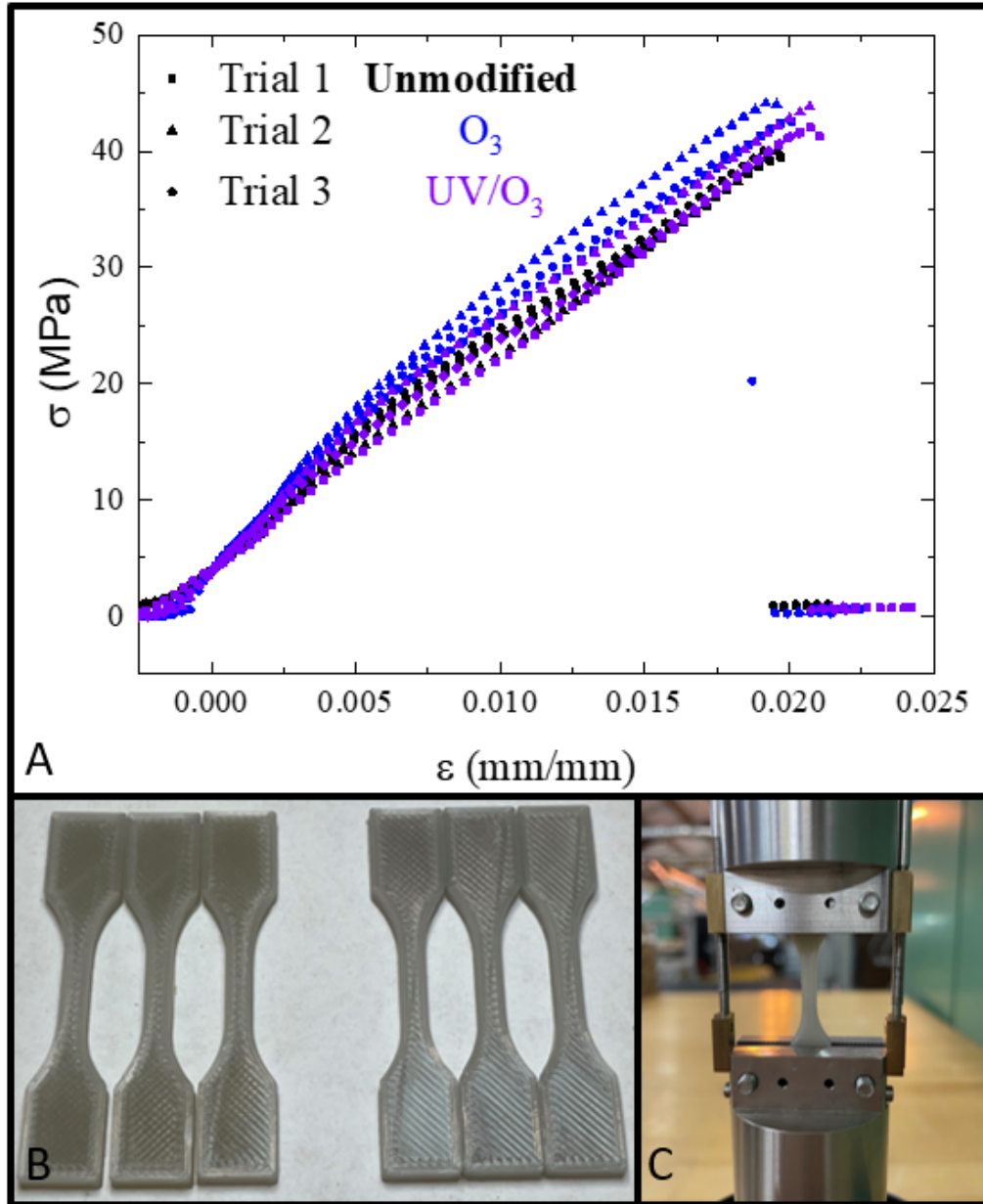

Figure 5 Tensile testing of unmodified, ozone modified, and UV/ozone modified BPA-PC/PS printed dogbone blends. Photographs of B) ozone modified (left) and unmodified (right) tensile bars and C) tensile bars loaded into the MTS Deben Microtest

Specimen Type	Modulus (GPa)	Ultimate Tensile Strength (MPa)	Strain at Failure(mm/mm)
Unmodified	**1.795 +/- 0.017**	**40.29 +/- 0.62**	**0.0198 +/- 0.001**
Ozone	**1.965+/ -0.070**	**42.48 +/- 1.48**	**0.0194 +/- 0.001**
UV/O$_3$	**1.831 +/- 0.033**	**42.45 +/- 0.99**	**0.0206 +/- 0.002**

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 1735 cm^{-1} indicating new C=O bond formation increasing 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 between unmodified, ozone and UV/ozone treated dogbone specimens as the phase to phase interfacial properties of the polymer blend continue to dominate the mechanical performance. In considering 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 dissimilar polymer crosslinking and increased compatibilization. The newly formed functional groups represent potential common reaction sites populated on each respective phase of the blend that could be crosslinked by a second gas phase reactant or a liquid phase reactant. It will be critical to further understand the effects 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 potential blend 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 properties of the blend may be improved. 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 functional 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.

Acknowledgements

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