

Summary

Poly(lactic acid) (PLA) composites were prepared by integrating quinoa chaff that had been refluxed in a toluene and ethanol solution, with differing ratios of the chaff. These composites have been evaluated by bomb calorimetry, infrared (IR) spectroscopy, water uptake, water contact angle & degradation, antioxidant assay and scanning electron microscopy (SEM) to determine chemical and physical properties. A cellulase enzyme was also purified from E-Coli bacteria for use in degradation studies. Current tests indicate that the refluxing of raw chaff increases homogenization of composites, which in turn allows for the increase of properties overall as well as increased degradation. This gives promising results concerning the future of biodegradable materials as they are able to keep favorable properties as well as decrease overall waste.

Introduction

- Poly(lactic acid) (PLA) is a bioplastic made from fermented plant biomass, having similar properties to petroleum based plastics, the main difference being the ability to degrade into lactic acid monomers and oligomers.
- While PLA takes less time for degradation than traditional plastics, without any special treatment, PLA can still persist for decades without any significant change or breakdown.
- Quinoa chaff is a byproduct of quinoa seed production that has no real use outside of cattle feed and is generally considered to be a waste product.
- The chaff protecting the seeds is naturally rich in saponin and cellulose which could give the product useful properties if integrated properly into a bioplastic such as PLA.
- Repurposing quinoa waste into a component of a bioplastic with PLA can reduce carbon emissions produced by typical petroleum based plastics.
- 5 to 10 tons per hectare of by-product chaff is produced from quinoa harvesting; and is used to feed livestock or as compost.
- Utilizing natural and eco-friendly materials can be a step toward reduction of demand for petroleum-based plastics.
- By integrating the quinoa chaff that contains cellulose into PLA composites, we hope to keep the current properties of the polymer, as well as use a cellulase enzyme to degrade the bioplastic in a shorter period of time compared to industrial treatment.

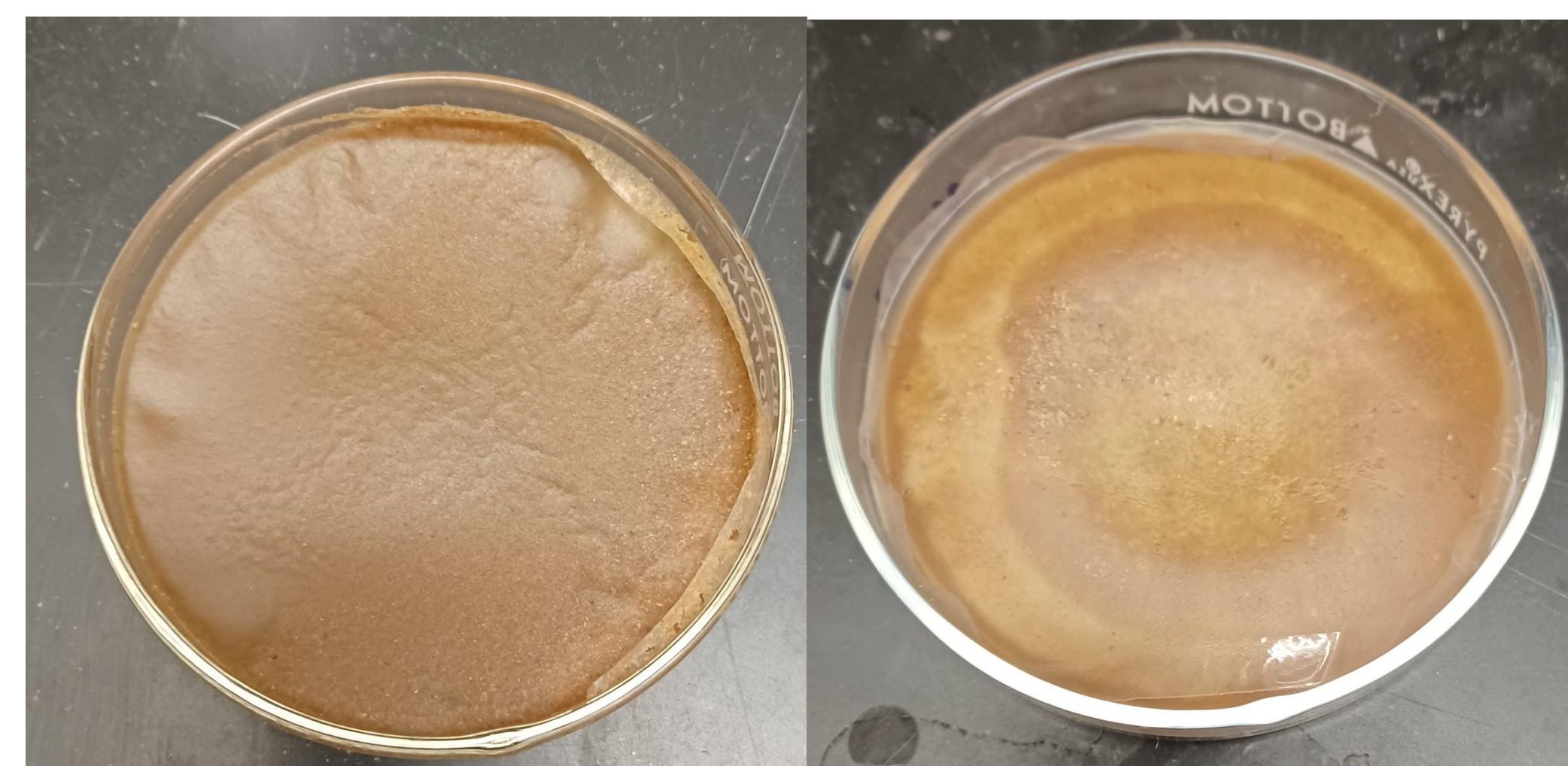


Figure 1. PLA-Quinoa composite films with reflux treatment (left) and without (right)

Methods

Preparation of bioplastic composites

- Raw quinoa chaff is refluxed in a toluene:ethanol solution, dried, then added to PLA dissolved in chloroform, sonicated overnight, before pouring and allowing to dry under vacuum
- The quinoa was added in different weight ratios with PLA being constant and having differing percentages of quinoa, giving 25%, 50%, and 75% quinoa composites

Bioplastic Characterization

- Samples were characterized using bomb calorimetry, infrared (IR) spectroscopy, water uptake, water contact angle & degradation, antioxidant assay and scanning electron microscopy (SEM).
- PLA quinoa composite powder is pressed into a starch based packing peanut prior to bomb calorimetry in order to maintain pill stability.
- Cellulase enzymes were extracted for use in ongoing composite degradation studies



Figure 2. Extracted oils and pigments after refluxing quinoa in toluene:ethanol wash.



Figure 3. Starch-based packing peanut pill containing 0.35 Quinoa : PLA composite powder.

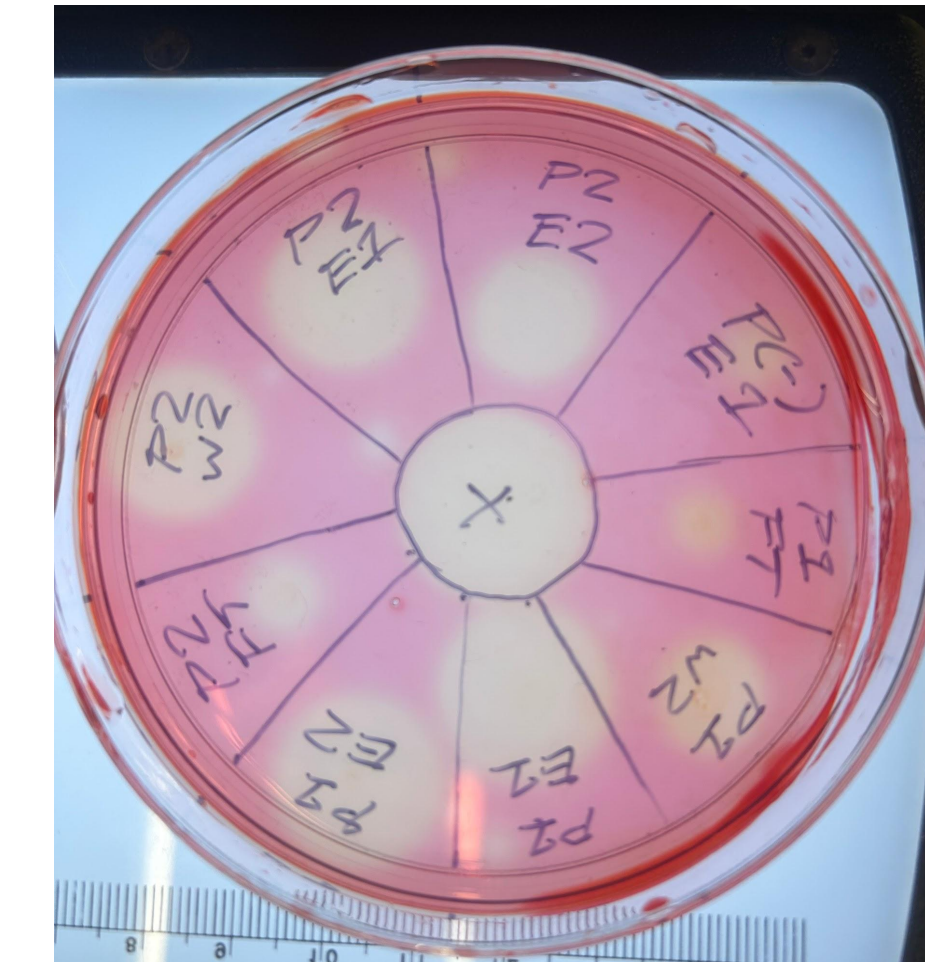


Figure 4. Carboxymethylcellulose (CMC) plate used to test for cellulase activity after staining with congo red solution.

Results

IR spectra of powdered samples and controls display distinct differences

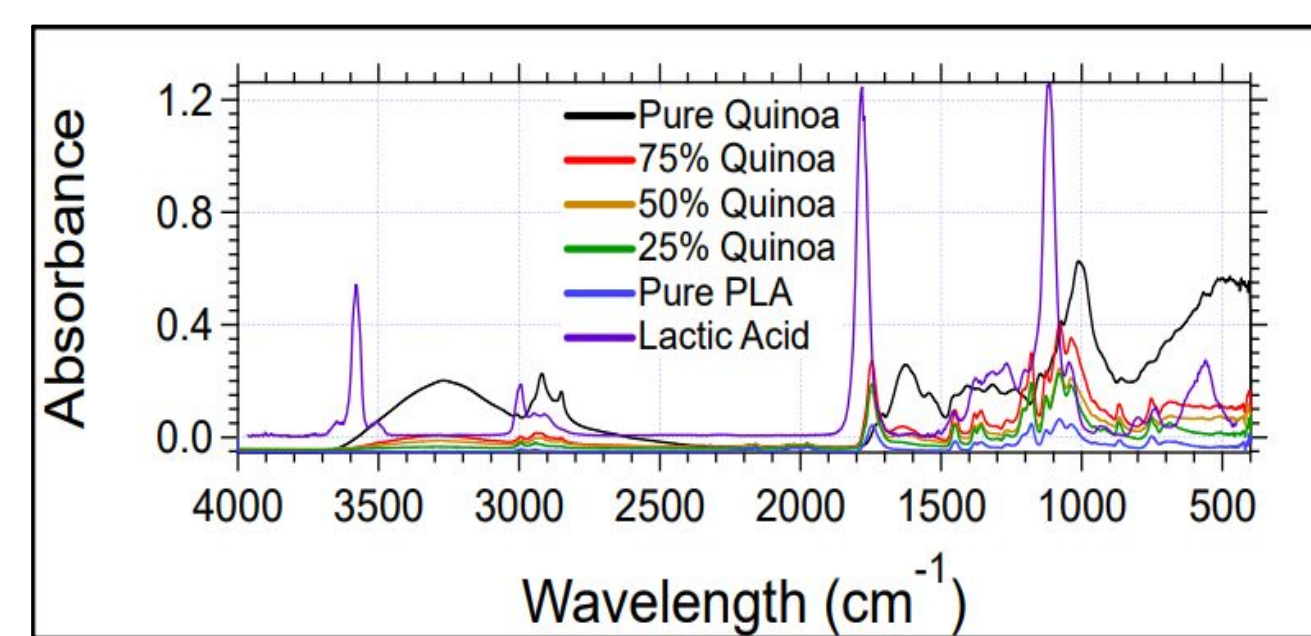


Figure 5. IR spectra of powdered samples and controls are shown. Distinct functional groups are observed for PLA (blue) versus PLA/quinoa composites (75% red, 50% orange, 25% green) and controls of pure Lactic acid (purple) and pure quinoa chaff (black).

Particle size increases as quinoa ratio to PLA increases

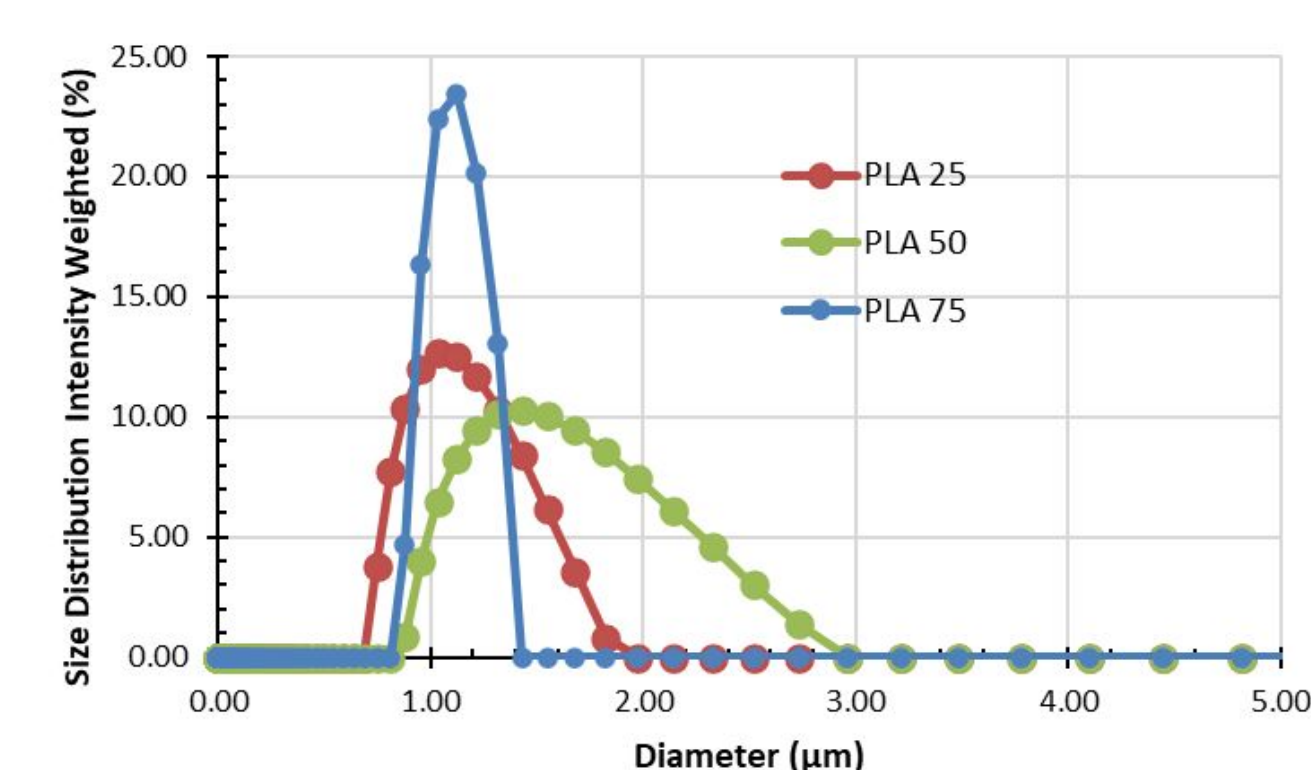


Figure 7. Dynamic Light Scattering particle size data shows distribution of particles increasing with quinoa concentration.

Bomb Calorimetry data from Quinoa PLA composites

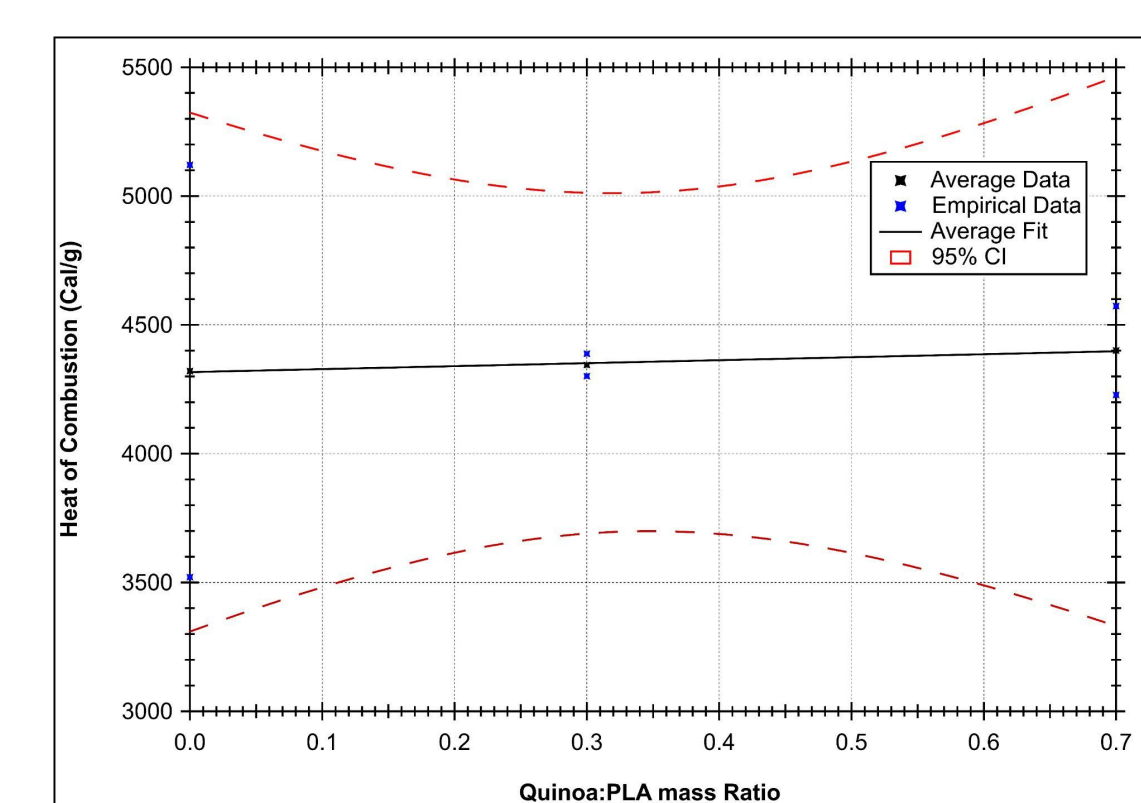


Figure 6. Heat of combustion data plotted against Quinoa:PLA ratio. Observed heat of combustion patterns indicate that the heat of combustion increases as the mass ratio of quinoa:PLA increases, this was modeled using a linear fit

Water permeability decreases with increased quinoa concentration and decreased PLA concentration

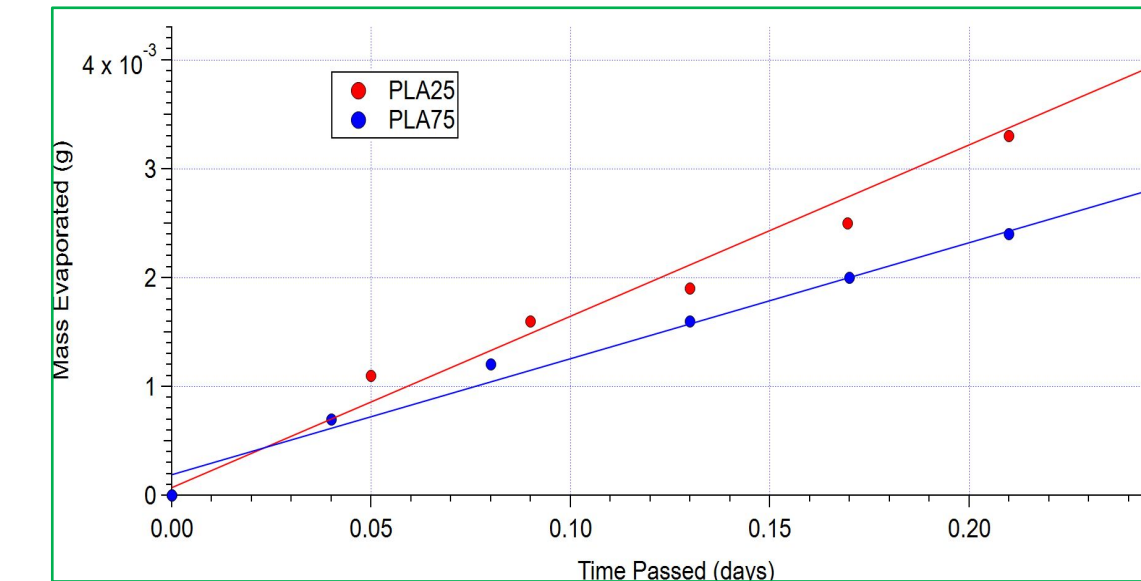


Figure 8. Water permeability data is shown for both PLA/Quinoa 25 & PLA/Quinoa 75. There is an increased permeability for PLA25 compared to PLA75.

Results

Morphological Characterization by scanning electron microscopy shows increasing roughness

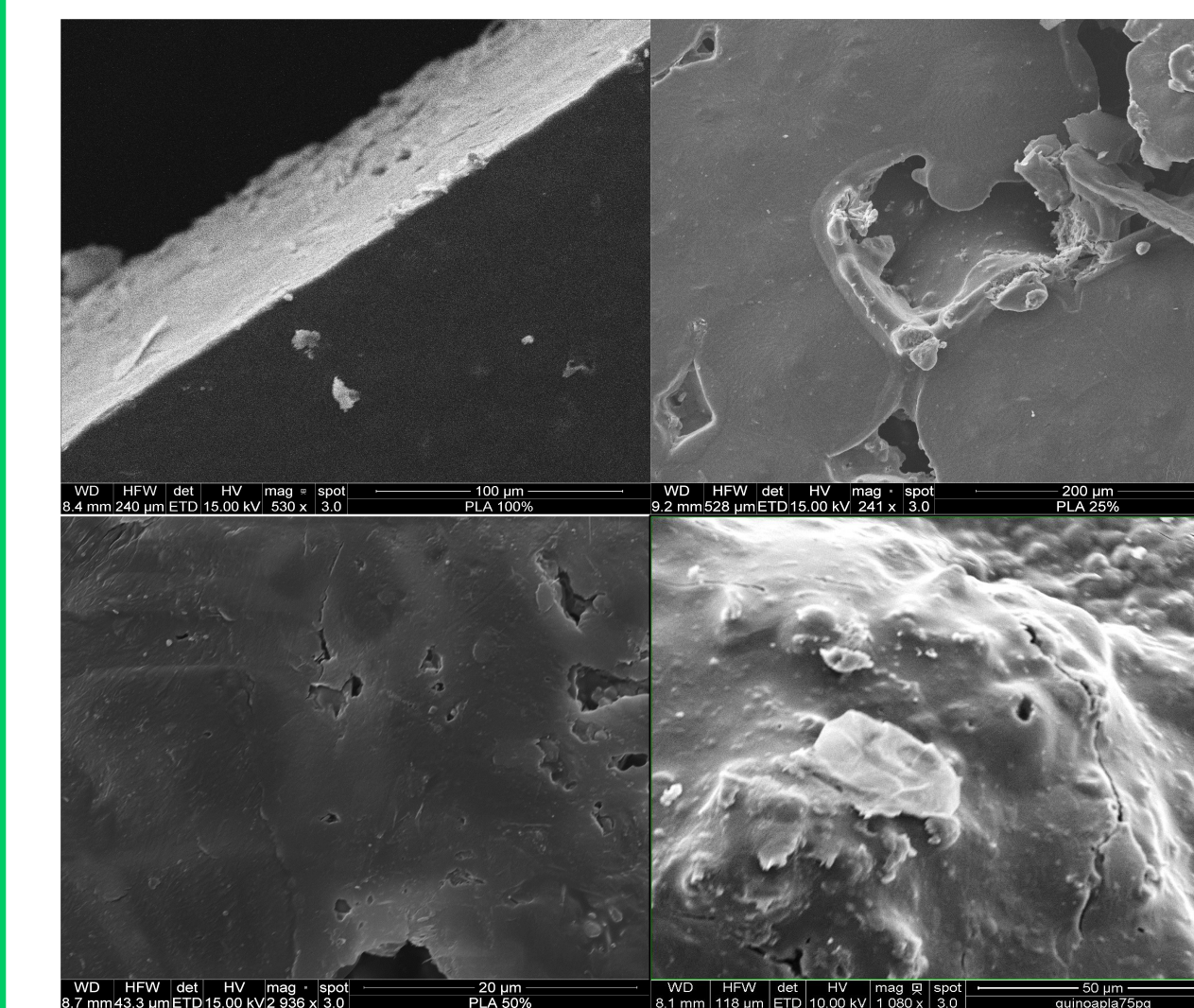


Figure 9. SEM of PLA and PLA/Quinoa Composite films. SEM images are shown above of A. PLA, B. Quinoa 25, C. 50 & D. 75) showing a more homogenous and regular surface morphology for pure PLA when compared with composites displaying increased roughness and agglomerations.

Antioxidant studies show increased activity compared to PLA alone

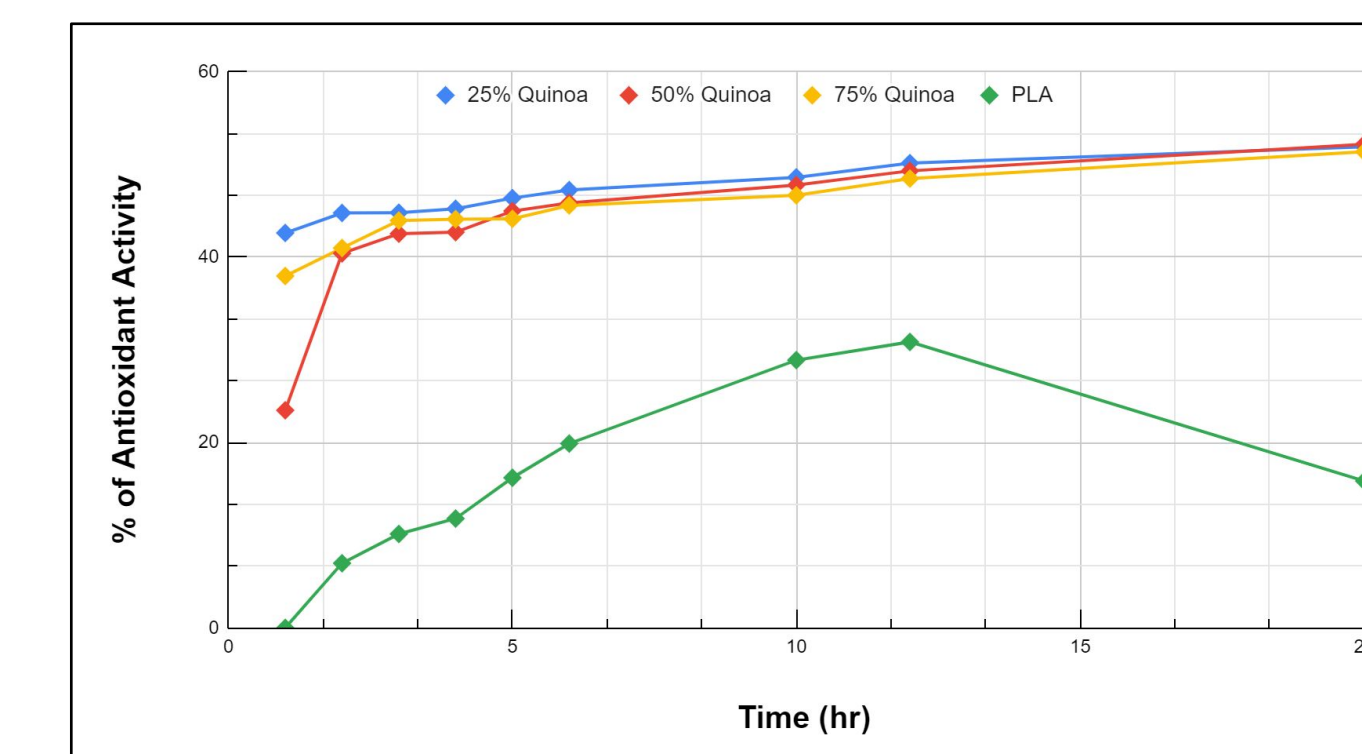


Figure 11. Antioxidant activity of PLA quinoa composites. Antioxidant activity was calculated from the absorbance at 517 nm of samples in the presence of DPPH free radicals minus DPPH in ethanol control.

Contact Angle studies show contact for PLA < PLA/Quinoa composites showing higher hydrophilicity

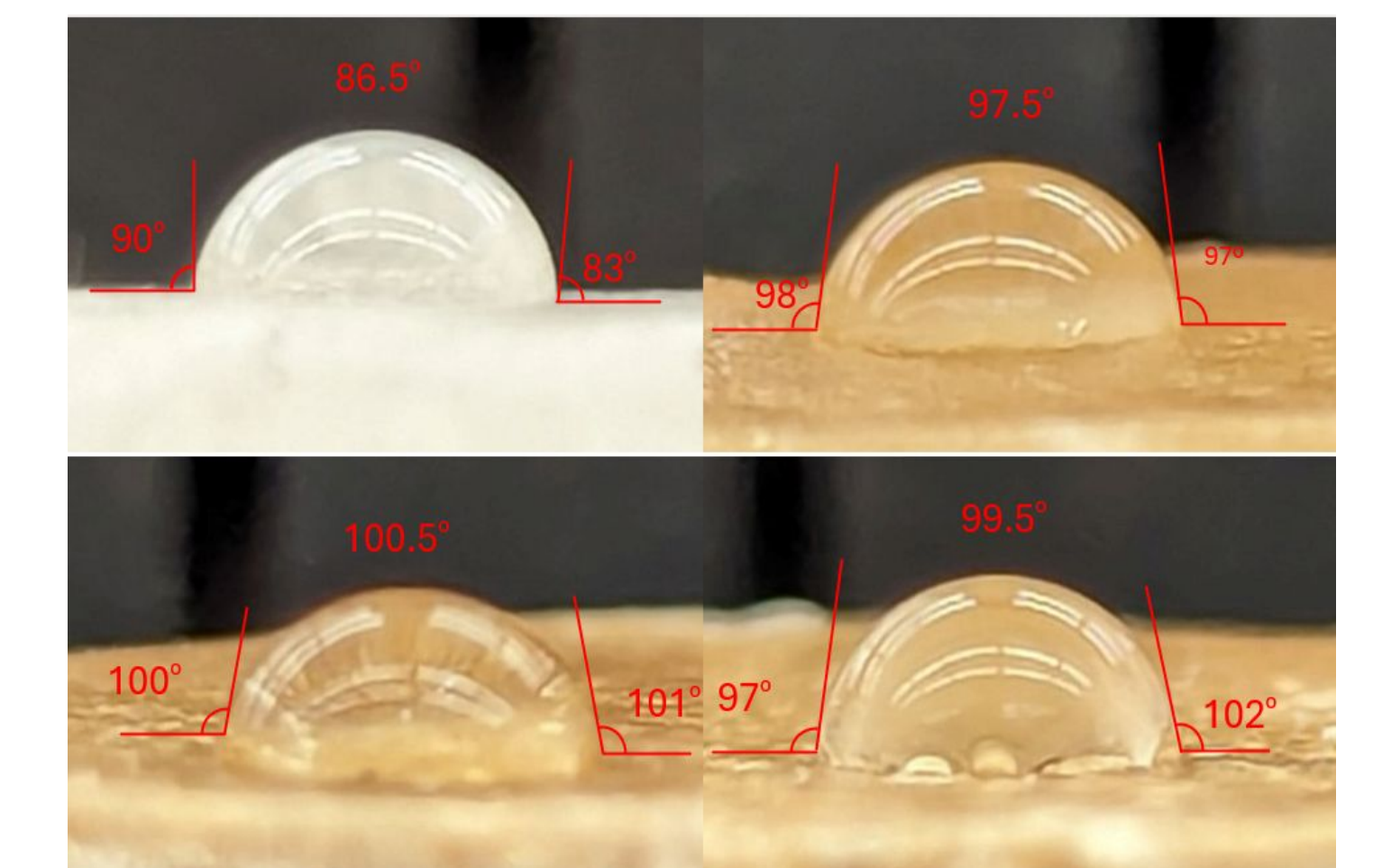


Figure 10. Water contact angle (WCA) images display higher WCA for PLA than for PLA/Quinoa composites. Hydrophobic > 90°; Hydrophilic < 90°

IR spectra after exposure of the samples to varying relative humidity shows more water absorption with increasing amounts of quinoa chaff

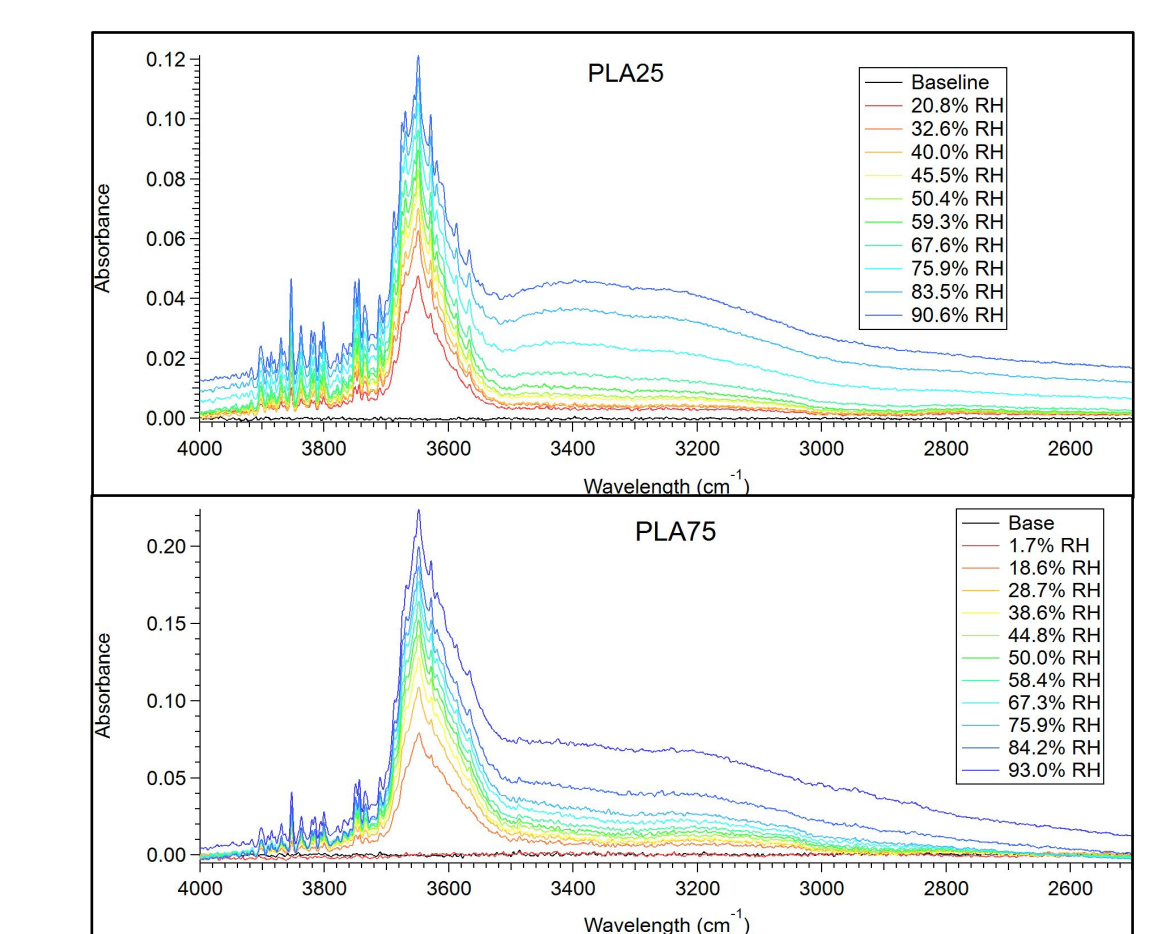


Figure 12. Water absorption determined by DRIFT spectroscopy. Absorption of water was measured using DRIFT spectroscopy for PLA25 and 75 at differing relative humidities (RH) from approximately 0 to 90% RH by monitoring the absorbance between 3000-3800 cm⁻¹

Conclusions

- Treating the raw chaff before mixing with PLA increase homogenization allowing for improved composite formation and overall properties
- Empirical data shows that as quinoa:PLA ratio is increased the heat of combustion increases. Higher heat of combustion allows the material to break down easier in high temperature environments
- Increasing the amount of quinoa chaff in the PLA composites led to increased water absorption. Additionally, the composite with 25% ratio quinoa had greater water permeability compared to composite with 75% ratio
- Antioxidant activity was determined using DPPH, and was significantly higher in quinoa containing composites vs PLA
- Water degradation study shows that composites containing higher amounts of quinoa will have particle size breakdown
- Future testing on the refluxed composites including tensile strength, cellulase degradation as well as repetition of previous tests
- Continued testing will allow for the determination of how effective the increased degradation of reusable polymer composites are after being integrated with natural cellulose

Acknowledgments

- We would like to thank the COMPASS program and Nievita Bueno Watts and Nanette M Durbin for providing support and guidance.
- Rafael Bernard was funded by a grant from California State University STEM Pathways and Research Alliance (CSU-SPaRA)
- Thank you Brandon Wilcox and Cristina Tusei for their amazing assistance in the Chemistry stockroom as well as Tyler Hooker in the Physics stockroom.
- Rachel Sechan for providing starch based packing peanuts.

References

1. (N.D.). Sustainable Active Food Packaging from Poly(Lactic Acid) and Cocoa Bean Shells. <https://doi.org/10.1002/acsami.200755> e001
2. Stern, T. (2017, January 08). DAV 23 - The Quinoa Processing Process. <https://www.linkedin.com/company/compass-program/>
3. How much oil is used to make plastic? (May 17, 2017). <https://www.youtube.com/watch?v=348585858>
4. Terech, G., Guzman-Parque, G., Paul, D. C., Barthelemy, M., Gabor, L., Gabor, G., Gabor, L., Alfaro-Sanchez, A., & Hernandez-Guerrero, J. A. (2018). Thermoplastic cellulose acetate blends with high barrier properties and ductile behaviour. *Chemical Engineering Journal*, 348, 461-468. <https://doi.org/10.1016/j.cej.2018.02.021>
5. Jaramilla, M., Terech, G., Alfaro-Sanchez, A., Gabor, L., & Gabor, G. (2012). Structural, mechanical and barrier properties of active PLA-Antioxidant Films. *Journal of Food Engineering*, 110(3), 380-389. <https://doi.org/10.1016/j.jfoodeng.2011.12.024>
6. Manjappa, R., Zouhar, A., Choudhary, A., & Gopal, K. (2020). Modified uptake color method for testing water vapor permeability in porous membranes. *Energy*, 195, 117057. <https://doi.org/10.1016/j.energy.2020.117057>
7. Balgieri, S., Maltarello, R., Pizzarello, A., Vignani, A., Quarta, A., Pizzarello, R., & Ching, C.M. Determination of Antioxidant by DPPH Radical Scavenging Activity and Quantitative Physicochemical Analysis of Flour pellets. *Molecules*, 2022 Feb 16;27(4):1206. doi: 10.3390/molecules27041206. PMID: 35020118; PMCID: PMC8878433
8. Tran, Q., Altmann, L., Dube, P., Molkentin, M., Salsinger, R., Koth, R., Phartyal, M. M. Direct Demonstration of Complete Combustion of Gas-Suspended Powder Metal Fuel Using Bomb Calorimetry. *Meas. Sci. Technol.* 2022, 33 (4), 047002. <https://doi.org/10.1088/1361-9162/ab9702>
9. Ren, H., Xu, Z., Du, C., Ling, Z., Yang, W., Pan, L., Tan, Y., Fan, W., Zhang, Y. Preparation and Characterization of Starch-Based Composite Films Reinforced by Quinoa (Chenopodium Quinoa Willd.) Starch Cellulose Nanocrystals. *International Journal of Biological Macromolecules* 2023, 242, 124908. <https://doi.org/10.1016/j.ijbiomac.2023.124908>