



UNIVERSITÀ DEGLI STUDI DI SALERNO

Department of Industrial Engineering

Master's degree in food engineering

Study of a biodegradable layer for silage covering

Thesis in
Transport Phenomena

Supervisors:

Prof. Ing. Gaetano Lamberti

Ing. Diego Caccavo

Ing. Raffaele Mancino

Candidate:

Joseph Chibueze OFOEGBU

0622800661

Academic Year 2022/2023



I dedicate this thesis to God for seeing me through this journey.

This text was printed in-house, in Times New Roman

The sceduled date for the thesis discussion is 17/07/2023
Fisciano, 07/07/2023

Tables of contents

Tables of contents	I
Table of figures	V
Table of tables	VIII
Abstract	X
Introduction	1
1.1 Silage _____	2
1.1.1 What is Silage?	2
1.1.2 How Is Silage Made?	2
1.1.3 Good Silage Quality	3
1.2 Types of Silage _____	4
1.2.1 Types of Silage Storage System	5
1.3. Tests for ascertaining or determining a good silage quality. _____	7
1.3.1. Silage DM content	8
1.3.2. Protein Analysis	8
1.3.3. Energy Value & Digestibility	8
1.3.4. Silage Fermentation Quality	9
1.3.5. Fiber Analysis	9
1.4. What is a Biodegradable Film _____	10
1.4.1. Benefits of Biodegradable Film	11
1.4.2. Types of Biodegradable Film	11

1.4.3. Applications of Biodegradable Films	12
1.5. Tests for Biofilms	13
1.5.1. Thermogravimetric Analysis (TGA)	14
1.5.2. Mechanical Analysis	14
1.5.3 Relative Humidity Testing	19
1.6. State of Art	20
1.7. Aims	23

Materials and methods 25

<i>In this chapter, the materials, methods, and equipment are discussed.</i>	25
2.1 Materials	26
2.1.1 Sodium Alginate	26
2.1.2 Glycerin	26
2.1.3 Cellulose	27
2.2 Apparatus	27
2.2.1 Texture Analyzer	27
2.2.2 Relative Humidity Testing Box	28
2.3 Methods	29
2.3.1 Preparation of Matrix layer with Silage	29
2.3.2 Cellulose Film Preparation	30
2.3.3 Cellulose Hydrogel Preparation	30
2.3.3 Sodium Alginate Film Preparation	30
2.3.4 Tensile Test	31
2.3.5 Humidity Test	32

Results and discussion 33

3.1 Tensile Test	34
3.2.1 Tensile Strength of Sodium Alginate Composite film	Errore. segnalibro non è definito.
3.2.2 Tensile Strength of Straw Fibers Composite Film.	42
3.2.3 Tensile Strength of Straw Powder Composite Film.	51

Table of contents	Page III
3.2.4 Tensile Strength of Stick Fiber Composite Film	65
3.2.5 Tensile Strength of Stick Powder Composite Film	67
3.2 Humidity Test _____	74
3.3 Elongation at Break Sodium Alginate vs Straw vs Stick _____	77
3.4 Tensile Stress of Sodium Alginate vs Straw vs Stick ____	79
3.5 Young Modulus of Sodium Alginate vs Straw vs Stick __	80
Conclusions	87
REFERENCES	90

Table of figures

Figure 1. Dog bone Specimen. Source: ASTM D-638. [39]	16
Figure 2. Tensile Stress vs Strain Curve. Source: Autodesk Instructables. [40] 16	
Figure 3. Stress-Strain Curve (Plastic Deformation). Source: Researchgate. [42]	19
Figure 4 Sodium Alginate Structure.....	26
Figure 5 Glycerin Structure.....	27
Figure 6 Cellulose Structure.....	27
Figure 7 Tensile Tester.....	28
Figure 8 Humidity Testing Box.....	Errore. Il segnalibro non è definito.
Figure 9 The chart shows the stress-strain curves for five Sodium alginate (SA) biofilm samples.	42
Figure 10 In (a) we have SA_StrawFiber 30g; In (b) we have SA_StrawFiber 15g; In (c) we have SA_StrawFiber 7.5g.	51
Figure 11 In (a) we have SA_StrawPowder 30g; In (b) we have SA_StrawPowder 15g; In (c) we have SA_StrawPowder 7.5g.....	58
Figure 12 In (a) we have SA_StickFiber 30g; In (b) we have SA_StickFiber 15g; In (c) we have SA_StickFiber 7.5g.	67
Figure 14 In (a) we have SA_StrawPowder 30g; In (b) we have SA_StrawPowder 15g; In (c) we have SA_StrawPowder 7.5g.....	74
Figure 15 The chart shows the Relative Humidity-Time of SA and its twelve composite samples.....	76
Figure 16 The chart shows on the x-axis the type of film and on the y-axis the elongation at break. In blue, the mean elongation of alginate biofilms was analyzed; in red, the mean elongation of SA straw powder composite samples was analyzed; in green, the mean elongation of SA straw fiber composite samples was analyzed; in yellow, the mean elongation of SA stick powder composite samples was analyzed; and in purple, the mean elongation of SA stick fiber composite samples was analyzed.....	77
Figure 17 The chart shows on the x-axis the type of film and on the y-axis the elongation at break. In blue, the mean tensile stress of alginate biofilms was analyzed; in red, the mean tensile stress of SA straw powder composite samples was analyzed; in green, the mean tensile stress of SA straw fiber composite	

samples was analyzed; in yellow, the mean tensile stress of SA stick powder composite samples was analyzed; and in purple, the mean tensile stress of SA stick fiber composite samples was analyzed. 79

Figure 18 The chart shows on the x-axis the type of film and on the y-axis the elongation at break. In blue, the mean young modulus of alginate biofilms was analyzed; in red, the mean young modulus of SA straw powder composite samples was analyzed; in green, the mean young modulus of SA straw fiber composite samples was analyzed; in yellow, the mean young modulus of SA stick powder composite samples was analyzed; and in purple, the mean young modulus of SA stick fiber composite samples was analyzed. 80

Table of tables

Table 1. Summary of an Ideal Silage [7]	4
Table 2 Sample Design	31

Abstract

In this work new recipes for the preparation of biodegradable silage coatings were tested.

In particular, biofilms were prepared using cellulose, the silage itself and the sodium alginate.

The cellulose extraction method known as the Kraft process can be suggested for use while attempting to extract cellulose from sticks, even though the cellulose film that was initially intended to be used was unsuccessful despite following the instructions outlined in literature.

The film prepared using silage was found to be too sensitive to water. The film is also expensive and consumes large quantities of silage, which could instead be used as animal feed.

The alginate biofilm was therefore found to be the cheapest, easiest to make and with the best properties. To limit the shrinkage of the film due to the removal of water and to make it more palatable to animals, a filler was added to the film. Two kinds of fillers were chosen, a wood-based material “stick” and dried hay-based material “straw” with two different shapes, fiber and powder. To compare sodium alginate (SA) with and without filler content, which served as control sample, several tests were performed: shrinkage tests, mechanical tests (Young modulus, the elongation at break, tensile stress) and water absorption tests. The tensile test suggests that SA/Straw powder is the best in maintaining the pure biofilm alginate mechanical properties having a young modulus and breakage stress close to the control sample. However, such film showed a decrease of the strain at the breakage due to increase of stiffness. According to the water absorption test, the addition of fillers, both straw and stick in the shape of fiber and powder, decreased the relative humidity of the sample with respect to the control one.

From these results, it can be concluded that the SA/straw powder is the best possible filler or additive to incorporate in the alginate film for a better silage covering.

Chapter One

Introduction

In this chapter, there is an overview of the silage storage system and its coverings.

REFERENCES

1. Denoncourt, P., S. Caillet, and M. Lacroix, *Bunker-stored silage covered with biodegradable coating. Part I. Laboratory assay*. Journal of the Science of Food and Agriculture, 2004. **84**(4): p. 300-306.
2. Wood, B.J., *Microbiology of fermented foods*. 2012: Springer Science & Business Media.
3. Denoncourt, P., B. Ouattara, and M. Lacroix, *Development of biodegradable coatings for covered horizontal bunker-stored silage*. Journal of the Science of Food and Agriculture, 2004. **84**(10): p. 1207-1215.
4. McDonnell, E.E. and L. Kung Jr, *An update on covering bunker silos*. 2006.
5. Park, R.S., C.S. Mayne, and T.W.J. Keady, *Silage production and utilisation*. 2005: Wageningen Academic Publishers.
6. Driehuis, F. and S.O. Elferink, *The impact of the quality of silage on animal health and food safety: a review*. Veterinary Quarterly, 2000. **22**(4): p. 212-216.
7. FarmLife, T. *Analysing your silage report*. 2016.
8. Authority, T.t.A.a.F.D., *Quality Grass Silage for Dairy and Beef Production Systems*
A Best Practice Guide 2016.
9. **Cornext**, *Types of Silage*.
10. Agro, I.S., *The applications of different types of silages*, in *Silage agro*. 2023, issuu: Online.
11. George, J.R., *Extension publications: forage and grain crops*. 1994.
12. Savoie, P. and J.C. Jofriet, *Silage storage*. Silage science and technology, 2003. **42**: p. 405-467.
13. Kaizer, A.G. and J.W. Piltz, *Feeding testing: Assessing silage quality*. Successful silage. The State of New South Wales, Department of primary industries and dairy Australia, 2004: p. 311-334.

14. Borreani, G., et al., *Silage review: Factors affecting dry matter and quality losses in silages*. Journal of Dairy Science, 2018. **101**(5): p. 3952-3979.
 15. Nutrition, L.A. *Interpreting Grass Silage Analysis*. 2023; Available from: <https://magniva.lallemandanimalnutrition.com/en/global/news/interpreting-grass-silage-analysis/>.
 16. de Oliveira, J.S., E.M. Santos, and A.P.M. dos Santos, *Intake and digestibility of silages*. Advances in silage production and utilization, 2016: p. 101-121.
 17. Amaral, R.C., et al. *Influence of covering strategies on feed losses and fermentation quality of maize silage stored in bunker silos*.
 18. Wisconsin, M.R.a.T.F. *Quality and Feeding*. 2023. 53706 (608) 262-1390.
 19. Johansson, C., et al., *Renewable fibers and bio-based materials for packaging applications—A review of recent developments*. BioResources, 2012. 7(2): p. 2506-2552.
 20. Compostables, G., *Biodegradable Films: Types, Applications and Benefits*. 2020, University of Wisconsin, Division of Extension.
 21. group, B., *Biodegradable Films: Different Types, Applications*. 2023.
 22. Otoni, C.G., R.J. Avena-Bustillos, and H.M.C. Azeredo, *Recent advances on edible films based on fruits and vegetables—A review*. Compr Rev Food Sci Food Safety 2017; 16 (5): 1151–69.
 23. Díaz-Montes, E., *Polysaccharides: Sources, characteristics, properties, and their application in biodegradable films*. Polysaccharides, 2022. 3(3): p. 480-501.
 24. Mangaraj, S., et al., *Application of biodegradable polymers in food packaging industry: A comprehensive review*. Journal of Packaging Technology and Research, 2019. 3: p. 77-96.
 25. Borreani, G. and E. Tabacco, *Bio-based biodegradable film to replace the standard polyethylene cover for silage conservation*. Journal of Dairy Science, 2015. **98**(1): p. 386-394.
 26. SpA, N. *Product : Mater-Bi*. Mater-Bi 2023; Available from: <https://www.novamont.com/eng/mater-bi>.
 27. Novamont, *From Agriculture for Agriculture: Advantages of Mater-Bi mulch film*, in *Mater-Bi*. 2018.
-

28. Letendre, M., et al., *Physicochemical properties and bacterial resistance of biodegradable milk protein films containing agar and pectin*. Journal of Agricultural and Food Chemistry, 2002. **50**(21): p. 6017-6022.
29. Liu, S., Y. Li, and L. Li, *Enhanced stability and mechanical strength of sodium alginate composite films*. Carbohydrate polymers, 2017. **160**: p. 62-70.
30. Bharath Rajaram, M.O.a.M.U., *Material Analysis for Bioplastics Quality Assurance and Degradation*. 2022.
31. Puglia, D., A. Tomassucci, and J.M. Kenny, *Processing, properties and stability of biodegradable composites based on Mater-Bi® and cellulose fibres*. Polymers for advanced technologies, 2003. **14**(11-12): p. 749-756.
32. Qi, R., et al., *Field test on the biodegradation of poly (butylene adipate-co-terephthalate) based mulch films in soil*. Polymer Testing, 2021. **93**: p. 107009.
33. Sarfraz, A., et al., *Electrode materials for fuel cells*, in *Reference Module in Materials Science and Materials Engineering*. 2020, Elsevier BV.
34. research, A., *Thermogravimetric analysis (TGA)*.
35. Wikipedia, *Thermogravimetric Analysis (TGA)*.
36. Twiglobal, *How does it work?*
37. Wikipedia, *Dynamic Mechanical Analysis (DMA)*.
38. Twiglobal, *What is Mechanical Testing? (A complete guide)*.
39. *Investigation of Mechanical Properties on Vinyl Ester Based Hybrid Composites*. 2017: p. 216-222.
40. Philipfigari, *Steps to Analyzing a Material's Properties From Its Stress/Strain Curve*. 2023, Autodesk Instructables.
41. Arham, R., et al., *Physical and mechanical properties of agar based edible film with glycerol plasticizer*. International Food Research Journal, 2016. **23**(4).
42. Tchakalova, B., *What is the relation between Tensile Strength and Youngs Modulus of a material*. 2018, Researchgate: Online.
43. Callahan, C.W., A.M. Elansari, and D.L. Fenton, *Psychrometrics*, in *Postharvest Technology of Perishable Horticultural Commodities*. 2019, Elsevier. p. 271-310.
44. Wikipedia, *Humidity*.
45. Choudalakis, G. and A.D. Gotsis, *Permeability of polymer/clay nanocomposites: A review*. European polymer journal, 2009. **45**(4): p. 967-984.

46. Bernardes, T.F., R.C.d. Amaral, and L.G. Nussio. *Sealing strategies to control the top losses in horizontal silos*.
 47. Larry L. Berger, N.P., and Jason Sewell M.S. *Edible Covers for Bunker Silos*. in *Southwest Nutrition and Management Conference Proceedings*. 2005. Sheraton Phoenix Airport Hotel
1600 South 52nd Street
Tempe, Arizona
(480) 967-6600: Reprinted from the 2005 Southwest Nutrition and Management Conference Proceedings,
February 24 & 25, 2005, Tempe, Arizona.
 48. Crawford, E., *Prevent Hardware Disease in Cattle*. 2012, North Dakota State University.
 49. Kaza, S., et al., *What a waste 2.0: a global snapshot of solid waste management to 2050*. 2018: World Bank Publications.
 50. Eurostat, W.S., Available online: https://ec.europa.eu/eurostat/statistics-explained/index.php/Waste_statistics_-_electrical_and_electronic_equipment (accessed on 7 August 2020), 2019.
 51. Levitan, L.C., D.G. Cox, and M.B. Clarvoe, *Agricultural plastic film recycling: Feasibility and options in the Central Leatherstocking-Upper Catskill region of New York State*. 2005, Recycling Agricultural Plastics Project (RAPP), Cornell University.
 52. Bhatti, J.A., *Current State and Potential for Increasing Plastics Recycling in the US Master's Thesis*. Columbia University, Sponsored by Earth Engineering Center, New York City, NY, USA, 2010.
 53. Holmes, B.J. and R. Springman, *Recycling silo bags and other agricultural plastic films*. 2009: Cooperative Extension of the University of Wisconsin-Extension.
 54. Borreani, G., et al. *Opportunities in developing novel biodegradable films to cover silages*. Applied Market Information Ltd.
 55. Font, R., et al., *Semivolatile and volatile compounds in combustion of polyethylene*. Chemosphere, 2004. **57**(7): p. 615-627.
 56. Colglazier, W., *Sustainable development agenda: 2030*. Science, 2015. **349**(6252): p. 1048-1050.
 57. *Break Free from Plastic Pollution Act of 2021*, in S. 984. 2021.
-

58. Westlake, J.R., et al., *Biodegradable Active Packaging with Controlled Release: Principles, Progress, and Prospects*. ACS Food Science & Technology, 2022.
59. Savoie, P., et al., *Evaluation of apple pulp and peanut butter as alternative bunker silo covers*. Canadian Biosystems Engineering, 2003. **45**: p. 2-17.
60. Garrison, T.F., A. Murawski, and R.L. Quirino, *Bio-based polymers with potential for biodegradability*. Polymers, 2016. **8**(7): p. 262.
61. Jeevahan, J. and M. Chandrasekaran, *Nanoedible films for food packaging: A review*. Journal of Materials Science, 2019. **54**(19): p. 12290-12318.
62. Baghi, F., et al., *Advancements in biodegradable active films for food packaging: Effects of nano/microcapsule incorporation*. Foods, 2022. **11**(5): p. 760.
63. Pandit, P., et al., *Functionality and properties of bio-based materials*. Bio-based materials for food packaging: Green and sustainable advanced packaging materials, 2018: p. 81-103.
64. Costa, M.J., et al., *Physicochemical properties of alginate-based films: Effect of ionic crosslinking and mannuronic and guluronic acid ratio*. Food hydrocolloids, 2018. **81**: p. 442-448.
65. Dhanapal, A., et al., *Edible films from polysaccharides*. Food science and quality management, 2012. **3**(0): p. 9.
66. Li, Z., et al., *Chitosan–alginate hybrid scaffolds for bone tissue engineering*. biomaterials, 2005. **26**(18): p. 3919-3928.
67. Nie, L., et al., *Effects of surface functionalized graphene oxide on the behavior of sodium alginate*. Carbohydrate polymers, 2015. **117**: p. 616-623.
68. Gavrilescu, D., *Pulping fundamentals and processing*. Pulp Production and Processing: High-Tech Applications, 2020: p. 19.
69. Sixta, H., *Handbook of pulp*. Wiley. 2006, Vch Verlag, Weinheim.
70. Cai, J., et al., *Dynamic self-assembly induced rapid dissolution of cellulose at low temperatures*. Macromolecules, 2008. **41**(23): p. 9345-9351.
71. Soongswang, P., et al., *Efficient test setup for determining the water-permeability of concrete*. Transportation research record, 1988. **1204**: p. 77-82.

72. Denoncourt, P., A. Amyot, and M. Lacroix, *Evaluation of two biodegradable coatings on corn silage quality*. Journal of the Science of Food and Agriculture, 2006. **86**(3): p. 392-400.
 73. Jin, H., C. Zha, and L. Gu, *Direct dissolution of cellulose in NaOH/thiourea/urea aqueous solution*. Carbohydrate research, 2007. **342**(6): p. 851-858.
 74. Xiong, B., et al., *Dissolution of cellulose in aqueous NaOH/urea solution: role of urea*. Cellulose, 2014. **21**: p. 1183-1192.
 75. Fridrihsone, V., et al. *Dissolution of various cellulosic materials and effect of regenerated cellulose on mechanical properties of paper*. Trans Tech Publ.
 76. Menu, B., M. Jolin, and B. Bissonnette, *Studies on the influence of drying shrinkage test procedure, specimen geometry, and boundary conditions on free shrinkage*. Advances in Materials Science and Engineering, 2017. **2017**.
 77. Bažant, Z.P. and A. Donmez, *Extrapolation of short-time drying shrinkage tests based on measured diffusion size effect: concept and reality*. Materials and Structures, 2016. **49**: p. 411-420.
 78. Shaari, N. and S.K. Kamarudin, *Characterization studies of sodium alginate/sulfonated graphene oxide based polymer electrolyte membrane for direct methanol fuel cell*. Malaysian Journal of Analytical Sciences, 2017. **21**(1): p. 113-118.
 79. Sanjeevi, S., et al., *Effects of water absorption on the mechanical properties of hybrid natural fibre/phenol formaldehyde composites*. Scientific Reports, 2021. **11**(1): p. 13385.
 80. Semugaza, G., *Comparative shrinkage properties of pavement materials including recycled concrete aggregates with and without cement stabilisation*. 2016.
 81. Gao, C., E. Pollet, and L. Avérous, *Properties of glycerol-plasticized alginate films obtained by thermo-mechanical mixing*. Food Hydrocolloids, 2017. **63**: p. 414-420.
 82. Ameen, S., et al., *Synthesis and characterization of novel poly (1-naphthylamine)/zinc oxide nanocomposites: application in catalytic degradation of methylene blue dye*. Colloid and Polymer Science, 2010. **288**(16): p. 1633-1638.
 83. Wang, L.-F., S. Shankar, and J.-W. Rhim, *Properties of alginate-based films reinforced with cellulose fibers and cellulose nanowhiskers isolated from mulberry pulp*. Food Hydrocolloids, 2017. **63**: p. 201-208.
-

