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# Sprayable Polysaccharide-Based Fiber Reinforced Emulsions for Environmentally Sound Plasticulture

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**Summary:** The increasing demand for mulching and solarization in agriculture is posing serious problems of environmental concerns. Practically all these films are collected by the farmers and left on the ground borders to be incinerated. The same collection by the farmer is difficult; these films being thinner and damaged, their removal through automatic means is almost impossible. The research has focused on an innovative approach where a sort of sprayable water-based varnish is applied on soil. Such varnish, made of biodegradable polysaccharides mixture, contains biodegradable plasticizers to allow the film to remain elastic for the time needed. Moreover, a set of fibrous natural fillers have been tested, which can be mixed in the varnish or can be preventively applied on soil. The agronomic performances have been measured, together with mechanical properties and degradation behavior. The results seem to confirm the technical feasibility of such approach in developing a sustainable plasticulture.

**Keywords:** Polysaccharides

## Introduction

The use of plastics in agriculture causes the bulky problem of the waste disposal. The growing interest in environmental protection has been orienting research to the development of coatings based on biodegradable and renewable agricultural raw materials. The introduction of waterborne spray formulation of biodegradable polymers can be a solution because the disposal of biodegradable spray mulching coatings could be accomplished by incorporating them into soil by tilling the field at the end of cultivation. The lecture examines the main results obtained during applications in field of water solution of natural biodegradable polymers sprayed on the cultivation area in order to form a mulch coating. Aim of the research is to evaluate the functionality, the mechanical and the physical properties of biodegradable spray for mulching coatings during two years crop cultivation cycles. The spray coatings were especially formulated to meet the requirement for installation, duration according to type and time of cultivation, safe disposal directly into the cultivation soil upon milling. Physical properties were investigated by means of laboratory tests. Radiometric analysis, SEM analysis, mechanical tensile tests and infrared reflectance spectroscopy were executed on the biodegradable spray coatings samples in order to evaluate the coating properties. In the present lecture, we report on some of the most relevant tests effected in order to characterize the materials.

## Materials and Techniques

### Mechanical Properties

The instrument used for tensile test is a dynamometer Instron Mod. 4301, which conforms to the ISO 5893 standard and is linked to a personal computer for data acquisition.

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The tests were performed on the specimens taken from the soil at successive times. It was so possible to collect a sampling, that throughout mechanical analysis, could give information about the effect of the aging due to the permanence of the materials on the soil. For the tensile analysis and for each time of drawing out, five samples were tested.

They were prepared with a regular punch cutter whose dimension are: 0.5 cm of width × 2.5 cm of length.

Before testing, the samples were conditioned at 48% relative humidity (RH) in a desicator containing a saturated solution of calcium nitrate. All the measurements were performed at room temperature (27–28 °C) and at relative humidity variable in the range of 35–40% RH.

As far as the MA samples is concerned, films removed both from strawberry cultivation (MAS) and from flower cultivation (MAF) were tested. Nevertheless the MA films show inhomogeneous surfaces and changeable thickness; they are realized spraying a polymeric solution on the soil previously treated with a base of fibres spread on it. The films obtained are cross-linked dried gel enriched with fibres particles; for this reason they exhibit several irregularities, so avoiding the usual mechanical testing.

Nevertheless the ICTP research group carried out a different type of mechanical characterization, by which the samples had been undergone to a "puncture test". It consists in penetrating the specimens until the laceration of the same.

Following the photos of a MA sample tested, of the apparatus used and of the circular cups where the samples were trapped are reported. To compare the mechanical performances of different films tested on the soil, the puncture analysis were carried out also on MC and on MS samples.

*Water Vapour Transmission Rate (WVTR)*
The WVTR apparatus consists of:

A **test chamber**, where the assembled test dishes are placed, kept at controlled atmosphere

A **balance** sensible to a change smaller than 1% of the weight changing during the period when a steady state is considered to exist.

A circular **test dish**, impermeable to water or to vapour water; the specimen is attached to the dish by sealing in such a manner that the dish mouth, of 44 mm diameter, defines the effective area of exposition to the water pressure.

The test specimen is sealed to the open mouth of a test dish containing distilled water (100% U.R.), and the assembly placed in a test chamber under controlled condition of temperature (38 °C) and relative humidity (10% RH). An air flow inside the room provides uniform conditions at all test location.

The film separates two environments differently conditioned: inside the test dish there is saturated air (100% U.R.) and a temperature of 38 °C with a water vapour pressure of 6629,8 Pa; in the test chamber there is an air flow at 10% of RH. and a temperature of 38 °C.

The vapour pressure difference allows the transfer of vapour through the specimen from the water to the controlled atmosphere with following weighing loses.

The WVTR calculates as follow:

$$\mathrm{WVTR}(g/24\ \mathrm{h}\cdot \mathrm{m}^2) = \mathrm{G/tA}$$

where

G = weight change, g, t = time during which G occurred, h, A = test area (cup mouth area), $m^2$

## Results and Discussion

### Mechanical Tests

*1 - Chitosan Based Compositions (MCh/PG/CB)*
By the results of tensile properties, it is evident that, the better compromise of mechanical performances is exhibited from the last composition including the carbon black; this material was actually employed for mulching applications.

 

***Table 1.***
Materials tested.

| Description | Code |
|---|---|
| Biodegradable formulations: | |
| **M**ulching **A**lginate based composite | MA |
| **M**ulching polysaccharide PSS20* mixture with cellulose **F**ibres | MF |
| **M**ulching polysaccharide PSS20 mixture with **G**el fibres | MG |
| **M**ulching films from **C**hitosan, **P**oly**g**lycerol and **C**arbon **B**lack of different composition | MCh/PG/CB |
| **M**ulching **S**pray water solution of polysaccharides and cellulosic fibres | MSO |
| **MSO**: The mulching is applied outside greenhouse | MSG |
| **MSG**: The mulching is applied inside greenhouse | |

* PSS20 is the trade name of a guar gum based formulation belonging to PSI AB (SWEDEN).

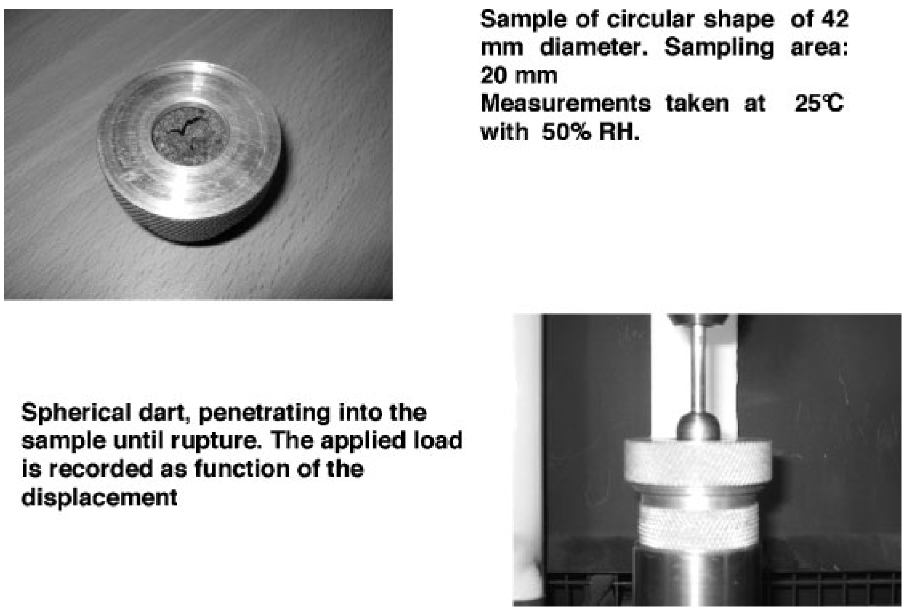


***Figure 1.***
Holder and testing setup for Alginate samples.

2 - *Puncture Test*

As far as MA samples is concerned, films removed both from strawberry cultivation (MAS) and from flower cultivation (MAF) were tested. Nevertheless the MA films show inhomogeneous surfaces and irregular thickness; they are realized spraying a polymeric solution on the soil previously treated with a base of fibres spread on it. The films obtained are cross-linked dried gel enriched with fibres particles; for this reason they exhibit several irregularities, so hampering the usual mechanical testing.

***Figure 2.***
Measuring cell for WVTR.

 

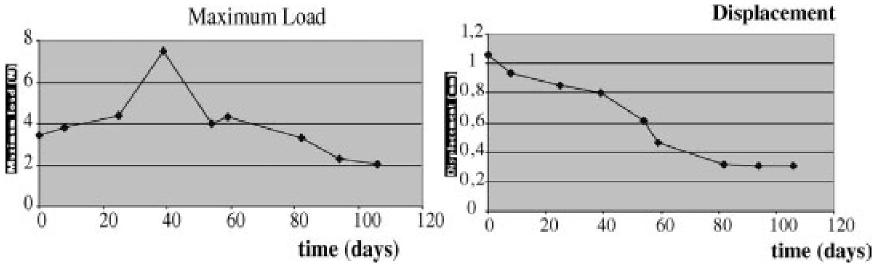


***Figure 3.***
Maximum Load and Displacement as function of time for MAS samples.

Nevertheless a different type of mechanical characterization has been set up, by which the samples undergoes a sort of ''puncture test''. It consists in penetrating the specimens until the laceration of the same.

The tests were performed on samples opportunely cut with a punch cutter of 42 mm circular section; the samples were trapped in cups fixed on the inferior traverse of the INSTRON instrument used for the previous tensile properties. They undertake the action of a force exerted by a spherical dart linked to a steel rod fixed on the upper traverse of the apparatus; the dart goes down moving at a rate of 2 mm/min and penetrate the sample until the rupture of the same. The applied load versus the displacement were recorded.

The parameters obtained were normalized respect to the 1/2 of the area of the sphere and respect to a estimated value of the displacement of 10 mm.

All the measurements were carried out at room temperature on specimens conditioned at 50% of RH. Following the tables of maximum load against the displacement both of MA and of MC samples are reported:

Fig. 3 shows the trend of MAS maximum load and displacement as function of the time. For the too few data of the MAF sample, it wasn't possible to plot the relative curve.

By the analysis of the curves, it is possible to individuate a quite regular trend toward lower values both of the load and of the displacements. This outline is consistent with the loosing of plasticizer during the time of permanence of the coating on the soil; so the film, resulting more rigid, shows both a lower resistance to rupture, and a lower displacement.

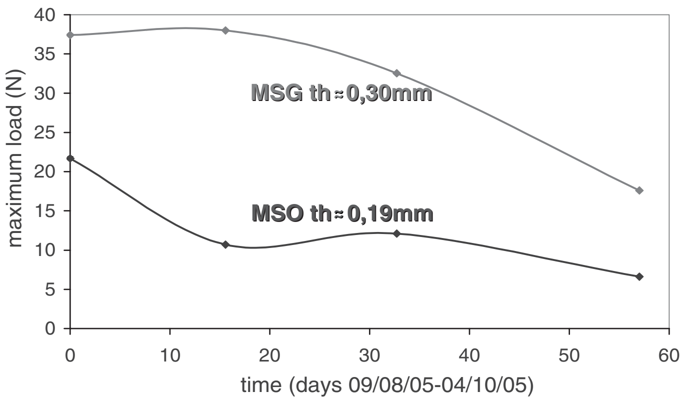


***Figure 4.***
Maximum Load as function of time for MSG and MSO samples.

 

**Table 2.**
Modulus, Stress and strain at break for Chitosan based samples as function of composition.

| Sample | Young Modulus (MPa) | Stress at break (MPa) | Strain at break (%) |
|---|---|---|---|
| Chitosan | 3417 ± 268 | 45.9 ± 3.71 | 13.1 ± 7.75 |
| Chitosan/PG 67/33 | 239.0 ± 62.4 | 28.5 ± 4.93 | 61.3 ± 12.6 |
| Chitosan/PG 50/50 | 72.4 ± 6.69 | 25.4 ± 3.22 | 78.1 ± 9.5 |
| Chitosan/PG/CB 40/40/20 (**MCh/PG/CB**) | 94.3 ± 4.7 | 8.16 ± 0.29 | 38.86 ± 1.55 |

In relation to MSO and MSG samples, it is necessary to emphasize both the different environmental condition of their application, (in open field and greenhouse, respectively), and the different thickness of the samples; these two effects reflect on the outcomes of their mechanical performances. Following the table of puncture test results of MSO and of MSG samples is detailed; in this case the maxima loads (N) versus the aging time of the two samples are reported to underline the substantial differences of loads values of the two samples:

Hereafter the curves of MSG and MSO maximum load in function of the time are reported.

The profile of the curves suggests that MSG samples show better mechanical performances than MSO films; this result is probably ascribed to the different environment in which both the films aged: differently to the films applied in open field, the samples aged in greenhouse didn't undergo the direct action of atmospheric agents (rain, wind, exposition to straight solar radiation); this important issue combined with the film thicknesses substantially different, gives rise both to the shift of the starting maximum load value and to the diverse outline of the curves.

**Table 3.**
Puncture Test results for MA applied on strawberry (MAS).

| MAS | Maximum load (N) | Displacement (mm) |
|---|---|---|
| Day 0 | 3.4 ± 1.6 | 1.058 ± 0.015 |
| Day 8 | 3.8 ± 1.6 | 0.937 ± 0.012 |
| Day 25 | 4.4 ± 6.3 | 0.855 ± 0.098 |
| Day 39 | 7.5 ± 2.2 | 0.803 ± 0.076 |
| Day 54 | 4.0 ± 0.9 | 0.613 ± 0.032 |
| Day 59 | 4.3 ± 3.0 | 0.467 ± 0.045 |
| Day 82 | 3.3 ± 1.5 | 0.318 ± 0.109 |
| Day 94 | 2.3 ± 0.4 | 0.309 ± 0.098 |
| Day 106 | 2.1 ± 1.0 | 0.311 ± 0.096 |

## Concluding Remarks

The results obtained highlighted that the innovative spray coatings can promote sustainable agriculture, environmentally friendly agricultural practices and the use

**Table 4.**
Puncture Test results for MA applied on flower (MAF); the films were tested until the 38$^{th}$ day, because after that date the samples resulted already broken.

| MAF | Maximum Load (N) | Displacement (mm) |
|---|---|---|
| Day 0 | 4.4 ± 1.1 | 0.994 ± 0.100 |
| Day 15 | 4.4 ± 3.3 | 0.836 ± 0.053 |
| Day 38 | 6.6 ± 4.8 | 0.830 ± 0.097 |

**Table 5.**
Puncture Test results for MSG and MSO samples.

| Time (days) | MSG Maximum load (N) ±20% | MSO Maximum load (N) ±20% |
|---|---|---|
| 0 | 37,4 | 21,7 |
| 16 | 38,0 | 10,7 |
| 33 | 32,5 | 12,1 |
| 57 | 17,6 | 6,6 |

 

of non-oil renewable raw materials for the mulching realization. It is of coarse a big challenge to compete with existing materials based on Polyethylene for performances and price, but the recent trend goes in the direction of cheaper polysaccharides (starch) and in the application in pot cultivations for flower and vegetables, where it is not possible to use plastics, and some of the formulations show promising effects against the development of spontaneous weeds.

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[1] C. Bastioli, *Macromol. Symp.* **1998**, *135*, 193–204.
[2] P. L. Nayak, *J.M.S.-Rev. Macromol. Chem. Phys.* **1999**, *C39*, 481–505.
[3] X. L. Wang, K. K. Yang, Y. Z. Wang, *J. Macromol. Sci. Part C* **2003**, *C43*, 385–409.
[4] O. Olabisi, L. M. Robinson, M. T. Show, "*Polymer-Polymer Miscibility*", Academic Press, **1979**,
[5] C. Xiao, Y. Lu, H. Liu, L. Zhang, *J.M.S. – Pure Appl. Chem.* **2000**, *A37*, 1663–1675.
[6] R. Chadra, R. Rustgi, *Progr. in Polym. Sci.* **1998**, *23*, 1273–1335.
[7] P. Halley, R. Rutgers, S. Coombs, J. Gralton, M. Jenkins, H. Beh, K. Griffin, R. Jayasekara, G. Lonergan, *Starch* **2001**, *53*, 362–367.
[8] D. L. Kaplan, J. M. Mayer, M. Greenberger, R. A. Gross, S. McCarthy, *Polym. Degrad. and Stability* **1994**, *45*, 165–172.
[9] D. Briassoulis, *J. Of Polym. And the Environment* **2004**, *12*, 65–81.
[10] B. Immirzi, M. Malinconico, G. Romano, R. Russo, G. Santagata, *J. Material Sci. Letter* **2003**, *22*, 1389–1392.
[11] J. Katan, A. Greenberger, H. Alon, A. Grinstein, *Phytopathology* **1976**, *66*, 683–688.
[12] J. Katan, A. Grinstein, A. Greenberger, O. Yarden, J. E. DeVay, *Phytoparasitica* **1987**, *15*, 229–255.
[13] J. I. Stapleton, J. Quick, I. E. DeVay, *Soil Biol. Biochem.* **1985**, *17*, 369–373.
[14] L. Pacini, *Plasticulture* **1993**, *100*, 13–16.
[15] K. I. Draget, G. Skjak Braek, O. Smidsrod, *Intern. J. Biol. Macromol.* **1997**, *21*, 47–55.
[16] H. Grasdalen, B. Larsen, O. Smidsrod, *Carbohydr. Res.* **1981**, *89*, 179–185.
[17] D. Gomez-Diaz, J. M. Navata, *J of Food Engin.* **2004**, *64*, 143–149.
[18] O. Holte, E. Onsoyen, R. Myrvold, J. Karlsen, *Eur. J. of Pharm. Sci.* **2003**, *20*, 403–407.
[19] W. R. Gombotz, S. F. Wee, *Adv. Drug Deliv. Rev.* **1998**, *31*, 267–285.
[20] P. Mormile, L. Petti, B. Immirzi, M. Malinconico, V. De Luca, C. Manera, *Appl. Spectroscopy* **2001**, *55*, 858–863.
[21] R. Avissar, Y. Maher, L. Margulies, J. Katan, *Soil Sci. Soc. Am. J.* **1986**, *50*, 202–205.
[22] R. Avissar, Y. Maher, L. Margulies, J. Katan, *Soil Sci. Soc. Am. J.* **1986**, *50*, 205–209.
[23] T. Takakura, K. Kurata, T. Honjo, HIS Acta Horticulturae 174 – Symposium Greenhouse Climate and its Control. Editor Germing G.H. **1985**, Physical models and the Greenhouse Climate.
[24] P. Mormile, L. Petti, B. Immirzi, M. Malinconico, C. Manera, E. De Luca, - 15th International Congress for Plastics in Agricolture (Plasticulture 2000), Pennsylvania – USA, September 23–27, **2000**.
[25] D. Briassoulis, An overview on the mechanical behaviour of biodegradable agricultural films. *J. of Polymers and the Environment* **2004**, *12*(2), 65–81.
[26] R. Chandra, R. Rustgi, Biodegradable polymers. *Progress in Polymer Science* **1998**, *23*, 1273–1335.
[27] P. Halley, R. Rutgers, S. Coombs, J. Gralton, G. Christie, M. Jenkins, H. Beh, K. Griffin, R. Jayasekara, G. Lonergan, Developing biodegradable mulch films from starch-based polymers. *Starch* **2001**, *53*, 362–367.
[28] D. L. Kaplan, J. M. Mayer, M. Greenberger, R. A. Gross, S. P. McCarthy, Degradation methods and degradation kinetics of polymer films. *Polym. Degrad. and Stability* **1994**, *45*, 165–172.
[29] J. M. Krochta, C. L. C. De Mulder-Jphnston, Biodegradable polymers for agricultural products. ACS Symposia (G. Fuller T.A. McKeon, D.D. Billis Eds) **1996**, 121.
[30] R. Narayan, Drivers for biodegradable/compostable plastics and role of composting in waste management and sustainable agriculture. Bioprocessing of Solid Waste and Sludge, 11 (1), **2001**, www.orbit-online.net/journal/archiv/index.html
[31] G. Scarascia Mugnozza, E. Schettini, G. Vox, Effects of the solar radiation on the radiometric properties of biodegradable films for agricultural applications. *Biosystems Engineering* **2004**, *87*(4), 479–487.
[32] R. S. Tocchetto, R. S. Benson, M. Dever, Outdoor weathering evaluation of carbon-black-filled, biodegradable copolyester as substitute for traditionally used, carbon-black-filled, non-biodegradable, high-density polyethylene mulch films. *J. of Polymers and the Environment* **2002**, *9*(2), 57–62.

 