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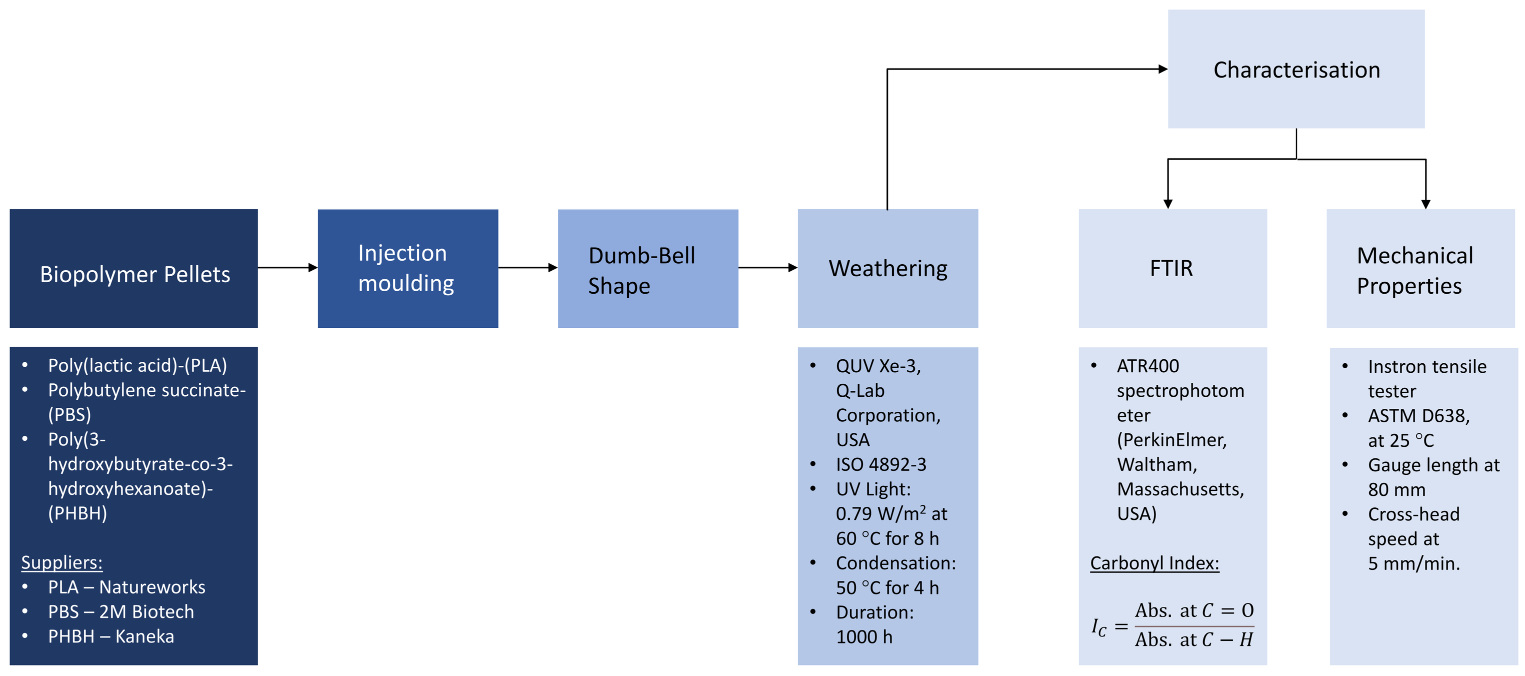
Effect of weathering on mechanical and surface properties of biopolymers

Monwabisi Cyril Nzimande[1,3], Asanda Mtibe[1], Shepherd Tichapondwa[3] and Maya Jacob John[1,2]*
[1]Centre for Nanostructures and Advanced Materials, Chemicals Cluster, CSIR, Pretoria, South Africa,
[2]Department of Chemistry, Nelson Mandela University, Port Elizabeth, South Africa, [3]University of Pretoria, Pretoria, South Africa

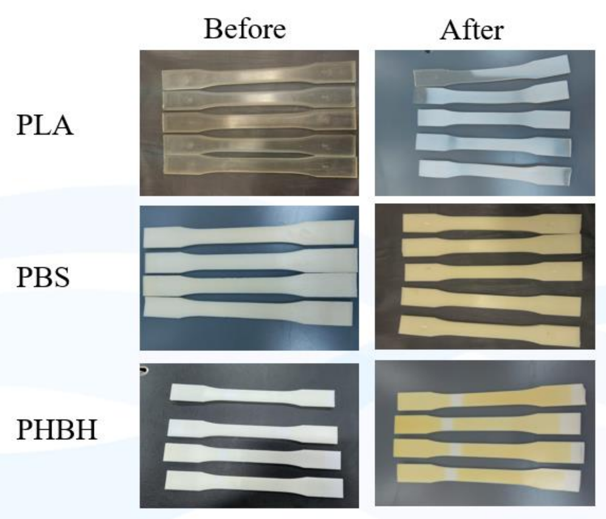
INTRODUCTION

- Plastics (both conventional and biopolymers) when exposed to environmental conditions undergo weathering and degradation processes, caused by elements such as sunlight (UV radiation), heat and moisture. Photo-degradation occurs by the action of UV rays of sunlight and can result in surface changes (loss of color, cracking) and loss of mechanical properties. As biopolymers are being used to replace conventional plastic products for a wide variety of applications, it is critical to study the long-term environmental impact of aging on properties of biopolymers.
- The aim of this study is to study the effects of long-term environmental aging on surface and mechanical properties of biopolymers, such as poly(lactic acid) (PLA), polybutylene succinate (PBS), and poly(3-hydroxybutyrate-co-3-hydro-xyhexanoate) (PHBH).

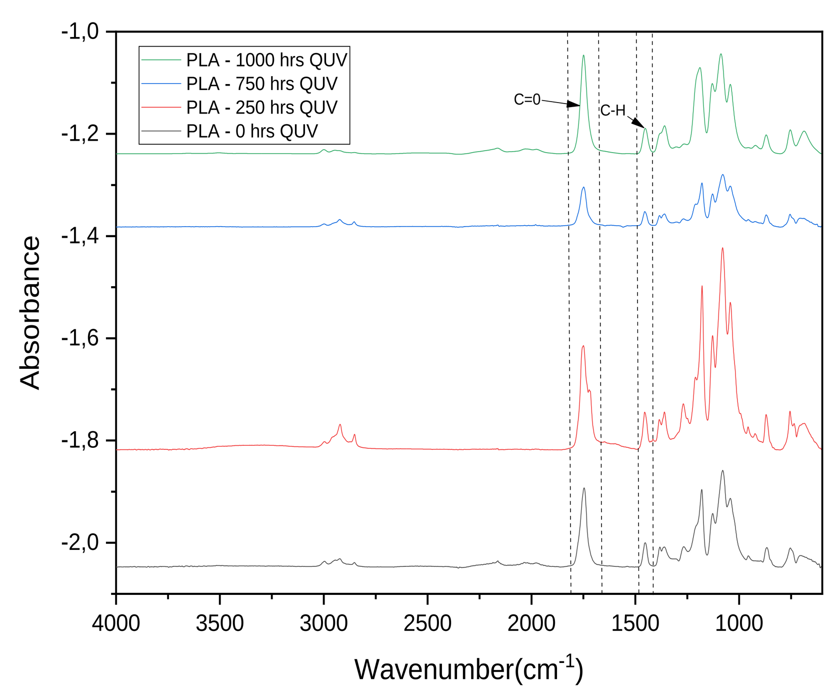
SAMPLE PREPARATION, INSTRUMENTATION AND CHARACTERIZATION TECHNIQUES



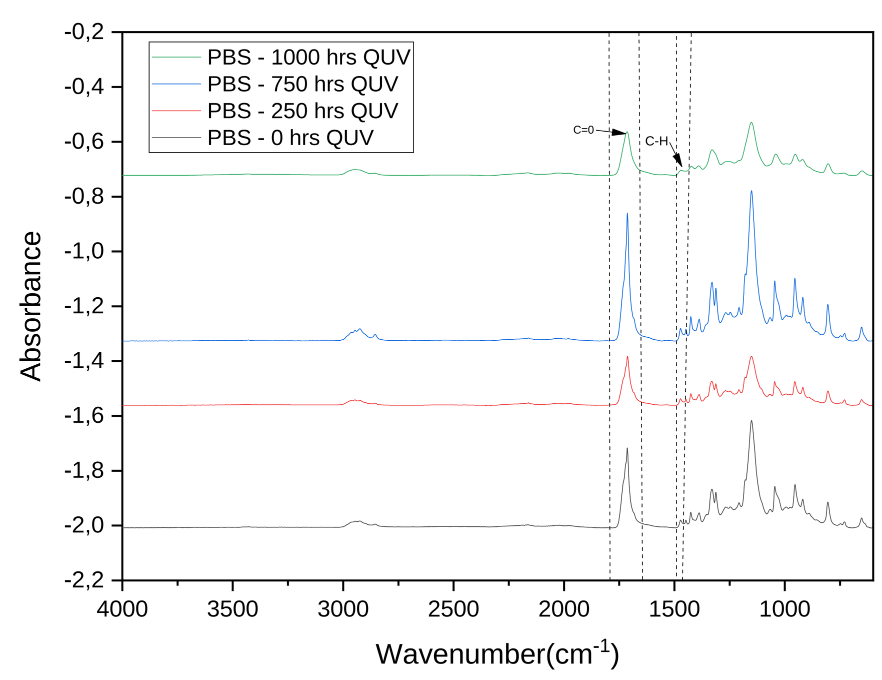
PICTURES OF SAMPLES: PLA,PBS AND PHBH BEFORE AND AFTER AGING



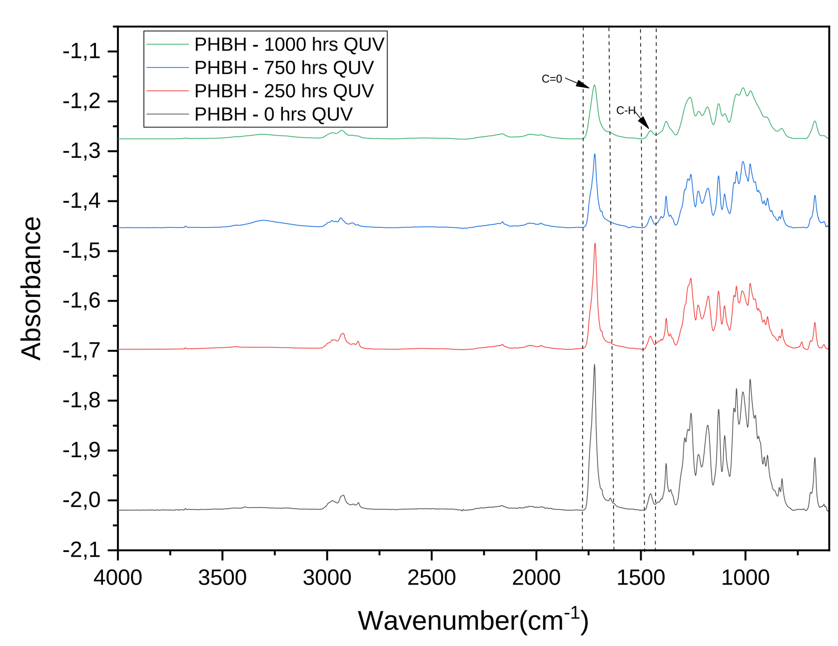
- PLA samples before aging are transparent because of its amorphous structure. The temperature in the chamber during accelerated weathering is 60 °C which is sufficient for the start of cold crystallization of PLA. After 1000 h period, due to the increased level of crystallinity, neat PLA specimen becomes opaque and white in color.
- PBS samples and PHBH samples indicate a change from white to yellow as weathering time increased. The colour change of the samples can be explained by the photo-oxidative reactions that create chromophore groups (e.g., carboxyl, carbonyl, ketone, aldehyde, hydroxyl, ester, etc.) and conjugated double bonds in the polymers over the accelerated weathering exposure.



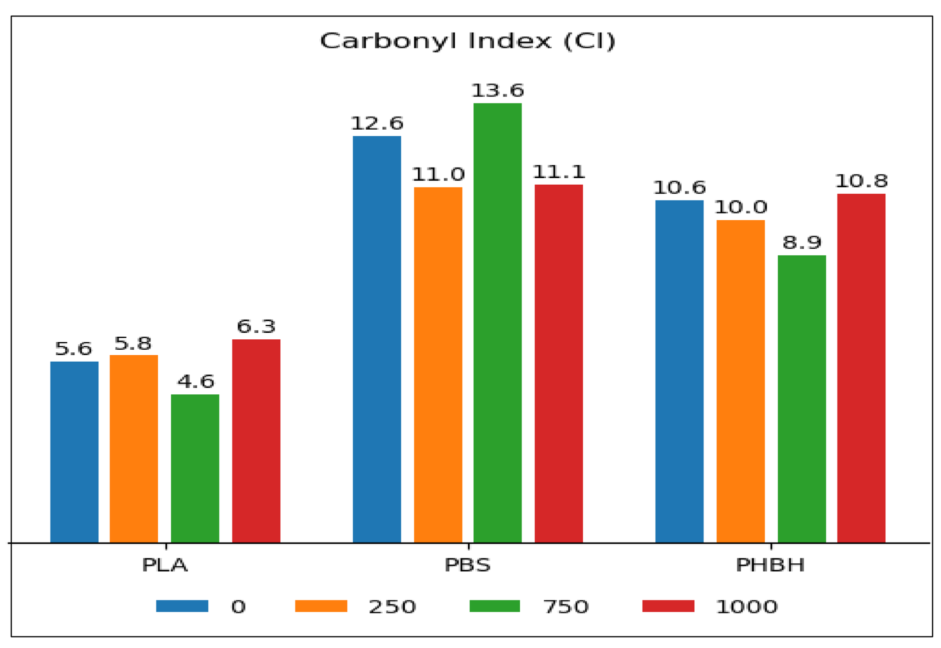
FTIR spectra of PLA samples: unaged and aged for 250, 750 and 1000 hours



FTIR spectra of PBS samples: unaged and aged for 250, 750 and 1000 hours



FTIR spectra of PHBH samples: unaged and aged for 250, 750 and 1000 hours



- The changes in carbonyl index (CI) of PLA over time show the formation of carboxylic end groups and ketones as a result of photo-oxidation, followed by a decline (250-750 hours) and a later increase (end) indicating dynamic photochemical transformations and degradation processes.
- PBS experiences initial oxidative reduction (250 h), followed by an increase in CI (250-750 h) due to extended UV exposure leading to carbonyl group formation, and then a decrease in CI indicating normal degradation.
- Initially, photo-oxidation causes CI of PHBH to rise from 10.6 to 10 over 250 hours. Following that, CI drops to 9.9 (250-750 hours), probably due to secondary reactions. The CI increases to 10.8 (750-1000 hours), indicating that photochemical reactions activity is back to normal.

TENSILE PROPERTIES OF PLA SAMPLES BEFORE AND AFTER WEATHERING

Aging time (hours)	Tensile stress at break (MPa)	Young's modulus (MPa)	Strain at break (%)
0	42.52±8.47	1953.83±108.34	16.24±7.63
250	44.30±33.02	1810.89±213.62	6.32±2.78
750	12.98±15.39	1169.18±608.79	7.85±5.69

- After 750 hours of aging, tensile strength and Youngs modulus reduced by 71% and 35% respectively. The presence of moisture during weathering results in swelling and plasticizing of PLA matrix leading to hydrolysis and breaking of C-O ester linkages in PLA resulting in weight and strength loss.
- PLA photodegradation occurs by Norrish II type photo-cleavage reaction resulting in formation of C=C bonds and hydroperoxides (O-H).
- At 1000 h, the PLA specimens were too brittle and could not be tested.

TENSILE PROPERTIES OF PBS SAMPLES BEFORE AND AFTER WEATHERING

Aging time (hours)	Tensile stress at break (MPa)	Young's modulus (MPa)	Strain at break (%)
0	35.42±2.44	383.51±19.63	175.92±11.94
250	26.33±6.88	463.51±49.29	9.61±4.26
750	14.13±0.88	595.44±35.15	3.27±0.43
1000	14.00±2.01	464.97±19.91	3.88±0.77

- The tensile strength of PBS reduced by 25 % after 250 h and after1000 h of exposure tensile strength was found to reduce by 46 %.
- The strain at break of neat PBS exhibited a substantial decrease of 95% after 1000 hours of aging.
- Since PBS is an aliphatic polyester, spraying with warm water and alternating with UV exposure might create an environment for hydrolytic degradation in which the amorphous zone was more useful than the crystallinity region for water molecules to penetrate.

TENSILE PROPERTIES OF PHBH SAMPLES BEFORE AND AFTER WEATHERING

Aging time (hours)	Tensile stress at break (MPa)	Strain at break (%)	Young's modulus (MPa)
0	31.81±0.44	8.67±2.01	1397.91±166.03
250	33.27±8.73	7.26±3.38	1629.28±146.33
750	29.84±0.56	3.38±0.31	1977.30±161.73
1000	29.16±0.90	3.17±0.16	1815.25±104.08

- The tensile strength of PHBH decreased by 10% after 1000 h of aging. During exposure, the C=O group in PHBH absorbed UV radiation, resulting in the cleavage of the C-O ester and the C-C bonds of the polymer main chain.
- Youngs modulus was found to increase after aging.

CONCLUSIONS

- After aging PLA specimens were found to change from transparent to opaque. This is attributed to the fact that cold crystallization of PLA is induced by accelerated weathering at 60 °C. Due to increased crystallinity, the PLA specimen turns opaque and white after 1000 hours of aging.
- Both PBS and PHBH samples experienced a change in color from white to yellow over time, which was caused by photo-oxidative processes that formed chromophore groups and conjugated double bonds in the polymers under rapid exposure.
- The tensile strength of PLA samples decreased by 70% after 750 hours of aging due to specimen ductility, while PBS samples decreased by 46%. Furthermore, in PHBH samples, it was reduced by 53%. This is attributed to degradation mechanisms including bond breakage and molecular structural weakening caused by heat, oxygen, and UV radiation.
- Carbonyl index (CI) values were found to increase with weathering times, indicating a gradual increase in oxidative degradation and the formation of carbonyl functional groups in the polymer structure.
- Among the different biopolymers, PLA exhibited the highest level of photodegradation after 1000 hours of exposure.

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