Fluid Biomulching Based on Poly(vinyl alcohol) and Fillers from Renewable Resources

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ABSTRACT: This article reports on the results obtained in an investigation on the application of biodegradable polymeric materials in the agricultural practice of mulching. Particular attention has been devoted to the effect of biobased mulching films generated *in situ* by low-pressure spraying of polymeric water dispersions on the various cultivars. In a field trial, the effectiveness of the hydromulching (liquid-mulching) technique was assessed by the monitoring of the growth and yield of lettuce and corn, which were used as reference plants. Conventional plastic films and straw mulching (SM) were compared with liquid-mulching treatments based on poly(vinyl alcohol) and natural fillers derived from agroindustrial wastes (sugar cane bagasse, wheat flour, saw dust, and wheat straw). An improvement of the biomass yield of the two selected plants with respect to conventional polyethylene mulching was attained in various liquid-mulching formulations with positive effects on the maintenance of soil structure. Alternative fluid-mulching treatments based on biodegradable components were effective in preserving soil aggregates and improving some crop growth parameters. © 2007 Wiley Periodicals, Inc. J Appl Polym Sci 108: 295–301, 2008

Key words: biodegradable; fibers; renewable resources; waste

INTRODUCTION

Synthetic polymeric materials are commonly used in a variety of agricultural applications, for which the term *plasticulture* has been coined. Thermoplastics, elastomers, fibers, and water-soluble polymers are presently used for the controlled release of fertilizers or pesticides, soil conditioning, plant protection, seed coating, gel planting, water transport, and packaging. Mulching sheets and films represent, however, the largest application share of plastics in agriculture.[1]

Mulching is aimed at controlling radiation, soil moisture and temperature, weed invasion, insect infestation, soil compaction, and the degree of carbon dioxide retention, and it has been adopted for different kinds of cultivation. Mulched crops ripen faster, their yields frequently are increased, and in some cases, the reduction or absence of soil contamination adds value to the harvested products.[2] In most cases, once the plastic films have exerted their role along with the crop life cycle, they are removed because they can have negative effects on soil tilling and seed bed preparation for the subsequent crop.

Where the recovery of plastic materials is not economically feasible, controllable, or attractive, the production of large amounts of waste materials may generate major environmental concerns if appropriate, labor-demanding, and costly disposal practices are not adopted. Low-density polyethylene, poly(vinyl chloride), poly(butylene), and copolymers of ethylene with vinyl acetate are generally used for the production of mulching films.

According to the European Community Directives, waste materials deriving from agricultural and agrochemical activities have been classified as special or dangerous wastes for which postconsumer reclamation and specific costly disposal treatments are required.[3,4] Costs of waste properly recovered either as feedstock material or by mechanical recycling may be in many instances even higher than the cost of the virgin material itself.

Furthermore, film deterioration due to thermal and photophysical oxidation during the service life, combined with soil contamination, can make the collection and recycling of mulching films even less attractive because of cleaning costs and downgrading of material characteristics.

Because the use of degradable polymers suitable to be biodegraded in place could reduce or even eliminate disposal and recycling costs, interest in the development of photobiodegradable,[5] biodegradable,[6]

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and, more recently, oxobiodegradable[7] materials with short and controllable service lifetimes have attracted a great deal of scientific and economic interest.

Although a large number of polymeric materials have been designed for controlled degradation, only a few have reached the commercialization stage on a large scale. Films based on starch with poly(vinyl alcohol) (PVA),[8] poly(ethylene-*co*-acrylic acid),[9] poly(vinyl chloride),[10] and photodegradable poly (1-butene)[11] have been developed in the past, but their biodegradation was seriously disputable.

A mulching effect or a conditioning effect on the soil structure can also be obtained by the technique referred to as *hydromulching* or *liquid mulching*.[12] Because of their water solubility, some synthetic degradable polymers such as polyacrylamide, PVA, carboxymethylcellulose, and hydrolyzed starch-*g*-polyacrylonitrile can be easily sprayed onto the soil surface with the aim of forming a film that can positively affect the soil structure. Nutrients, fillers, and tackifiers can also be included in the mixture to obtain a sort of thatch layer with improved properties of soil protection, moisture retention, and nutrient availability for cultivars.[13,14]

A wide number of natural polymers, together with different materials from renewable resources, such as agricultural byproducts, can be used as fillers in blends or composites with synthetic polymers.[15]

Among these last, PVA is known to display a positive effect on the soil structure[16,17] and on the stability and porosity of loamy and clay soil.[18,19] PVA, being a nontoxic, biocompatible, and biodegradable material,[20] appears to be a suitable ingredient for soil application. Moreover, because of its functionality, PVA is suitable to be blended with natural materials such as starch,[21] pectin,[22] cellulose,[23] chitin,[24] soy protein,[25] gelatin,[26] and sugar cane bagasse (SCB) and agriculture byproducts such as apple and orange peels from fruit juice extraction[27] and corn fibers from ethanol production.[28]

This contribution is aimed at reporting on an ongoing investigation[29–32] relevant to the formulation and applicability of mixtures of PVA as synthetic water-soluble polymeric materials and biobased fillers in hydrobiomulching practice by highlighting the advantages with respect to the traditional mulching technology.

EXPERIMENTAL

Materials

PVA (grade 8/88 Mowiol, number-average molecular weight = 67 kD, hydrolysis degree = 88%) was purchased from Erkol (Tarragona, Spain) and used as received. Wheat flour (WF) was a commercial product (Rovato, BS, Italy) with the following composition: 45.5% starch, 34.8% hard fibers, 2.0% ash, 2.2% cellulose, and 15.5% moisture. SCB was kindly supplied by Copersucar (Sao Paulo, Brazil). Before use, SCB fibers were conditioned in an oven at 50°C for 24 h, crushed by a blade grinder, and sieved. The fraction passing through a 70-mesh ASTM sieve (<0.212 mm) was collected. SCB powders were composed of dark brown fibers about 100–150 μm long and 10–50 μm wide. The composition of the sieved sample was 42.6% hard fibers, 29.2% cellulose, 10.5% lignin, 9.1% protein, 2.6% fat, and 6.0% ash. Figure 1 presents a scanning electron microscopy picture of SCB powders (T300 scanning electron microscope, JEOL, Tokyo, Japan).

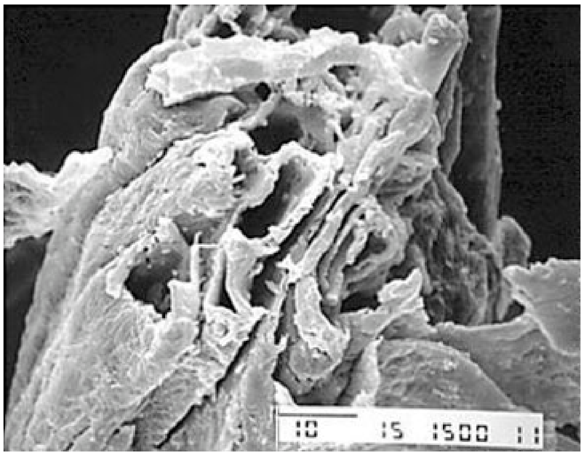

Figure 1 Scanning electron microscopy image of SCB fibers.

The saw dust (SD) was a commercial daily-use product. The wheat straw (WS) was a commercial product (Experimental station of University of Pisa, Rotala, PI, Italy) used both as a raw material (stem average length = 1 m) and as a coarsely ground material (20-mm particle size).

Poly(potassium aspartate) (Pasp) was prepared by hydrolysis of polysuccinimide according to the procedure reported by Alford et al.[33]; polysuccinimide (QR-1420) was kindly supplied by Rohm & Haas (Philadelphia, PA) (weight-average molecular weight = 10 kD).

The urea–formaldehyde (UF) resin was a solid product kindly supplied by Sadepam SRL (Mantova, Italy). Elemental analysis of the resin gave the following results: C, 33.18%; H, 6.70%; and N, 31.22%.

The black polyethylene (PE) film was a commercial mulch film (75 μm thick).

The area or open field trial was located at the Department of Agronomy, Faculty of Agriculture, University of Pisa (43° 40′ N, 10° 23′ E, 6 m asl).

The characteristics of the soil were as follows: 38% sand, 21% silt, and 41% clay.

Thermogravimetric analysis

A Mettler TA4000 system (MettlerToledo, Greifensee, Switzerland) consisting of a TG50 furnace, M3

TABLE I
Composition of the Mulching Formulations Used in the Comparative Field Trial

Hydrobiomulching treatment	PVA (g/m^2)	Organic filler		Water (g/m^2)
		Type	g/m^2	
SCB UF	20	SCB	40[a]	340
SCB Pasp	20	SCB	40[b]	340
SCB	20	SCB	40	340
WF UF	20	WF	40[a]	340
WF Pasp	20	WF	40[b]	340
WF	20	WF	40	340
WS UF (milled)	20	WS (milled)	500[a]	380
WS Pasp (milled)	20	WS (milled)	500[b]	380
WS (milled)	20	WS (milled)	500	380
SD UF	20	SD	500[a]	380
SD Pasp	20	SD	500[b]	380
SD	20	SD	500	380

[a] UF (2 g/m^2) was added.
[b] Pasp (2 g/m^2) was added.

microbalance, and TA72 GraphWare was used for thermogravimetric measurements. Samples (ca. 10 mg) were heated from 25 to 600°C at a 10°C/min scanning rate under a nitrogen atmosphere (flow rate $\approx$ 200 mL/min). The onset temperature was determined as the temperature evaluated at the crossover of tangents drawn on both sides of the decomposition trace.

Field trial experiment

In a field trial carried out at Pisa University between June and September, two conventional mulching materials were compared with 12 innovative hydrobiomulching formulations. Black PE film and straw mulching (SM) (SW; 1000 g^{-2} WS as the raw material) were used as control conventional mulching practices based on synthetic and natural products. PVA was chosen as a biodegradable synthetic polymer capable of consistent film formation when applied to soil. Commercial WF, SCB, SD, and WS were used as low-cost organic fillers. For each of the organic fillers, three different formulations were prepared by inclusion in the UF mixture (C, 33.18%; H, 6.70%; N, 31.22%) or Pasp produced by the hydrolysis of polysuccinimide[33] or with no chemical additives. The addition of the aforementioned compounds was intended to enhance the compatibility of PVA and organic fillers and to contribute to the formation of relevant films following the application of the mixtures. Furthermore, UF resins are commonly used as slow-release fertilizers, and Pasp is a water-soluble and degradable polymer[33] that has been found to enhance the absorption of nutrients by plants.[34] Details of the mulching formulations used in the comparative field test are shown in Table I.

For mixture preparation, an appropriate amount of a 10 wt % PVA water solution was introduced into a conical flask, and then the desired amount of the filler, UF or Pasp, and water up to a final 15 wt % concentration were added under stirring. The resulting viscous suspension was kept under stirring for 1 h at 80°C, and then water was added to compensate for any evaporation during the heating process.

SCB and WF were used as filler components of the liquid-mulching treatment. They were dispersed in the PVA water solution (as described previously), and the mixture was sprayed onto the soil surface at a rate of 40 g/m^2 of organic filler with a type EC attack OL 195 23050 Eu RC compressor (Fini, Bologna, Italy) working at a pressure of 3 bar and equipped with a 2.5-mm nozzle.

SD and coarsely ground WS were used for a semidry treatment in which the organic fillers were manually spread on the soil at a level of 500 g/m^2. For this treatment, a 5 wt % PVA/additive water suspension was prepared with the same method used previously and applied via spraying on the organic filler previously spread on the soil surface.

Treatments were applied to plots having a 1-m^2 surface area arranged in a randomized block experimental layout with three replications [Fig. 2(a,b)]. Control plots of untreated soil were included in the experiment. *Zea mays* L. and *Lactuca sativa* L. were chosen to test the agronomic effect of the mulching treatments on a seeded crop and a transplanted crop, respectively. For each plot, three corn plants were established by sowing, and three plants of *L. sativa* were established by seedling transplantation [Fig. 2(c)]. The fluid suspensions were applied after sowing and immediately before transplantation. Seedbed fertilization consisted of 200 kg/ha nitrogen from a slow-release source, 150 kg/ha P_2O_5, and 50 kg/ha K_2O. No topdressing fertilization was applied. Irrigation was performed to prevent water stress.

At 30 and 60 days after sowing, the corn plant height and fresh and dry biomass were measured. At 60 days after sowing, the total leaf area was also determined.[35]

All the lettuce plants were harvested 50 days after transplantation, and fresh and dry biomass was measured and reported as the average plant biomass.

Samples of the soil surface were collected at the end of the trial, and the aggregate stability was determined by the wet-sieving method.[36] Data were tested with an analysis of variance, and the least significant difference for $P \leq 0.05$ was used to detect differences between treatment means.

RESULTS AND DISCUSSION

Previous studies performed in our laboratories confirmed the strong interaction of PVA with soil as a

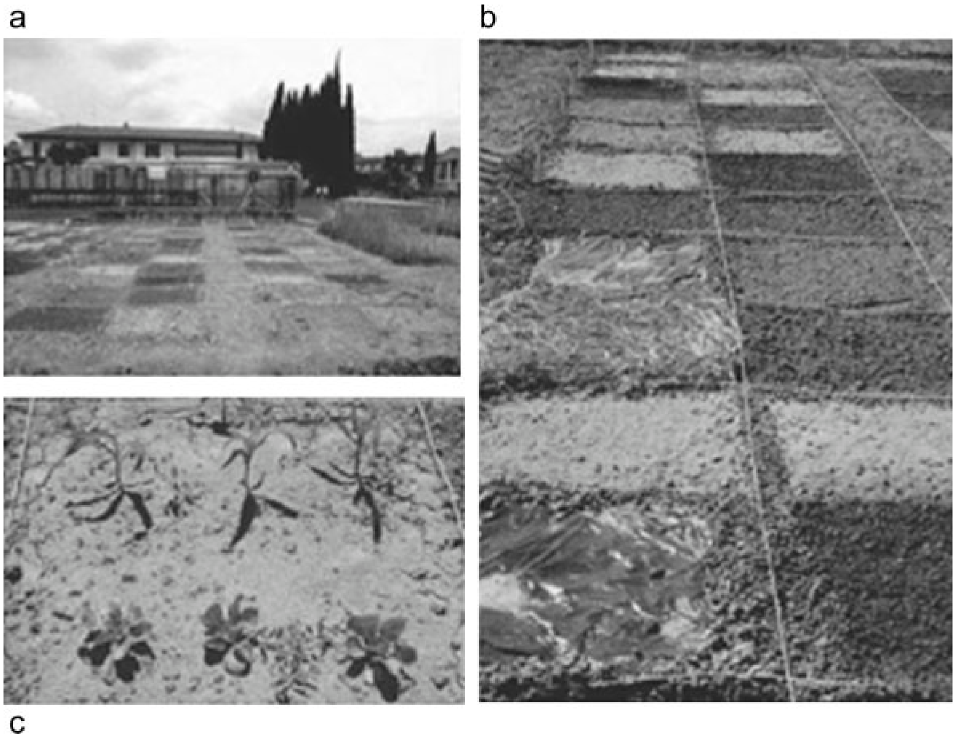

Figure 2 Images of the field trial.

binding agent and suggested that the filler was improving the time that PVA lasted on the soil surface and the consequent structuring effect. PVA, SCB, and WF decomposition starts over 200°C (Fig. 3); thus, the thermal stability is suitable for processing by the casting of a water solution and for applications in the open field.

Liquid mulch (SCB, SCB UF, SCB Pasp, WF, WF UF, and WF Pasp) formed a uniform cover on the soil surface. Formulations containing SCB conferred a brown color to the soil. The semidry mulch (WS, WS UF, WS Pasp, SD, SD UF, and SD Pasp) uniformly covered the surface of the plots and appeared very well aggregated, forming a flexible, cohesive

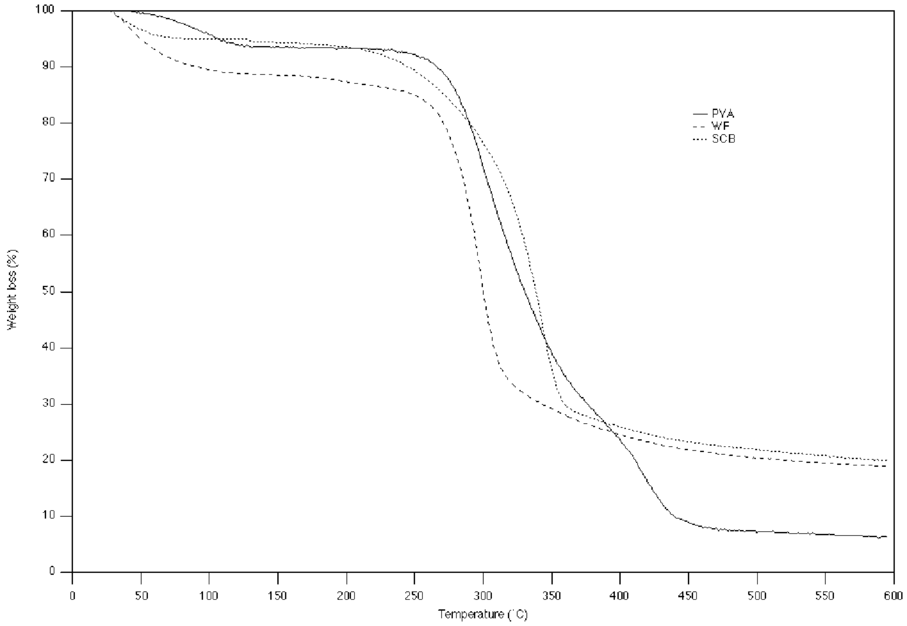

Figure 3 Decomposition curves of PVA, SCB, and WF.

TABLE II
Agronomic Parameters in the Field Mulching Tests Carried Out on *Zea mays* and *Lactuca sativa*

	Z. mays				*L. sativa*
Hydrobiomulching treatment	Plant height at 30 days after sowing (cm)	Dry biomass at 30 days after transplanting (g/plant)	Dry biomass at 60 days after sowing (g/plant)	Total leaf area at 60 days after sowing (m^2/plant)	Dry biomass at 50 days after transplanting (g/plant)
SCB	17.9	0.4	70.7	0.51	15.9
SCB UF	16.7	0.6	73.7	0.47	10.8
SCB Pasp	17.8	0.7	47.7	0.34	12.2
WF	17.6	0.5	55.3	0.40	15.9
WF UF	16.4	0.4	49.4	0.38	11.1
WF Pasp	13.6	0.4	49.0	0.37	12.7
WS (milled)	19.0	0.5	58.2	0.36	20.1
WS UF (milled)	19.3	0.8	47.0	0.33	16.2
WS Pasp (milled)	19.8	0.8	65.6	0.42	24.0
SD	17.9	0.8	70.3	0.52	17.9
SD UF	20.2	0.8	61.6	0.39	19.4
SD Pasp	16.8	0.5	39.1	0.29	18.1
PE film	23.1	0.9	91.4	0.54	14.3
SM	22.4	1.0	47.8	0.36	11.4
Control	14.1	0.5	31.8	0.25	8.2

layer. When the plots were irrigated, water dwelt on the layer and slowly percolated down to the soil. These mixtures were revealed to be very effective in water retention and at the same time did not require elaborate watering methods.

Corn plant height

The height of the corn plants as measured 30 days after sowing was significantly affected by the treatments. In plots in which the SM and PE film were adopted, plants reached the heights of 22.4 and 23.1 cm, respectively, versus 14.1 cm recorded in the untreated soil (Table II). Two of the hydrobiomulching formulations, WS Pasp and SD UF, performed significantly better than the control and reached the results obtained with the conventional techniques. The plant height recorded for WF with both the Pasp and UF additives (WF Pasp and WF UF, respectively) was similar to that of the control and significantly lower than that of the PE and SM.

The other fluid treatments, even if producing results similar to the SM and PE treatments, did not differ statistically from the untreated soil. The plant height determined 60 days after seeding did not show any significant effect related to the different treatments.

Corn leaf area

As observed for the previous measurements, the total leaf area per plant also showed the positive effect of the PE treatment on plant growth, with this technique showing the highest value. Many of the fluid-mulching treatments compared in the trial produced a similar positive effect on this parameter (SD, SCB, SCB UF, WS Pasp, WF, SD UF, and WF UF). For the leaf area, SM did not produce an effect statistically different from the control.

Corn fresh and dry biomass

Corn plant biomass production showed similar trends for fresh and dry weights. Data for the dry weight are reported in Table II. Data for the fresh weight 60 days after sowing are shown in Figure 4.

Thirty days after sowing, SM and PE values were significantly higher than the value recorded for the control.

Sixty days after sowing, although SM no longer differed from the control, six fluid treatments (SCB UF, SCB, SD, SD UF, WS Pasp, and WS) performed

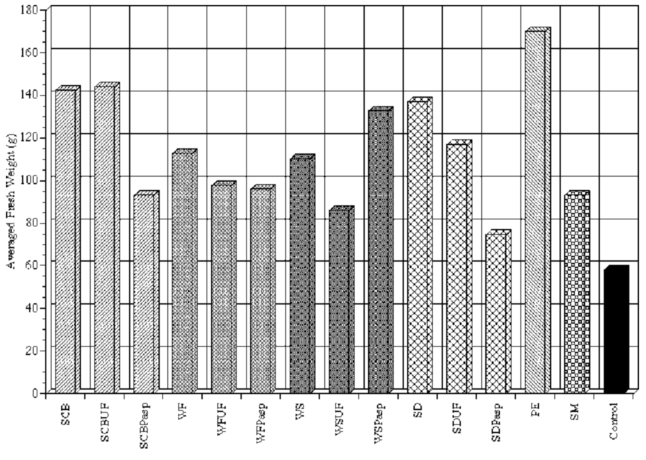

Figure 4 Average fresh weight of corn (60 days from seedling).

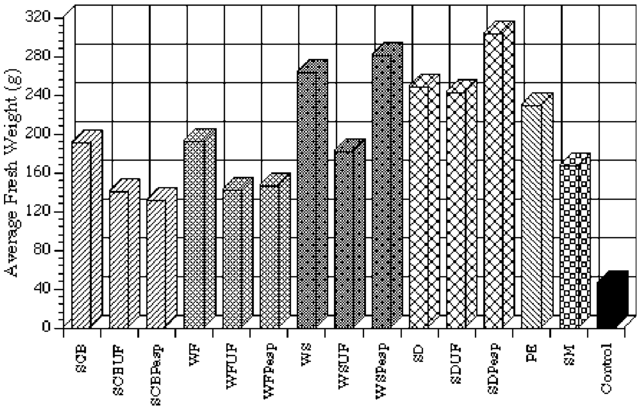

Figure 5 Average fresh weight of lettuce.

better than the untreated soil and similarly to PE, which, once again, represented the best technique.

Lettuce fresh and dry biomass

The effects of the mulching treatments on this crop were different in comparison with corn, as outlined by the results collected for the dry weight (Table II), and the fresh weights are shown in Figure 5. Although PE again promoted growth significantly higher than that of the control, the WS Pasp and WS treatments allowed even higher biomass production. Furthermore, the performance of many treatments equaled that of PE (SD UF, SD Pasp, SD, WS UF, WF, and SCB). The effect of SM did not have a difference statistically significant from the control.

Aggregate stability

During the experiment period, the treatments suffered rather harsh weather conditions, especially in the month of June, as reported in Table III. However, the mulching effect of the different composites was quite evident, and at the end of the experiment, plots treated with the fluid mixtures had maintained a much better structure in comparison with the untreated control. This effect was probably due to the PVA soil conditioning action, as reported previously. When the experiment was stopped and the mulches were removed, it was interesting to observe that WS and SD semidry mulches had partially migrated into the soil, forming a 1–2-cm-thick layer of a soil–filler mixture; under this layer, the soil was wet and very well structured.

Despite evident differences in the soil structure as determined on the basis of visual assessments, the measurement of the soil structure stability was difficult to perform because of the presence of the natural fillers used in the mulch (WF, SCB, SD, and WS), and determinations carried out on soil samples did not show statistically significant differences.

The pictures shown in Figure 6 refer to the soil surface at the end of the trial in plots that had received SCB or WF treatments or no mulching treatment (control). Soil aggregates were apparently still present in treated soil, whereas they were completely disrupted in the control plot, thus indicating clearly the beneficial effect played by the hydrobiomulching treatments.

CONCLUSIONS

Traditional mulching methods such as those based on the use of PE films and straw mats can modify the soil conditions and improve plant growth. Alternative fluid-mulching treatments based on biodegradable components may allow for the achievement

TABLE III
Weather Conditions Recorded in the Period of the Mulching Experiments

Month	Period (days)	Relative humidity (%)	Rain collected (mm)	Global radiation (MJ/m^2)	Air temperature (°C)	Soil temperature 25 cm from the surface (°C)
June	1–10	73.8	31.6	19.2	26.1	22.3
	11–20	66.7	24.3	22.5	24.1	25.3
	21–30	67.1	3.1	20.5	22.0	24.0
	1–30	69.2	59.0	20.8	22.3	23.9
July	1–10	67.2	3.9	24.3	21.8	24.3
	11–20	69.5	6.5	24.3	24.2	26.5
	21–31	65.5	1.5	23.2	25.6	27.2
	1–31	67.4	11.9	23.9	23.9	26.0
August	1–10	63.2	0.0	21.6	26.1	28.0
	11–20	59.1	3.5	19.6	25.6	27.4
	21–31	65.9	22.3	19.6	24.0	26.3
	1–31	62.7	25.8	20.21	25.2	27.2
September	1–10	70.4	0.1	19.4	24.1	26.0
	11–20	66.9	93.6	17.3	21.2	23.6
	21–30	64.9	0.0	15.0	20.2	21.8
	1–30	67.4	93.7	14.9	21.8	23.8

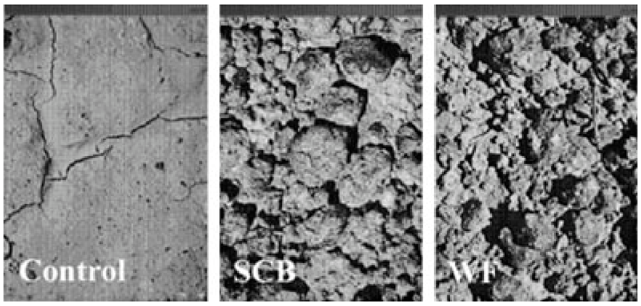

Figure 6 Appearance of the soil surface 100 days after the mulching application: comparison of the control and some fluid-mulching treatments.

of similar enhancement in crop production while at the same time being faster and easier than SW and leading to fewer environmental concerns and higher cost effectiveness than plastic films.

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