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Liquid Mulch Based on Poly(Vinyl Alcohol). PVA-Soil Interaction

Emo Chiellini,[1] Patrizia Cinelli,[1] Salvatore D'Antone,[1] Vassilka I. Ilieva,[1]*
Simone Magni,[2] Sergio Miele,[2] Silvia Pampana[2]

[1] UdR-INSTM Consortium @ Department of Chemistry & Industrial Chemistry, University of Pisa, Via Risorgimento 35, 56126 Pisa, Italy.
[2] Department of Agronomy & Agroecosystem Management University of Pisa, Via San Michele 2, 56124 Pisa, Italy

Summary: This study is meant to provide a contribution in recent developments of biodegradable polymeric materials applied in agricultural practices with particular reference to the mulching segment. Special attention has been devoted to material based on renewable resources or utilization of waste products from agro-industrial activities, thus suggesting cost-effective and environmentally sound solutions to specific social needs. In the present contribution PVA solubility at room temperature has been improved by premixing with chemical additives and proteic materials. Waste materials from ethanol production by corn fermentation and from wood industries have been used as, respectively starch-based and lignocellulosic additives. The prepared formulations were applied on the soil by conventional spraying agricultural equipment. Time of permanence of the film formed on the soil was monitored as well as the effect on corn growth and yield production. Finally, in order to investigate the final fate of the PVA applied on the soil, a test was performed in lysimeters, with half of the lysimeters cropped with maize plants. PVA amount applied for the mulching test was in order of 5-10 g PVA/1 m^2; under those conditions it resulted completely absorbed and no presence of PVA was recorded in the leached solutions

Keywords: lignocellulosic; mulch; poly(vinyl alcohol); renewable resources; soil

Introduction

Semi-dry and liquid mulches have a large range of application, chiefly as soil structuring agents or binders for seedling on soil where structure and slope can be limiting factors for seedling establishment [1-6]. The stabilization of friable soils has a great importance in order to avoid soil slippage. Thus soil erosion threatens water quality and agricultural productivity because of the runoff of chemicals and the loss of valuable top soil. Few soils possess the optimum physical and chemical characteristics for maximum productivity with no previous addition of some type of amendments. Most of these amendments are chemicals but several studies have been conducted to

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evaluate the influence of both mineral and organic polymers on soil physical properties [7]. Improvements in soil conservation have been achieved by addition of polymeric materials to the in irrigation systems [8-10].

Polymers may also be present as tackyfiers to help holding the mulching materials in place once applied. In some cases, a type of thatch is formed that protects seeds and soil against erosion. Hydrophilic polymers, such as poly(acrylamide) (PAM), poly(vinyl alcohol) (PVA), carboxymethyl cellulose, and hydrolyzed starch-*g*-poly(acrylonitrile) copolymers (HSPAN) have been proposed as soil conditioners in these techniques called hydro-mulching [11,12]. The successful use of PAM in irrigation water raises the interest for the use of other polymers with similar properties, but concerns have increased about the widespread use of PAM in open agricultural environment since the monomer, acrylamide, is a neurotoxin [13]. Even the use of PAM almost devoid of monomer (<0.05%) does not eliminate the concern that the monomer can occur as a degradation product by early removal of the amine group from the polymer backbone [13]. Thus the interest for the final fate of polymers applied in agriculture and possible ecotoxicity of degradation products is raising [14].

Poly(vinyl alcohol) (PVA) has shown a positive structuring effect on soil [15-19] moreover it is a non toxic, biocompatible material, thus it appears suitable for application in open fields.

Previous studies indicated that the introduction of natural fillers in the sprayed mixtures allowed for a longer lasting of PVA structuring effect on the soil [20]. Mixture based on PVA and wheat flour or sugarcane bagasse evidenced a promoting effect on lettuce growth and particularly on the conservation of soil structure [21].

For these reasons in the present work were investigated formulations of mixtures based on PVA, supported with proteins and natural fillers whichwere selected in order to reduce final costs of the formulations and beside to provide organic matter in the soil, combining a structuring effect with a covering, colouring and fertilizing one. Moreover the possible final fate of PVA was investigated with particular attention at the possibility of PVA leaching in water tables.

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Materials

Polyvinyl alcohol (PVA Mowiol 05/88, Hoechst) was 88% hydrolyzed with an average molecular weight of 37 KD.

Lignocellulosic based and starch based materials were respectively by-products of wood industry (Nuova Rivart, Italy) and of ethanol biorefinary, from maize fermentation (corn condensed soluble distillate, Williams, IL, USA).

Proteic materials of animal source were by-products of leather industry, proteic hydrolizate (PH), (S.Croce, Italy).

Boric Acid, KI and I_2 resublimed were Carlo Erba products.

Experimental

Conditioning effects on soil structure were evaluated in a field trial while a lysimetric plant was used to collect water leached from the soil surface in order to investigate the possible ground water contamination. In both trials, bare soil application was compared with the distribution to soil on which maize (*Zea mais* L.) was cultivated in order to investigate possible effects due to the crop.

Soil was respectively a loamy soil, in the field, and a sandy loam soil in the lysimeters. Soil characteristics are reported in Table 1.

Table 1. Soil Characteristics

Soil	**Field**	**Lysimeter**
Sand (%)$^+$	42.8	59.3
Silt (%)	40.2	30.2
Clay (%)	17.0	10.5
pH^a	8.2	7.7
Nitrogen (%)^b	1.2	1.3
EC (1:2) (mS)	0.2	2.0
Lime Content	1.8	9.2

$^+$USDA Soil Texture Classification, ^{a} 2.5:1, soil:water, ^{b}Kjeldhal Method

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Starch and lignocellulosic based mixtures were tested in two different PVA application rates equivalent to 5 (optimal, SO, LCO) and 10 (double, SD, LCD) g/m^2, as reported in Table 2.

Table 2. Mixture composition

Mixture	PVA	S	LC	PH
LCO	5.0	-	8.0	1.5
LCD	10.0	-	8.0	1.5
SO	5.0	10.0	-	1.0
SD	10.0	10.0	-	1.0

S= Corn Condensed Soluble Distillate, LC= Wood industry by-products, PH= Proteic Hydrolizate, LCO = Lignocellulosic Optimal PVA amount, LCD = Lignocellulosic Double PVA amount, SO = Starch Based Optimal PVA amount, SD = Starch based Double PVA amount

Field Trial

The field trial was carried out from June to September 2001 in the experimental station of DAGA in Rottaia – Pisa (43° 67' N, 10° 30' E). The climate in the area is typically mediterranean with a dry-warm period in summer and a cool-rainy one in autumn.

A split-split-plot experimental design with three replications was adopted, with mixture as main treatment and PVA application rate and crop presence as secondary and tertiary treatment respectively. Plot size was 2 x 2.5 m. Mixtures (LCO, LCD, AO, AD) were applied on plots, respectively with and without crop. No mixtures application was performed on control plots.

The ingredients were introduced in a sprayer tank, mixed with the appropriate amount of water and applied on the soil surface by a five nozzles (Ø 0.1 mm) sprayer (20 bar, 20ml/min).

The crop was managed as ordinary in the area for what concerns tillage, fertilization and irrigation.

The conditioning effects on soil structure produced by the different mixtures were monthly evaluated by the collection of soil core samples taken at different depths in the soil profile (0-20 and 20-40 cm depth respectively). Moisture content was determined on a dry weight basis.

Special attention was dedicated to soil moisture since water availability plays a major role in determining crop yield.

At the end of the crop cycle total biomass production and grain yield were also recorded.

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Data were subjected to analysis of variance and LSD with P≤ 0.05 was used to detect differences between means. Significant effects of treatments are discussed below. For the data of June 29th the DMS was 1.5, for the data of August 3rd DMS was 1.0.

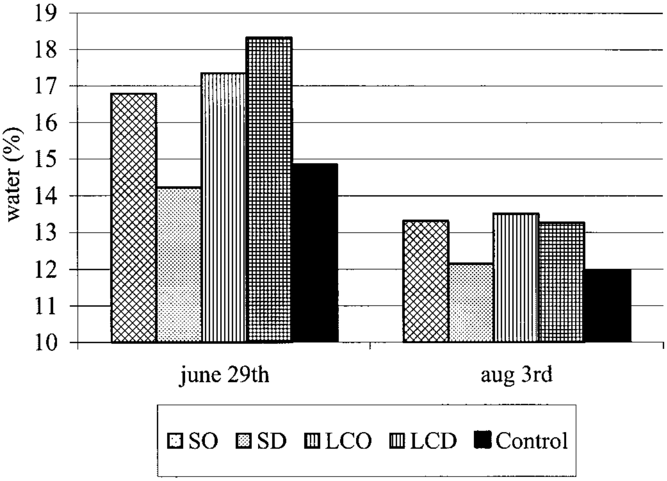

Figure 1. Soil moisture content at 0-20 cm depth.

As shown in Figure 1, SO, LCO and LCD mixtures determined in the first layer of the soil profile (0-20 cm depth) a moisture percentage higher than the one recorded for no-treated plots. This effect was recorded until full summer (August), a period in which water availability is very important in determining crop production. Nevertheless maize did not reach statistically different yield levels (data not shown) possibly because the seeding took place late in the spring (May the 30th) and plants were not able to take advantage of larger water availability in soil due to the mixtures effect. For mixtures based on lignocellulosic filler, no difference was produced by the PVA application rates (LCO, LCD) while, when starch fillers are used, the double PVA application rate (SD) accounted for sensible reduction of soil moisture. This unexpected effect could be attributed to evident cracking of soil observed in SD conditioned plots. More uniform soil structure obtained with the application of lignocellulosic based mixtures suggested that this type of fillers appears more promising for liquid mulch formulations.

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Lysimetric Trial

As previously discussed the possible leaching of soil structuring polymers, or their constituent monomer (as a result of degradation, or synthesis impurities) induced concerns on their use in agriculture. In order to investigate the fate of the PVA after application on the soil, a trial was performed in lysimeters (0.6 m wide, 0.6 m long, 0.75 m deep). Mixtures were applied by using an air compressor (Fini, Italy), working at 3 bar pressure and equipped with a 2.5 mm nozzle (Figure 2).

Figure 2. Mixtures Application by Spraying in Lysimetric Trial.

An experimental design as described for the field trial, with two replicates, was adopted. Each cropped every lysimeter contained four maize plants. The lysimeters were irrigated weekly and the leached solution was collected 7 times during the experiment duration (about 4 months). The total amount of leached solution collected was about 100 L for the uncropped lysimeter, and about 50 L for the cropped ones, because of water consumption by the crop.

A sample of 500 ml was isolated from each of the seven collected fractions. This sample was purified from soil debris by filtration and concentrated by rotavapor (Rotavapor BUECHI R-114), water bath 35 °C about 2 h for each sample. The concentrated solution (2 ml) was then frozen and liophilized. Solid residues of about 1g/500g solution and 0.5g/500g solution were recorded for respectively samples from plots without and with maize. No significant difference

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was recorded on the solid residue in controls and conditioned plots. PVA presence in the leached solutions was investigated by the absorbance (690 nm) of PVA-iodine complex, as reported by Finley [22]. A calibration curve has been drawn by use of a PVA standard solution (0.100 mg/ml) prepared with PVA Mowiol 05/88, Hoechst. From the calibration curve (Figure 3), derived from the PVA-iodine complex absorbance values at 690 nm plotted against the quantity of PVA contained in the 50 ml volumetric flask, utilized for the analysis, the following formula was obtained: Abs = 0.60142 [PVA] + 0.014621.

The leached solution collected from the control showed no absorbance at 690 nm, and when a determined amount of PVA was introduced in this solution its presence was regularly revealed by the standard procedure. 25 ml of each collected fraction were intorduced in a 50 ml volumetric flask, and analyzed according to the standard procedure[22]. Similarly the residue (of 500 ml) was dissolved in 100 ml of water (5 times concentrated) and 25 ml of this solution were analyzed. No PVA presence was revealed both in the normal and in the concentrated solutions. These results may be attributed to a complete adsorption of PVA by the soil since PVA is known to interact strongly with single soil components [23].

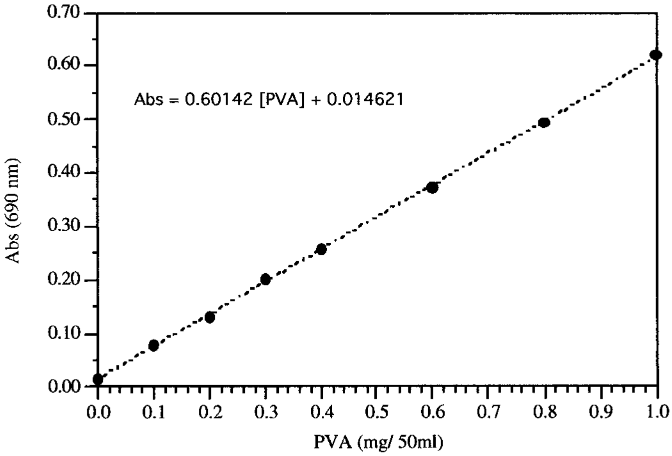

Figure 3. Calibration Curve of PVA 05/88, Mowiol, Hoechst, Absorption at 690 nm.

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In order to evaluate the capacity of adsorption of the agricultural soil present if the lysimeters two experiment were performed in lab-scale 10 g of agricultural soil were placed in a 250 ml conical flask in the presence of 100 ml of a water solution containing respectively 25, 50, 75 and 100 mg of PVA, and stored in the dark. Three ml of the solution were collected, clarified and 1ml of the supernatant was analyzed by the absorbance (690 nm) of PVA-iodine complex. By correlation of the PVA content with the calibration curve, the PVA adsorption by the soil was recorded. Results are shown in Figure 4.

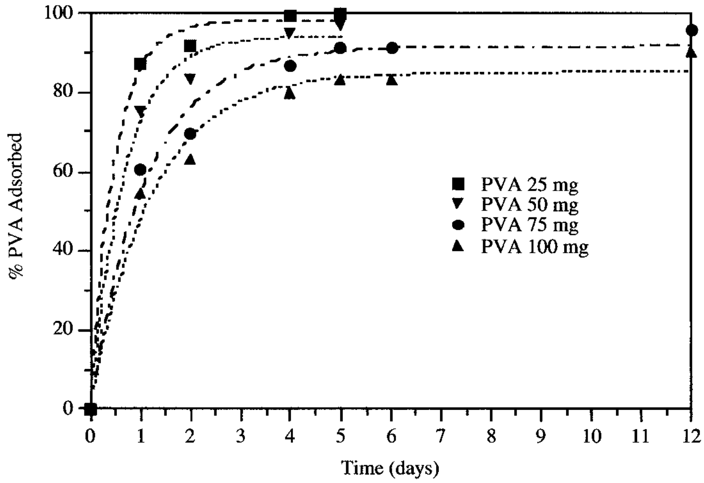

Figure 4. Adsorption Rate of PVA on 10 g of Agricultural Soil.

In a few days the PVA was completely adsorbed by the soil, the rate of adsorption being faster for the more dilute solutions. In the second experiment 100 ml of a solution containing 100 mg of PVA (1mgPVA/1ml) were placed in 250 ml conical flasks containing respectively 10, 30 and 50 g of soil. Similarly to the previous experiment, PVA was completely adsorbed in a few days and at a faster rate for higher soil/PVA ratio (Figure 5).

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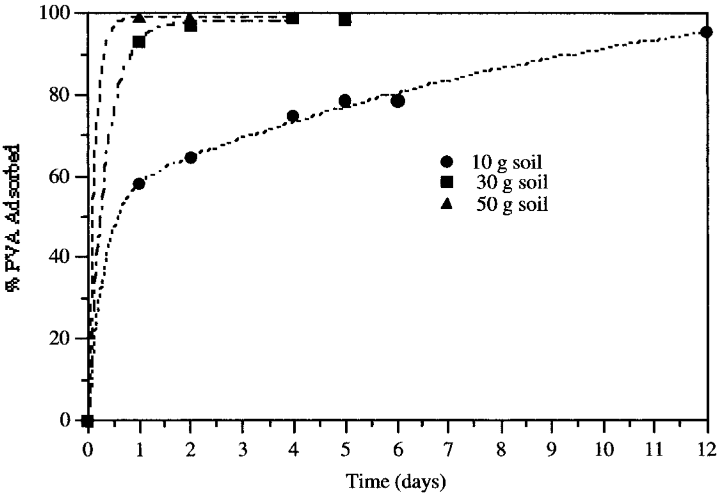

Figure 5. Adsorption Rate of PVA on respectively 10, 30 and 50 g of Soil.

On the basis of these preliminary results, the amount of PVA applied either in the field or in the lysimeters (5-10 g/m^2) should be rapidly adsorbed by just 1-2 Kg of soil. Thus any attempt to recover the adsorbed PVA from the soil, e.g. by suspension of the soil in hot water, gave negative results.

Conclusions

Mixture based on powdered low molecular weight PVA, premixed with proteins and natural fillers proved to be suitable for application, in the form of water suspensions at room temperature, by conventional spraying equipments. Results from field test pointed out a larger water availability in the treated soils than in the control plots, when the fillers had a lignocellulosic nature.

PVA used in the present study was rapidly adsorbed by the soil. No presence of PVA was recorded in the leached solutions. The role of soil adsorption was reported in the present work, while analysis on PVA degradation by microorganisms are in progress.

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On the basis of these observations, the risk of ground water contamination by PVA or any degradation products doesn't seem to constitute a major environmental concern related to the use of PVA based films for agricultural applications.

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