A spray-on environmentally friendly degradable mulch material and its weed suppressing effect in greenhouse experiments

Michael Kirchinger
michael.kirchinger@tfz.bayern.de

https://orcid.org/0000-0002-9935-6095
Elias Holzknecht
Markus Redl
Siegrid Steinkellner
Peter Emberger
Edgar Remmele

Research Article

Keywords: Mulch film, Biocomposite, Weed control, Renewable Resources, Sustainable agriculture

Posted Date: October 10th, 2023

DOI: https://doi.org/10.21203/rs.3.rs-3412232/v1

Version of Record: A version of this preprint was published at Journal of Plant Diseases and Protection on April 2nd, 2024. See the published version at https://doi.org/10.1007/s41348-024-00900-6.

Abstract

This study describes a novel spray-on mulch material as an alternative to currently used weed control methods. The mulch material is based on renewable raw materials, mainly rapeseed oil, starch and sodium alginate. Laboratory tests were conducted to evaluate the mulch material's heat and water resistance as well as any mold growth. Furthermore, the aerobic degradability of the mulch material was recorded using the DIN EN ISO 17556 method. In addition, the mulch material was spread on an experimental field and its durability was tested under natural conditions over the vegetation period. The weed suppressing effect of the mulch material was investigated in greenhouse experiments. The formulation of the mulch material was optimized for heat and water stability. Mould resistance was improved by adding sodium benzoate. In the laboratory experiment, the CO_2 decomposition rate was about 30% after seven weeks. In the field, the mulch material maintained its function for six months. In the greenhouse, it was found that the mulch material showed a high efficiency in controlling aboveground biomass of *Elymus repens, Amaranthus retroflexus*, and *Setaria viridis*. In addition, the biomass of the roots of *Amaranthus retroflexus* and *Elymus repens* was reduced. Further studies are on the way to elucidate field suitability and the weed suppressive effect under different environmental conditions.

Introduction

Suppressing of weed growth is an important procedure for enhancing crop production in agriculture and horticulture. Beside using herbicides and mechanical weeding, the concept of soil mulching, whereby the soil is continuous covered with mulch films or mulch materials, offers another option. Soil mulching suppresses weed growth, reduces the loss of moisture from the soil and protects plants and their edible products from dirt [1]. From 2013 to 2019, the global demand of agricultural plastic films, which are used to a large extent for ground cover, grew at an average annual rate of 7.6% [2] and global demand for plastic films is expected to increase by a further 59% from 2018 to 2026 [3].

Low density polyethylene (LDPE) films are the most commonly used form of mulch films [4]. LDPE films have appropriate mechanical characteristics to assure an easy handling, functionality and resistance throughout the cultivation period. However, they also have a number of disadvantages, such as their production based on petroleum products or the release of microplastics [5]. After the use, the LDPE films are dirty of soil, organic matter and agro-chemicals [6]. Therefore, they must be carefully collected, which is time-consuming and expensive for farmers. In many cases, the only option is disposal, as the films often cannot be recycled due to heavy contamination. A promising alternative is the use of biodegradable mulch films. After the cultivation period, films can be incorporated into the soil, where microorganisms convert the mulch material in carbon dioxide, methane, water and biomass [7]. Unlike plastic films, this avoids waste, and neither macro- nor microplastics accumulate in soil and water. Currently, there are biodegradable mulch materials available consisting of polymers such as natural rubber [8], starch [9–11], cellulose [12], polylactic acid (PLA) [13], polyvinyl alcohol (PVOH) [14] or hydrolysed proteins [15]. These materials can contain natural fillers such as cellulose fibers to increase mechanical strength and even coloured pigments to block the transmitted light to inhibit weed growth [16]. However, the films must be partially buried in the ground so that they are not blown by the wind. This causes the underground part of the film to degrade more quickly, because there is more contact with microorganisms. Consequently, the films may detach from the ground or shred. In addition, some mulch films can disintegrate into very small particles. Thus, the film itself is decomposed, but the material is not degraded [2].

Recently, sprayable mulch films containing polysaccharides, proteins or other polymers in water has been developed [15, 17–19]. Unlike conventional films, the mulch film is formed in situ on field [20]. Mulch materials containing polymers like sodium alginate, glucomannan, chitosan and cellulose have been described [15]. The spray technology has several advantages over using conventional films: sprayable materials are not affected by strong winds and degrade more evenly compared to degradable films. In addition, they can be applied by using techniques that farmers are familiar with, such as application of liquid fertilizers or plant protection products. It is also less labour-intensive, so a single person is quite sufficient for the application. In addition, they can be tailored to specific crops and environmental conditions, providing a more customized solution for farmers.

From an agricultural perspective, weeds compete with crops not only for resources such as light, water and nutrients, their management also leads to an increase in production costs [21]. For weed control, their germination and growth behavior as well as their longevity play a crucial role. Different weed species are adapted to different development conditions, e.g. annual summer weeds germinate in spring, while annual winter weeds germinate mainly in autumn. Some weed species must go through dormancy; perennial species, on the other hand, can spread by seeds or reproduce by creeping roots, stolons, or rhizomes [22]. Therefore, weed control based on only one measure is often insufficient, and each individual measure has its strengths and weaknesses. There are some indications, that mulching films are more effective against annual weeds, as perennial weeds might penetrate films more easily [23]. However, good efficacy against a range of weeds is critical for adequate acceptance of new mulch materials.

The aim of this study was to develop a spray-on mulch material based on rapeseed oil and starch and to optimize it with regard to field-relevant parameters, such as extreme heat, water resistance and reduction of mould infestation. Furthermore, the aerobic degradability was investigated in laboratory and in a field trial (Fig. 1) and the suitability of the material for weed suppression was tested in a greenhouse trial.

Materials and Methods

Materials

Rapeseed oil was obtained by a local vegetable oil supplier (Franz Braun, Oberharthausen, Germany) in animal feed quality, as a cold processed and not refined oil. Sodium alginate was supplied from Lanuco (Hamburg, Germany), starch was supplied from Kroener (Ibbenbueren, Germany), sorbitol, sodium benzoate, sodium phosphate and calcium sulfate were obtained from Carl Roth (Karlsruhe, Germany), all chemicals had a purity of 99%. Glycerine was supplied from Distripark (Duisburg, Germany). Cellulose fibers (200 µm) were obtained from J. Rettenmaier & Söhne (Rosenberg, Germany).

Mulching Material

Mulching material is composed of two components, a water-based starch compound and an oil-based sodium alginate compound. In order to find the most suitable ratio of the components, test samples with different compositions were produced and tested for their properties. For each component, the liquid phase (water or rapeseed oil) was filled in a beaker, the solid ingredients were added, followed by stirring with a mechanical stirrer (Hei-Torque 200, Heidolph, Germany). After the two components had been homogeneously mixed individually, the oil phase was added to the aqueous phase with constant stirring. Immediately after mixing, the not yet completely solid mass was poured into round glass dishes and allowed to harden at room temperature. Numerous formulations with different compositions were investigated (Table 1). Only those formulations are shown which have also proved suitable for practical application.

For further development of the formulation, round samples were cast to investigate the characteristics of the material. To cast test samples, 250 g of freshly mixed mulch material were put into a glass form with a diameter of 17 cm and a depth of 1 cm and were allowed to harden.

Table 1
Formulation of mulch material tested for field relevant parameters. All values are given in mass-%.

Formulation	Water	Rapeseed oil	Starch	Sodium Alginate	Sorbitol	Glycerine	Filler
F1	51	28	11	1.1	0	4.1	2.2 [a]
F2	47	26	12	1.3	0	5.9	4.7 [b]
F3	47	32	13	0.9	0	4.7	2.5 [a]
F4	58	21	9.3	1.0	0	4.6	3.7 [a]
F5	49	25	11	1.1	5.9	3.9	2.3 [a]
F6	45	30	12	1.2	2.2	4.5	2.3 [a]
F7	36	35	14	1.0	2.6	5.2	2.7 [a]
Filler: a cellulose fiber, b sawdust							

Characterisation of the mulching material

The test samples were analysed for shrinkage, heat resistance, swelling behaviour, and mould growth. Shrinkage was analysed by measuring the diameter of the sample on days 1, 2, 3, and 7. For investigate the resistance to extreme heat, the test samples were placed in a drying oven at 60°C for three hours. Changes in mass were determined after 30 min, 1 h and 3 h. To determine the swelling behaviour, the test samples were cut in 7 x 7 cm squares, weighed, and placed in 600 mL-beakers containing 400 mL water. On days 1, 2, 3, and 7, the test samples were removed from the water, wiped with wet filtered paper, weighed, and put back into the solution. For the evaluation of the tests on shrinkage, swelling behaviour and the influence of heat on the samples, the difference in diameter or mass was calculated according to the following formula:

$$S = \frac{(d_0 - d_t)}{d_0}$$

1

where S is the change in shrinkage in %, d_0 is the diameter at time 0 and d_t is the diameter after time t in days. The swelling behaviour and the influence of heat were calculated with the masses according to the time points 0 and t.

To investigate the tendency to mould, various preservatives were added to the test samples. Subsequently, an aqueous solution from mouldy biowaste was sprayed onto the test samples. Test samples were stored for three weeks in a darkened, humid box at room temperature. For these tests, the formulation F6 was used, as it performed best in the previous tests. The preservatives citric acid, propionic acid, potassium hydroxide, tannic acid, zinc oxide, and sodium benzoate were added in 5 different mass concentrations (0.5%, 0,75%, and 1%, 2% and 3%). The material was visually inspected to determine whether or not mold was present. The investigations were carried out as triplicates.

Biodegradability

Aerobic degradability was investigated in accordance with DIN regulation 17556 [24]. A sealed Erlenmeyer flask was filled with 200 g of soil. The soil (a loess) was taken from a field 2 km south of Straubing, Germany (maximum depth 10 cm). The soil was sieved to 2 mm particle size before filling. The pH was determined (pH = 6.1) and the soil moisture was adjusted to 50% with distilled water. A total of six Erlenmeyer were prepared, three flasks with soil as reference and three flasks with soil and additional 2.5 g of shredded mulch material. The flasks were sealed with a frit and continuously flushed with synthetic air (v = 0.05 L/min). A gas wash bottle containing 100 mL of 5 M KOH solution was placed ahead of the flask with soil to remove CO_2 from the air. Two additional gas bottles, each containing 100 ml of 0.1 M KOH solution, were placed next to the bottom of the flask to collect the CO_2 produced. The resulting solution in the KOH-bottle was titrated (888 Titrando, Metrohm, Herisau, Switzerland) weekly with 0.1 M HCl solution [24, 25]. The CO_2 trapping was done in two reaction steps:

$KOH + CO_2 \rightarrow KHCO_3$ (1)

$KHCO_3 + KOH \rightarrow K_2CO_3 + H_2O$ (2)

During the titration, CO_2 is removed through the reaction with HCl. This reaction also proceeds in two steps:

$K_2CO_3 + HCl \rightarrow KHCO_3 + KCl$ (3)

$KHCO_3 + HCl \rightarrow KCl + H_2O + CO_2$ (4)

According to that reaction steps, the volume of HCl between the two equivalence points was used for determining the amount of CO_2 [26]. The mass of CO_2 was calculated with the following formula (5) [24, 27]:

$$m_{CO_2} = \frac{V_{HCl} \bullet c_{HCl} \bullet 44}{1000}$$

5

In addition, the mulch material was applied to an agricultural experimental area 2 km south of Straubing, Germany. Three strips of mulch were applied to the soil, each 10 m long, 40 cm wide and 5 mm thick (5 L/m^2). The two components were prepared in separate buckets, mixed with a hand mixer applied with a commercial airbrush (TSP - DGKD030063, Schneider Druckluft GmbH, Reutlingen, Germany). The soil was treated with a rotary tiller 2 days before application and was free of weeds. A fixed point was marked on each strip and recorded photographically (Canon EOS 750D, Canon, Japan) each week. The observation period was from April to October.

Plant Grow Experiment in Greenhouse

Under greenhouse conditions, the effect of the mulch material on different weeds was investigated. The glasshouse experiments were carried out at the BOKU University of Natural Resources and Life Sciences, Vienna. Three weed species were used for this experiment: the creepy perennial species *Elymus repens*, *Amaranthus retroflexus* (annual dicot species) and *Setaria viridis* (annual monocot species). The seeds of *Amaranthus retroflexus* and *Setaria viridis* were collected in Vienna (48°17'19.8"N 16°25'37.9"E) and rhizomes of *Elymus repens* in Krems (48°25'35.8"N 15°36'50.4"E) in Austria.

The pots with a total volume of two litres and a height of 20 cm were filled with a mixture of sand, expanded clay and soil, in a ratio of 1:1:1. In this process, the pots for *Amaranthus retroflexus* and *Setaria viridis* were filled with 1.6 L of substrate, on top of which about 25 to 30 seeds were placed, and finally these were overlaid with another 0.15 L of substrate, resulting in a sowing depth of about 1 cm. Once the plants had reached a height of 3 cm, the were thinned to 2 per pot. The rhizome pieces of *Elymus repens* were treated with idolbutyric acid (Cryzotop grün, Kwizda Agro, Vienna, Austria) for better root formation. One rhizome piece was placed on 1.3 L of substrate per pot and then covered with 0.4 L of substrate. The average temperature in the greenhouse was 20.5°C (minimum 14.7°C, maximum 45.1°C). The plants were watered regularly as needed.

A total of 3 treatments were investigated: an untreated control, herbicide (glyphosate) and the mulch material. One treatment consisted of 18 pots with 2 plants each. The application of the mulch and the herbicide glyphosate occurred 49 days after seeding. At this point, the plants were 10–50 cm (*Elymus repens*), 9–25 cm (*Amaranthus retroflexus*), and 4–21 cm (*Setaria viridis*) in height, respectively. Glyphosate (Glyphos, 360 g/L) was applied in a concentration of 2% solution) and a water amount of 22 mL/m^2 (220 L/ha) with a hand held sprayer (Solo 456, Stuttgart, Germany) by moving pots with weeds with a speed of 3km/h under a fan nozzle (Agrotop SprayMax 110 03, Obertraubling, Germany). Mulch was applied with a spray gun resulting a theoretical layer thickness of 5 mm (5 L/m^2).

The efficiency of weed control was estimated by visually assessing the percentage of dead leaf area. The evaluation was made 22 days after the application of glyphosate or mulch. Afterwards, the weeds were harvested. Since an aboveground dry matter determination was not possible due to the treatment with mulch material, only the below ground biomass was analysed. It was dried for 3 days at 60°C in a drying oven (Memmert U30, Schwabach, Germany) and then weighed (Sartorius GP5202-0CE, Göttingen, Germany).

Statistical analysis

Statistical analyses were performed using origin 2021b (OriginLab Corporation, Northampton, USA). Analysis of variance was performed using one-way ANOVA. Mean comparisons between treatments were performed using Tukey tests. Differences with $p < 0.05$ were considered to be significant. Values given throughout the text are means+-standard deviation.

Results and Discussion

Mulch material preparation and characterisation

Sprayable mulch coatings are increasingly gaining global attention as a next-generation alternative due to their environmental benefits and ease of application [28, 29]. In some applications, the formation of the mulch layer takes a few hours to a few days, as the water has to evaporate during the process. Materials based on aqueous solutions of chitosan or starch are often dried for a few days at room temperature [30] or for a few hours at higher temperatures in a drying oven [31]. To maximise the speed of the gelling process, a two-component mixture was used in this study. As gelling agent, sodium alginate was used. In general, sodium alginate forms a three-dimensional hydrophilic hydrogel, which is able to swell and adsorb large amounts of water without dissolving [32]. The polymer is the sodium salt of alginic acid composed of β-D-mannuronate and α-L-guluronate. In aqueous solution and in the presence of divalent cations, especially calcium, insoluble gels are formed. Due to the strong network formed between the divalent cations and the (COO)-groups of the guluronic acid, they can entangle the cations into a stable arrangement, called egg box [33–35]. In order to specifically control the gelling process, the sodium alginate and the calcium salt are added in a non-aqueous component, in this case rapeseed oil. The gelling process then starts immediately when the oil-containing component is mixed with the aqueous component. This causes the material to solidify within seconds.

After the mulch material is applied, it is exposed to numerous environmental and weather conditions, especially temperature and humidity. According to our observations, freshly applied mulch still contains sufficient water to keep the cover flexible and elastic. However, due to evaporation and infiltration of the water, the material becomes increasingly brittle. This leads to shrinkage of the layer and thus to cracks. Weeds can grow through these cracks, weakening the effectiveness of the material. In order to minimize shrinkage of the mulch material layer, different formulations were investigated (Fig. 2). The diameter of all test sample shrank for all the formulations investigated after just one day and continued to decrease over the test period of 7 days. The shrinkage was probably caused by evaporation of water. The formulations F3 and F6 showed the least changes. Since many components influence the properties of the material in this system, it is difficult to estimate a cause for individual improvements. Averous et al. (2000) described different thermoplastic blends containing starch and polycaprolactone. Shrinkage during the 8-day preparation period was reported in a similar scale between 0.1 and 14.4% [36].

Depending on the region and weather conditions, maximum ground temperatures of 60°C may occur in rare cases [37]. For this reason, the influence of temperature on the mulch material was studied in the drying oven. After 30 min, the test specimens lost on average 2–4% of their mass (Fig. 3). This loss of mass can be explained by the evaporation of water. Above 50°C, weakly bound water molecules weakly absorbed by the gel evaporate [38]. F2 and F6 showed the lowest mass losses within 3 hours in the drying oven with 4 and 5%, respectively, while F4 and F5 lost more than 10% of their mass as water after 3 hours. These mass losses are comparable to other covering materials based on sodium alginate. Immirzi et al. (2009) published a test series with 4 material formulations based on sodium alginate, hydroxyethyl cellulose and mixtures of both. In thermal tests, a loss of mass of approx. 10% was found at comparable temperatures, which was also due to water [6].

The mulch material should remain stable even in the rain. Therefore, swelling tests were carried out to investigate the influence of water on different formulations. These tests showed, on the one hand, the ability to absorb water and, on the other hand, the resistance to water, so that no components are extracted (Fig. 4). The formulations showed completely different behaviour in water. While the mass of some test samples decreased from day to day, which might be explained by the release of water-soluble ingredients (F5), most of the test samples initially increased in mass due to the uptake of water. After a few days, however, ingredients were released, so that the mass decreased again. Most of the test samples were able to absorb approx. 10% of their mass in water before the first ingredients were released on the second or third day. Formulation F6 was able to withstand the water the longest, as a reduction in mass was observed on the third day. The ability to absorb water in the formulations used is significantly lower than in other studies with sodium alginate gels, which can take up water several times their mass [39].

The major difference in this case is the presence of hydrophobic vegetable oil in the mulch material, which prevents such high levels of water uptake.

F6 showed the best results in the shrinkage and swelling tests. In the heat resistance tests, F2 was the best material. However, this formulation showed significantly worse results in the shrinkage tests. The shrinkage tests were rated higher because this material property has to prove itself over the entire period of use; swelling behaviour and heat resistance are only important in rare cases. For this reason, F6 was considered the preferred formulation.

The experiments to prevent mould growth were carried out with the preferred formulation F6. Various preservatives used for example in the food sector (citric acid [40], propionic acid [41], potassium hydroxide [42], tannic acid [43], zinc oxide [44], and sodium benzoate [45]), were added in different concentrations to F6 for the examination of microbial growth on test material. When tannic acid, citric acid, propionic acid and potassium hydroxide were added, the samples did not harden as much as without these preservatives. Since this soft material did not seem suitable for us as mulch material, these preservatives were excluded. The tests were carried out with sodium benzoate and zinc oxide. The test samples were visually evaluated to determine whether mould infestation occurred or not (Table 2).

Table 2
Results of the mould resistance experiment displaying the mass proportion and the preservatives. Test samples that have not solidified are marked with ns (not solidified), mould formation is marked with - and no mould formation is marked with +.

Amount preservative / mass%	Citric acid	Propionic acid	Potassium hydroxide	Tannic acid	Zinc oxide	Sodium benzoate
0.5	ns	ns	ns	ns	-	-
0.75	ns	ns	ns	ns	-	-
1.0	ns	ns	ns	ns	-	+
2.0	ns	ns	ns	ns	-	+
3.0	ns	ns	ns	ns	-	+

The most suitable preserving agent in these experiments was sodium benzoate. This substance showed a better effect against mould formation than zinc oxide. The limiting concentration was 1% of total mass. Below this level, the effect decreased strongly. Figure 5 shows two test samples, the left one with 1 mass-% sodium benzoate, the right sample containing no preservative. Compared to food, this concentration is high. In food, the usual concentrations are up to 0.1% [46]. The main reason for this, however, is that an undesirable aftertaste occurs at sodium benzoate concentrations above 1% [47].

Based on the test results, F6 with an addition of 1 mass percent sodium benzoate was selected as the best formulation. The final formulation is shown in Table 3.

Table 3
Final formulation of rapeseed oil-based and the water based component in mass percent.

Oil-based component		**Water based component**	
Ingredient	**Mass-%**	Ingredient	Mass-%
Rapeseed oil	30.1	Starch	12.3
Sodium alginate	1.2	Water	44.6
Calcium sulfate	1.5	Glycerine	4.5
Cellulose fibers	2.3	Sodium phosphate	0.3
		Sodium benzoate	1.1
		Sorbitol	2.2

Biodegradability

The developed mulch material should decompose by itself after a few months. This is to ensure that no residues remain in the soil. The ingredients were selected to the fact that mainly renewable raw materials were used. The mulch material contains several ingredients that are carbon-based and consequently release CO_2 during decomposition. According to the composition in Table 3, the mulch material consists of 35% carbon by mass. Theoretically, a maximum of 3.08 g of CO_2 can be formed during the degradation of the 2.5 g of mulch material used. This theoretical maximum value would be detectable in the case of complete degradation in a perfectly sealed system. As described in Modelli et al. (1999), a KOH solution was used fpr titration [25].

During the experiment, there was a steady increase of CO_2 released. In the first 7 weeks, about 30% of the theoretically available carbon was converted (Fig. 6). After that, however, the release of CO_2 stagnated, resulting in a flattening of the curve. The experiment was therefore terminated. However, when the Erlenmeyer flasks were opened, it was observed that the soil was dry. Humidification of the air by the gas wash bottle with water was apparently not sufficient to keep the soil’s water content high enough. The dry soil could therefore be the cause of the stagnation of the decomposition. Nevertheless, the degradation of the mulch material was comparatively high in the time interval studied. Our data is in line with Costa et al. (2014), who studied different mulch films in strawberry cultivation using the same method and compared these results with cellulose [48]. After 7 weeks, almost 40% of the cellulose had degraded, but only just under 2% of the mulch films. The mulch material presented in our work contains many substances that are readily available to microorganisms, such as starch, rapeseed oil and cellulose, which might be beneficial also for degradation on a laboratory scale. Nevertheless, these results show a good aerobic degradability of the mulch material.

In the second experiment on biodegradability, the mulch material was applied in strips to an experimental field. This application is very close to practice, so that the observations on degradability should be very close to reality. Photographs were taken at the same location for each strip (Fig. 7). This made it easy to see the change over the observed period. The material was applied to the ground in April. At the time of application, it was sunny with temperatures of 15°C. The weather during the observation period was consistently very dry and hot. This also affected the condition of the mulch material. Two months after application, the first cracks (June) already appeared in the material. Due to the dryness, however, hardly any weeds grew through the cracks. During the summer months, there were some thunderstorms with short-term rainfall. After that, it was observed that the mulch material could absorb water and thus became less brittle. The water was absorbed into the sodium alginate gel. This also allowed some of the very small cracks to close again. From August onwards, there was already a visible reduction in the thickness of the mulch material. Heavy rains set in during October and temperatures dropped significantly. From this time on, the mulch material also became very dark. This color change was caused by microorganisms that decomposed the material. The field trial showed that the material was stable for a complete growing season, but then degraded rapidly during wet and cool weather. A mulch material based on chitosan remained stable for 2 months and then degraded rapidly [18]. Spray mulch experiments done with locust bean gum, guar gum or sodium alginate showed a shelf life of 6 months for locust bean gum, guar gum and 5 months for sodium alginate [49]. Biodegradable polymeric materials based on hydrolyzed proteins had a durability of almost 9 months [15] and sprayable mulches based on sodium alginate showed a decomposition after 109 days [6]. The mulch material developed in this study is thus in the upper range of durability compared to other sprayable mulch materials.

Greenhouse Experiment

The weed suppressing effect of the developed mulch material on *Amaranthus retroflexus*, *Setaria viridis* and *Elymus repens* was studied in a greenhouse experiment. The evaluation of the dead leaf area (Fig. 8) after 22 days showed that the herbicide treatment (glyphosate) controlled weeds very well (*Amaranthus retroflexus* 100%, *Elymus repens* 97.5%, *Setaria viridis* 100%). The untreated control showed no necrotic leaves. The developed mulch material also resulted in efficacy of 95% for *Amaranthus retroflexus* and *99%* for *Setaria viridis*. and 76% for *Elymus repens*.Hodge et al. (2019) showed that rapeseed oil, the main component of the developed mulch material, causes necrotic leaves and reduces the biomass of different weeds [50]. In our study, *Elymus repens*, although most of the leaves were necrotic, developed some new sprouts through the mulch. A similar effect was also shown by Gloeb et al. (2023) [51]. In this study, a sprayable material made of starch, glycerol and soy protein was used on *Guillenia flavescens* under field conditions. It is known that creepy perennials, like *Elymus repens*, are difficult to control by mulch films when they are established in a field [52] because they have a high vegetative reproduction ability in contrast to annual weeds, like *Amaranthus retroflexsus and Setaria viridis* [53].

The results of root biomass (Fig. 9) varied depending on the weed species. *Amaranthus retroflexus* showed no significant differences between the treatments. Nevertheless, the root mass of the control was higher than in the two other treatments. For *Elymus repens*, the root biomass of the control was significantly higher than that of glyphosate and the mulch material treatment. For both weeds, the application of glyphosate and the mulch material showed a reduction of below ground biomass. The results were different for *Setaria viridis*. In this case, the treatment with glyphosate showed a reduction in root mass, but the application of mulch material resulted in a higher biomass. In case of *Setaria viridis*, the application of mulch material did not have a major effect on biomass, so that at least the roots were able to produce more below ground biomass. Most studies examined the pre emergence effect of mulching films on weed control. A COCu-K hydrogel mulching film also inhibit the germination of weeds very well in a pot trial. The inhibition capacity was affected by the strength of the hydro gel and the coverage rate [54]. Therefore, increasing the layer thickness of the material tested in our study could improve the rate of weed control could, especially for *Elymus repens*. In another study the rate of emerged seedlings of *Amaranthus retroflexus* was significantly reduced by the application of a hydromulch [55]. We also found a good control of this weed species, but we examined the post emergence effect of the mulch material. Information about weed control of well-established weeds by mulch films is rare [51]. In this study the above ground biomass of *Sorghum bicolor* and *Abutilon theophrasti* was reduced by an application of a biodegradable spray mulch after the emergence of the weeds. This is in accordance with our results, but we examined beside the percentage of dead above-ground plant material the below-ground biomass. To the best of our knowledge this is the first report about the effect of mulch films on creepy perennials under controlled conditions [18, 50, 51, 55, 56]. We found that the tested mulch material reduced the below ground biomass of *Elymus repens* as well as glyphosate. Therefore, the mulch material is effective in controlling this weed under controlled conditions.

Overall, the good efficacy of the developed mulch material on *Amaranthus retroflexus* and *Elymus repens* was demonstrated and the effectiveness of the developed mulch material was comparable to other materials that have been published. A sprayable chitosan-based mulch was described suppressing the weed growth in containers [18]. During the first two month, the effectiveness of the mulch was better than the herbicide treatment(oxadiazon). A sprayable mulch consisting of aqueous dispersion of polyurethane consisting of carboxylate, sulfonate and ammonium suppressed weed growth to a similar rate as a PE film [28]. Paper pulp mulch were wound to allowed only 11% of the weeds to grow through the mulch layer [55]. A commercially available was applied at 1.25 and 2.0 kg/m^2. Thereby, the mulch layer reduced weed growth to approx. 10% compared to the untreated control [56].

Conclusion

In this study, a novel sprayable mulch material based on renewable raw materials was developed. Due to its property as a two-component material, it solidifies on the ground within seconds even though it is applied in liquid form. This advantage comes into play especially in steeper cultivation sites and can thus form a clear advantage over previous weed suppression methods. The mulch material is very easily degradable due to its components made from renewable raw materials. In the laboratory tests on maximum degradability, almost 30% was degraded within the first 7 weeks. In the field trials, the mulch material was able to last for a complete vegetation period. Degradation started after about half a year.

Due to these properties, the mulch material can be used in further field trials without foreign substances remaining and accumulating in the field. Further trials in permanent crops in orchards and vineyards are planned. The weed suppressing effect could be shown in greenhouse trials. The efficiency of weed control was comparable to glyphosate control in almost all trials. Future research will be addressed at improving the mechanical properties, in order to lengthen their lifetime.

Declarations

Author Declarations

Fundings

This work has been carried out under the Project “Alternatives Beikrautmanagement im Obst- und Weinbau mit ökologisch unbedenklichen Substanzen und einem alternativen Mulchverfahren auf Basis Nachwachsender Rohstoffe – ABOW“ (G2/N/18/09) funded by the Bavarian State Ministry of Food, Agriculture and Forestry and by the Austrian Federal Ministry of Agriculture and Forestry, Regions and Water Management, research contract of the BMNT and Josephinum Research (GZ BMNT - LE.1.3.2/0023-PR/8/2019).

Conflict of interests

The authors have no conflicts of interest to declare that are relevant to the content of this article.

Authors' contributions

All authors contributed to the study conception and design. Material preparation, data collection and analysis were performed by MK, EH and MR. The first draft of the manuscript was written by MK and MR. All authors commented on previous versions of the manuscript. All authors read and approved the final manuscript.

Availability of data and material

The authors declare that the data supporting the findings of this study are available within the paper. Should any raw data files be needed they are available from the corresponding author upon reasonable request.

References

1. Kasirajan S, Ngouajio M (2012) Polyethylene and biodegradable mulches for agricultural applications: A review. Agron. Sustain. Dev. 32(2):501–529. doi: 10.1007/s13593-011-0068-3
2. Sintim HY, Flury M (2017) Is Biodegradable Plastic Mulch the Solution to Agriculture's Plastic Problem? Environ Sci Technol 51(3):1068–1069. doi: 10.1021/acs.est.6b06042

3. Sintim HY, Bary AI, Hayes DG et al. (2020) In situ degradation of biodegradable plastic mulch films in compost and agricultural soils. Sci. Total Environ. 727:138668. doi: 10.1016/j.scitotenv.2020.138668
4. Menossi M, Cisneros M, Alvarez VA et al. (2021) Current and emerging biodegradable mulch films based on polysaccharide bio-composites. A review. Agron. Sustain. Dev. 41(4):53. doi: 10.1007/s13593-021-00685-0
5. Li S, Ding F, Flury M et al. (2022) Macro-and microplastic accumulation in soil after 32 years of plastic film mulching. Environ. Pollut. 300:118945. doi: 10.1016/j.envpol.2022.118945
6. Immirzi B, Santagata G, Vox G et al. (2009) Preparation, characterisation and field-testing of a biodegradable sodium alginate-based spray mulch. Biosyst. Eng. 102(4):461–472. doi: 10.1016/j.biosystemseng.2008.12.008
7. Santagata G, Malinconico M, Immirzi B et al. (2013) An overview of biodegradable films and spray coatings as sustainable alternative to oil-based mulching films. Acta Hortic 1037:921–928. doi: 10.17660/ActaHortic.2014.1037.122
8. Pillai, T., P. Padmaja, and P. J. Ruhoff (2014) Blends of acrylic lattices polyurethane dispersions for coatings(US8637609B1)
9. Gáspár M, Benkő Z, Dogossy G et al. (2005) Reducing water absorption in compostable starch-based plastics. Polym. Degrad. Stab. 90(3):563–569. doi: 10.1016/j.polymdegradstab.2005.03.012
10. Marques PT, Lima AMF, Bianco G et al. (2006) Thermal properties and stability of cassava starch films cross-linked with tetraethylene glycol diacrylate. Polym. Degrad. Stab. 91(4):726–732. doi: 10.1016/j.polymdegradstab.2005.05.020
11. Bastioli C (1998) Properties and applications of Mater-Bi starch-based materials. Polym. Degrad. Stab. 59(1-3):263–272. doi: 10.1016/S0141-3910(97)00156-0
12. Moeller HW (2008) Progress in polymer degradation and stability research. Nova Science Publ, New York, NY
13. Rocca-Smith JR, Whyte O, Brachais C-H et al. (2017) Beyond Biodegradability of Poly(lactic acid): Physical and Chemical Stability in Humid Environments. ACS Sustainable Chem. Eng. 5(3):2751–2762. doi: 10.1021/acssuschemeng.6b03088
14. Kukal SS, Sarkar M (2010) Splash erosion and infiltration in relation to mulching and polyvinyl alcohol application in semi-arid tropics. Arch. Agron. Soil Sci. 56(6):697–705. doi: 10.1080/03650340903208871
15. Sartore L, Vox G, Schettini E (2013) Preparation and Performance of Novel Biodegradable Polymeric Materials Based on Hydrolyzed Proteins for Agricultural Application. J Polym Environ 21(3):718–725. doi: 10.1007/s10924-013-0574-2
16. Brault D, Stewart KA, Jenni S (2002) Optical Properties of Paper and Polyethylene Mulches Used for Weed Control in Lettuce. HortSci 37(1):87–91. doi: 10.21273/HORTSCI.37.1.87
17. Johnston P, Freischmidt G, Easton CD et al. (2017) Hydrophobic-hydrophilic surface switching properties of nonchain extended poly (urethane) s for use in agriculture to minimize soil water

evaporation and permit water infiltration. J. Appl. Polym. Sci. 134(45):44756. doi: 10.1002/app.44756

18. Giaccone M, Cirillo C, Scognamiglio P et al. (2018) Biodegradable mulching spray for weed control in the cultivation of containerized ornamental shrubs. Chem. Biol. Technol. Agric. 5(1):1–8. doi: 10.1186/s40538-018-0134-z
19. Roeder O, Remmele E, Kirchhoff et al. (2007) Abdeckmaterial für Biomasse und Verfahren zu dessen Herstellung B32B 27 / 00 (2006.01)(EP 1 998 955 B1)
20. Avella M, Di Pace E, Immirzi B et al. (2007) Addition of glycerol plasticizer to seaweeds derived alginates: Influence of microstructure on chemical–physical properties. Carbohydr. Polym. 69(3):503–511. doi: 10.1016/j.carbpol.2007.01.011
21. Zimdahl RL (2007) Fundamentals of Weed Science. Elsevier Inc
22. Liebman M, Mohler CL, Staver CP (2001) Ecological management of agricultural weeds. Cambridge university press
23. Schonbeck MW (1999) Weed suppression and labor costs associated with organic, plastic, and paper mulches in small-scale vegetable production. J. Sustain. Agric 13(2):13–33. doi: 10.1300/J064v13n02_04
24. Deutsches Institut für Normung e. V. Plastics – Determination of the ultimate aerobic biodegradability of plastic materials in soil by measuring the oxygen demand in a respirometer or the amount of carbon dioxide evolved (ISO 17556:2019) ICS 83.080.01(17556)
25. Modelli A, Calcagno B, Scandola M (1999) Kinetics of aerobic polymer degradation in soil by means of the ASTM D 5988-96 standard method. J. Environ. Polym. Degrad. 7:109–116. doi: 10.1023/A:1021864402395
26. Kale G, Auras R, Singh SP et al. (2007) Biodegradability of polylactide bottles in real and simulated composting conditions. Polym. Test. 26(8):1049–1061. doi: 10.1016/j.polymertesting.2007.07.006
27. ASTM International Standard Test Method for Determining Aerobic Biodegradation of Plastic Materials Under Controlled Composting Conditions, Incorporating Thermophilic Temperatures 83.080.01(D5338-15)
28. Braunack MV, Filipović V, Adhikari R et al. (2021) Evaluation of a Sprayable Biodegradable Polymer Membrane (SBPM) Technology for soil water conservation in tomato and watermelon production systems. Agric. Water Manag. 243:106446. doi: 10.1016/j.agwat.2020.106446
29. Adhikari R, Mingtarja H, Freischmidt G et al. (2019) Effect of viscosity modifiers on soil wicking and physico-mechanical properties of a polyurethane based sprayable biodegradable polymer membrane. Agric. Water Manag. 222:346–353. doi: 10.1016/j.agwat.2019.05.020
30. Xu YX, Kim KM, Hanna MA et al. (2005) Chitosan–starch composite film: Preparation and characterization. Ind. Crops Prod. 21(2):185–192. doi: 10.1016/j.indcrop.2004.03.002
31. Gao X, Fu C, Li M et al. (2022) Effects of Biodegradation of Corn-Starch–Sodium-Alginate-Based Liquid Mulch Film on Soil Microbial Functions. Int J Environ Res Public Health 19(14):8631. doi: 10.3390/ijerph19148631

32. Coviello T, Matricardi P, Marianecci C et al. (2007) Polysaccharide hydrogels for modified release formulations. J Control Release 119(1):5–24. doi: 10.1016/j.jconrel.2007.01.004
33. Grasdalen H, Larsen B, Smisrod O (1981) 13C-NMR studies of monomeric composition and sequence in alginate. Carbohydr. Res. 89(2):179–191. doi: 10.1016/S0008-6215(00)85243-X
34. Grasdalen H (1983) High-field, 1H-nmr spectroscopy of alginate: Sequential structure and linkage conformations. Carbohydr. Res. 118:255–260. doi: 10.1016/0008-6215(83)88053-7
35. Grant GT, Morris ER, Rees DA et al. (1973) Biological interactions between polysaccharides and divalent cations: The egg-box model. FEBS Lett. 32(1):195–198. doi: 10.1016/0014-5793(73)80770-7
36. Averous L, Moro L, Dole P et al. (2000) Properties of thermoplastic blends: Starch–polycaprolactone. Polym. J. 41(11):4157–4167. doi: 10.1016/S0032-3861(99)00636-9
37. Kerridge BL, Hornbuckle JW, Christen EW et al. (2013) Using soil surface temperature to assess soil evaporation in a drip irrigated vineyard. Agric. Water Manag. 116:128–141. doi: 10.1016/j.agwat.2012.07.001
38. Karlsson LE, Wesslén B, Jannasch P (2002) Water absorption and proton conductivity of sulfonated acrylamide copolymers. Electrochim. 47(20):3269–3275. doi: 10.1016/S0013-4686(02)00244-X
39. Samanta HS, Ray SK (2014) Synthesis, characterization, swelling and drug release behavior of semi-interpenetrating network hydrogels of sodium alginate and polyacrylamide. Carbohydr. Polym. 99:666–678. doi: 10.1016/j.carbpol.2013.09.004
40. Brul S, Coote P (1999) Preservative agents in foods: Mode of action and microbial resistance mechanisms. Int. J. Food Microbiol. 50(1-2):1–17. doi: 10.1016/S0168-1605(99)00072-0
41. Kung Jr L, Sheperd AC, Am Smagala et al. (1998) The effect of preservatives based on propionic acid on the fermentation and aerobic stability of corn silage and a total mixed ration. J. Dairy Sci. 81(5):1322–1330. doi: 10.3168/jds.S0022-0302(98)75695-4
42. Hinton Jr A, Ingram KD (2006) Antimicrobial activity of potassium hydroxide and lauric acid against microorganisms associated with poultry processing. J. Food Prot. 69(7):1611–1615. doi: 10.4315/0362-028X-69.7.1611
43. Abd El-aal HA, Halaweish FT (2010) Food preservative activity of phenolic compounds in orange peel extracts (Citrus sinensis L.). Lucrări Ştiinţifice-Seria Zootehnie 53(15):233–240
44. Pasquet J, Chevalier Y, Couval E et al. (2015) Zinc oxide as a new antimicrobial preservative of topical products: Interactions with common formulation ingredients. Int. J. Pharm. 479(1):88–95. doi: 10.1016/j.ijpharm.2014.12.031
45. Shahmohammadi M, Javadi M, Nassiri-Asl M (2016) An overview on the effects of sodium benzoate as a preservative in food products. Biotechnol. Healthc. 3(3):7–11. doi: 10.17795/bhs-35084
46. Lennerz BS, Vafai SB, Delaney NF et al. (2015) Effects of sodium benzoate, a widely used food preservative, on glucose homeostasis and metabolic profiles in humans. Mol. Genet. Metab. 114(1):73–79. doi: 10.1016/j.ymgme.2014.11.010

47. Khayatzadeh J, Afshar M, Moallem SA et al. (2011) Effect of potassium benzoate on BALB/c mice placenta: A histopathological study. J Gorgan Univ Med Sci 13(1):8–15
48. Costa R, Saraiva A, Carvalho L et al. (2014) The use of biodegradable mulch films on strawberry crop in Portugal. Sci. Hortic. 173:65–70. doi: 10.1016/j.scienta.2014.04.020
49. Vox G, Santagata G, Malinconico M et al. (2013) Biodegradable films and spray coatings as eco-friendly alternative to petro-chemical derived mulching films. J. Agric. Eng. 44(s2). doi: 10.4081/jae.2013.286
50. Hodge S, Merfield CN, Bluon A et al. (2019) The potential of culinary vegetable oils as herbicides in organic farming: The effect of oil type and repeated applications on plant growth. Org. Agr. 9(1):41–51. doi: 10.1007/s13165-018-0208-z
51. Gloeb E, Irmak S, Isom L et al. (2023) Biobased Sprayable Mulch Films Suppressed Annual Weeds in Vegetable Crops. Horttechnology 33(1):27–35. doi: 10.21273/HORTTECH05112-22
52. Zwerger P, Arlt K (2002) Unkraut: Ökologie und Bekämpfung. Eugen Ulmer
53. Holzner W, Glauninger J (2005) Ackerunkräuter: Bestimmung, Biologie, landwirtschaftliche Bedeutung. Stocker
54. Li S-S, Wang S-B, Chen Y et al. (2023) Biodegradable, anti-freezing and self-healable hydrogel mulch film for weed control. Chemical Engineering Journal 462:142211
55. Claramunt J, Mas MT, Pardo G et al. (2020) Mechanical characterization of blends containing recycled paper pulp and other lignocellulosic materials to develop hydromulches for weed control. Biosyst. Eng. 191:35–47
56. Shen K, Zheng Y (2017) Efficacy of Bio-based Liquid Mulch on Weed Suppression and Water Conservation in Container Nursery Production1. J. Environ. Hortic. 35(4):161–167. doi: 10.24266/0738-2898-35.4.161

Figures

Figure 1

Application of the mulch material with an air brush for the field trial

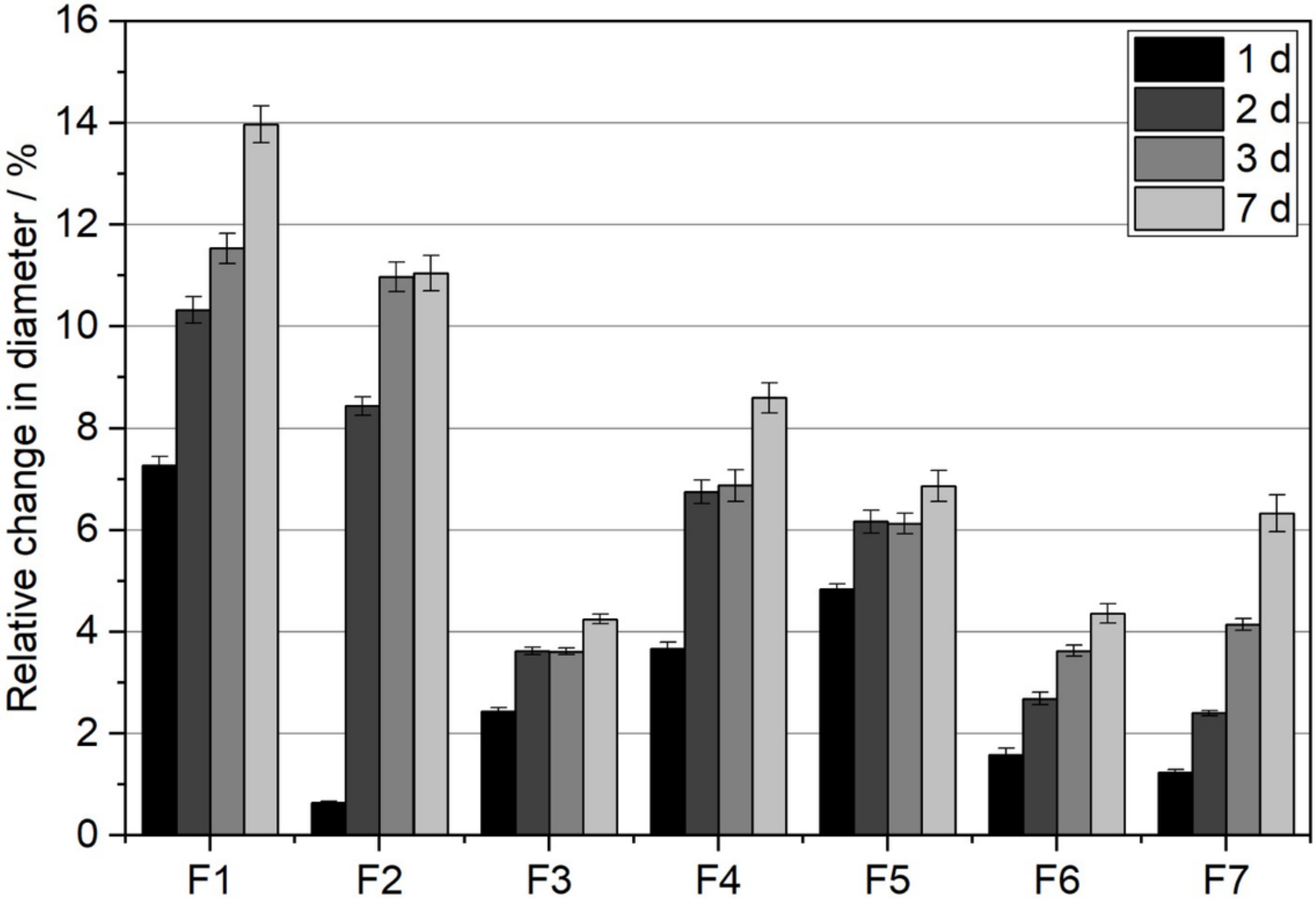

Figure 2

Properties of the different rapeseed oil/starch formulations with regard to shrinkage behavior. Error bars show the standard error, all values shown are the mean values from a triple determination.

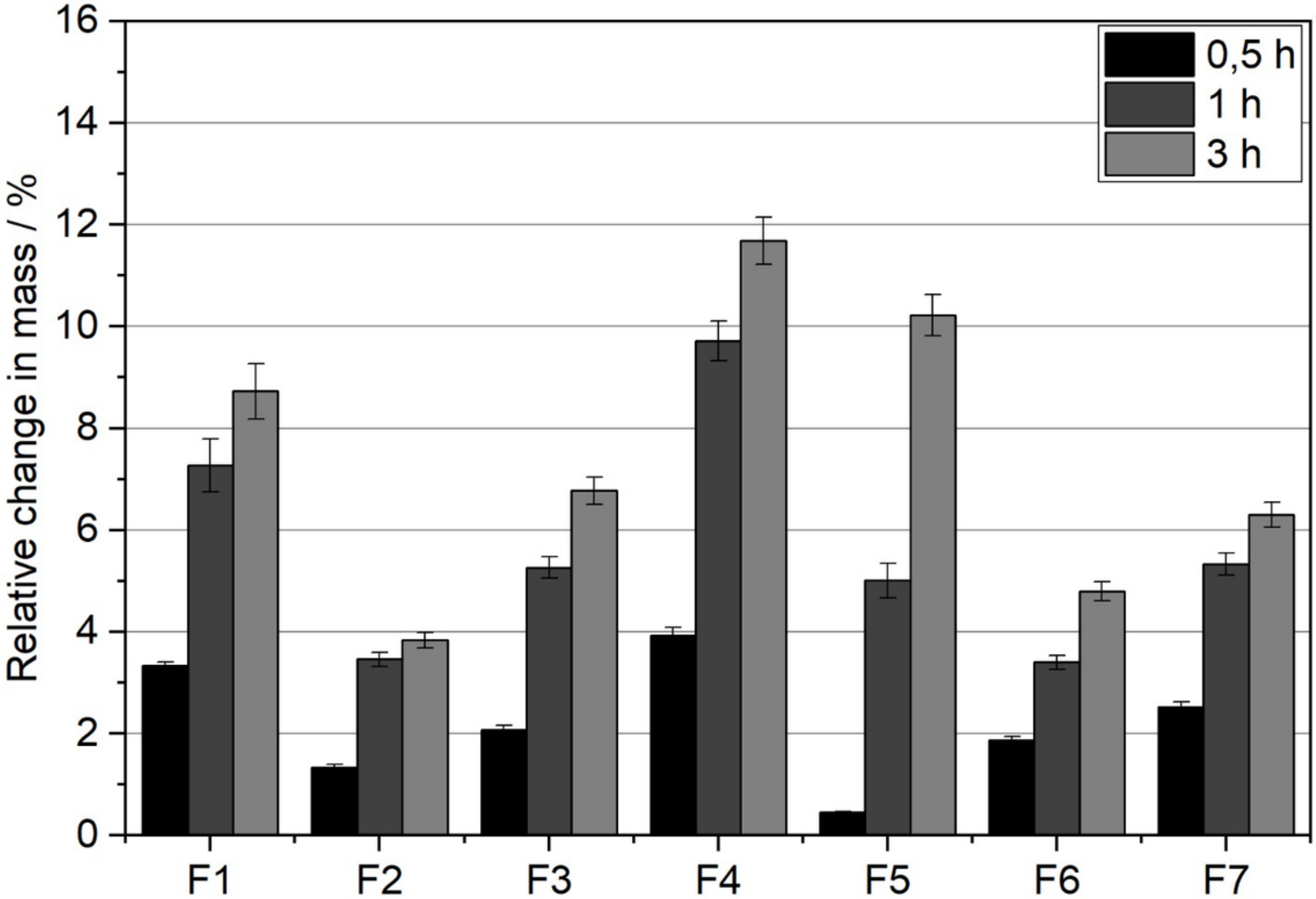

Figure 3

Properties of the different rapeseed oil/starch formulations with regard to heat resistance. Error bars show the standard error, all values shown are the mean values from a triple determination.

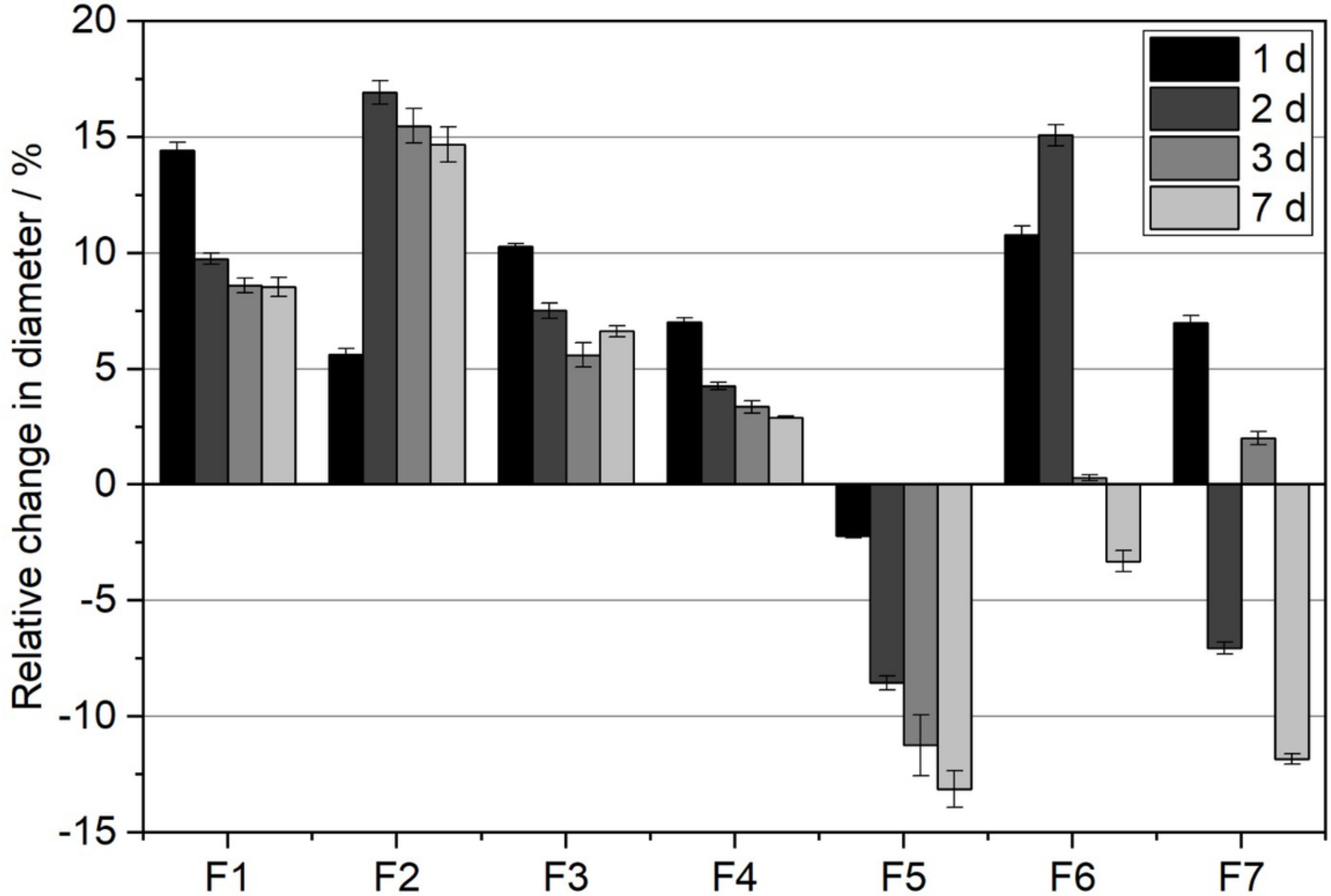

Figure 4

Properties of the different rapeseed oil/starch formulations with regard to swelling behavior. Error bars show the standard error, all values shown are the mean values from a triple determination.

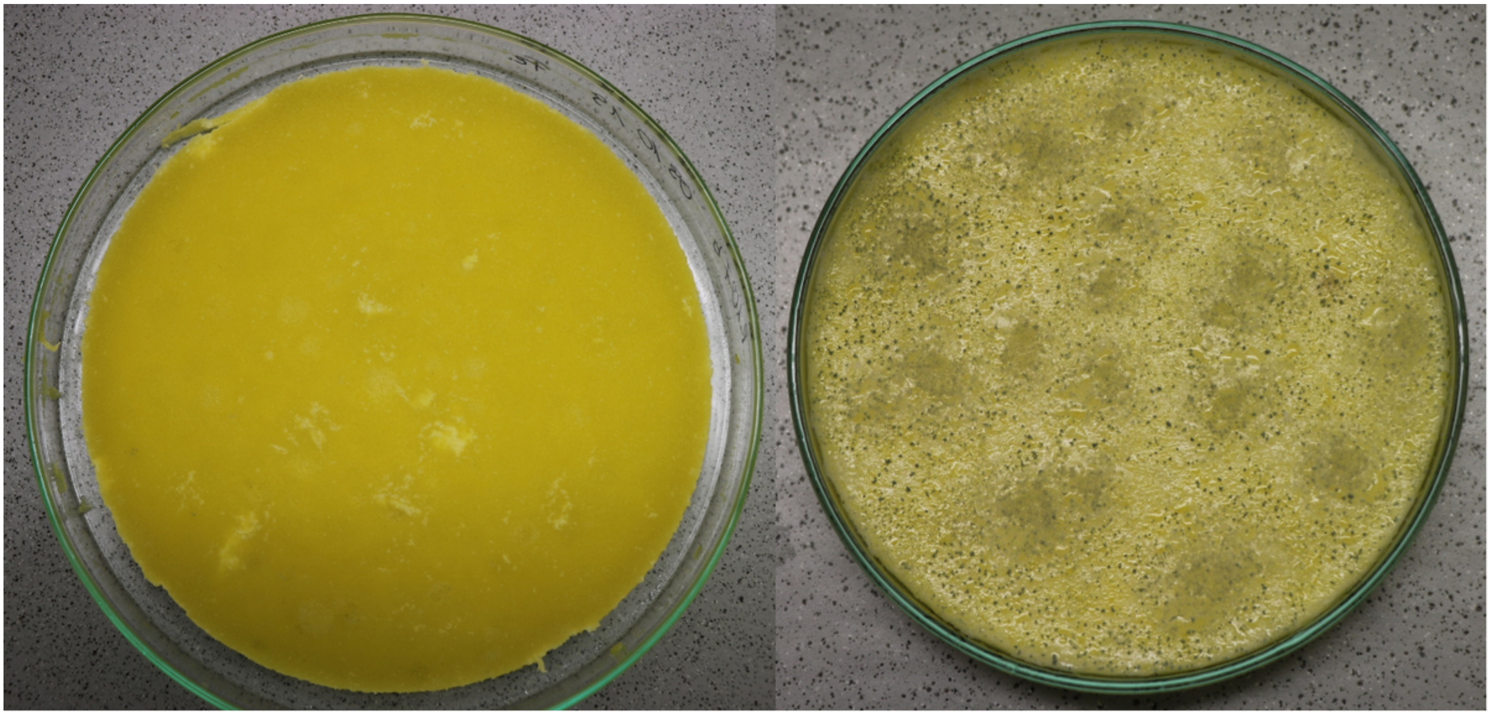

Figure 5

Comparison of two formulations when testing the tendency of mould growth. The test samples shown differ only in the presence of a preserving agent (left - 1 % sodium benzoate, right - without preserving agents).

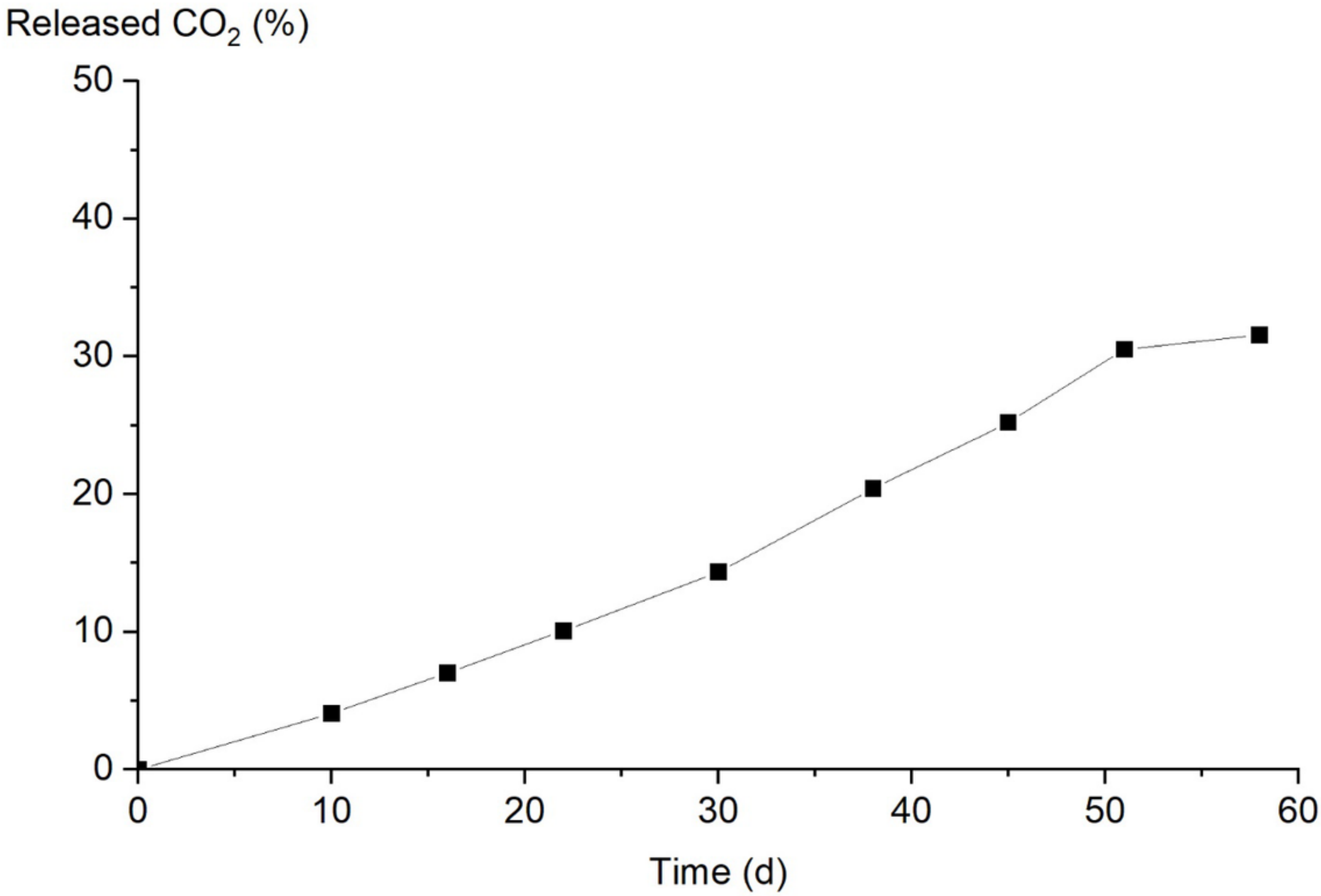

Figure 6

CO_2 released as a percentage of the theoretical maximum amount of carbon available.

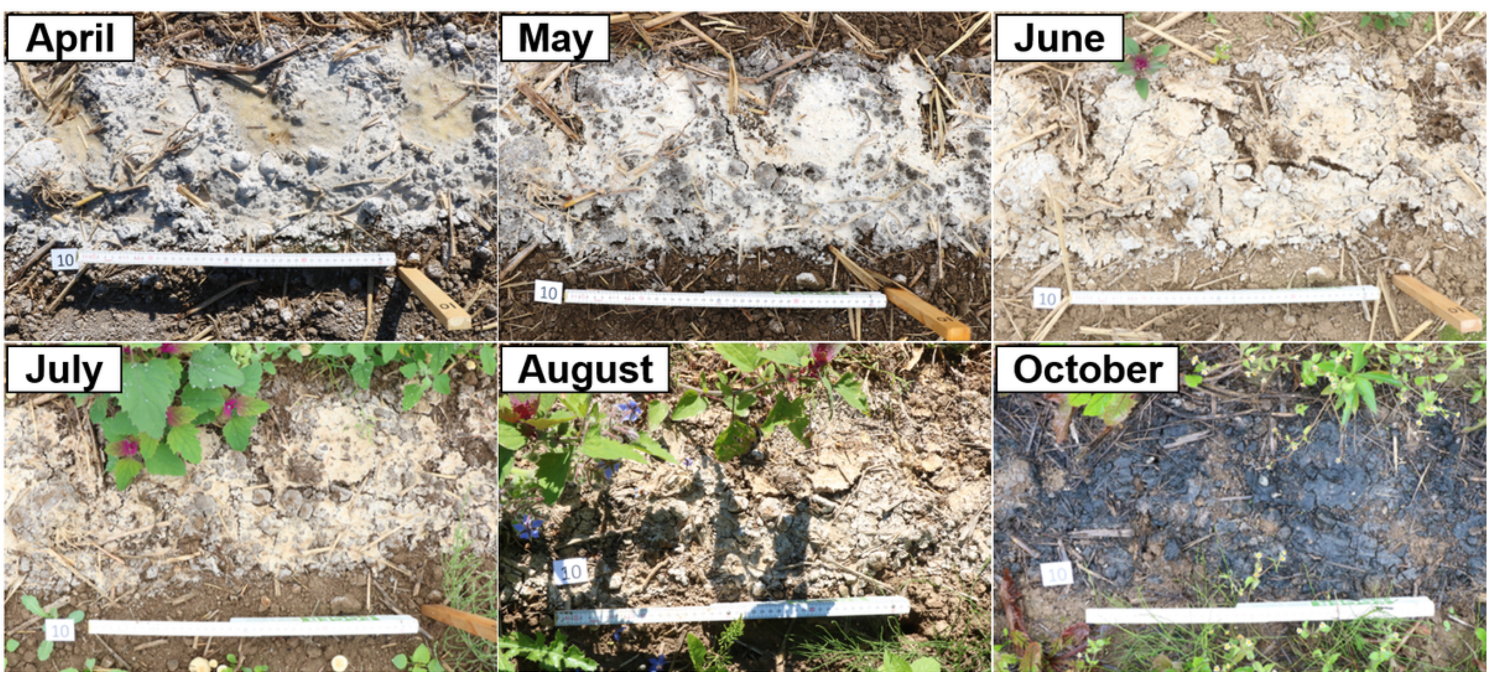

Figure 7

Alteration in the mulch material (layer thickness 5 mm) during the observation period April to October.

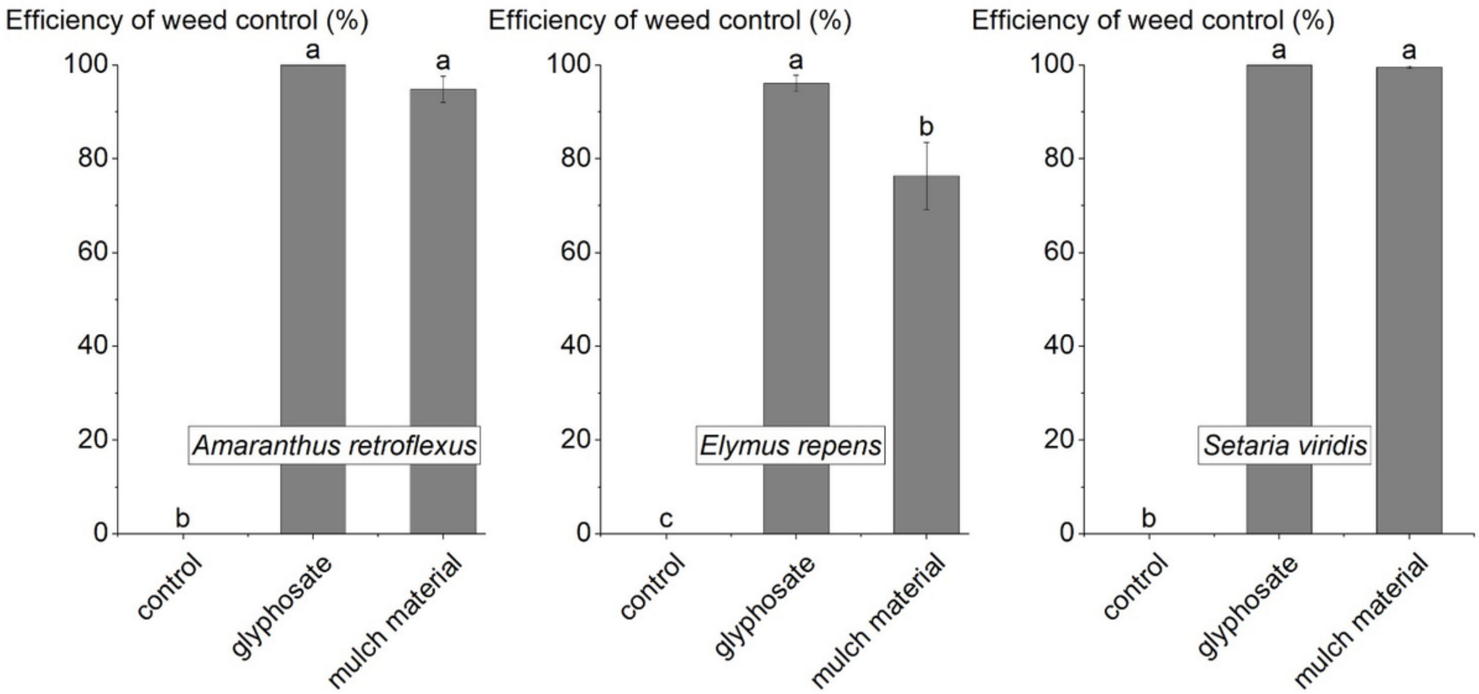

Figure 8

Efficiency of weed control (mean ± SE) from the visual score of dead leaf area of *Amaranthus retroflexus*, *Elymus repens* and *Setaria viridis* of the treatments control, glyphosate and mulch material 22 days after the application.

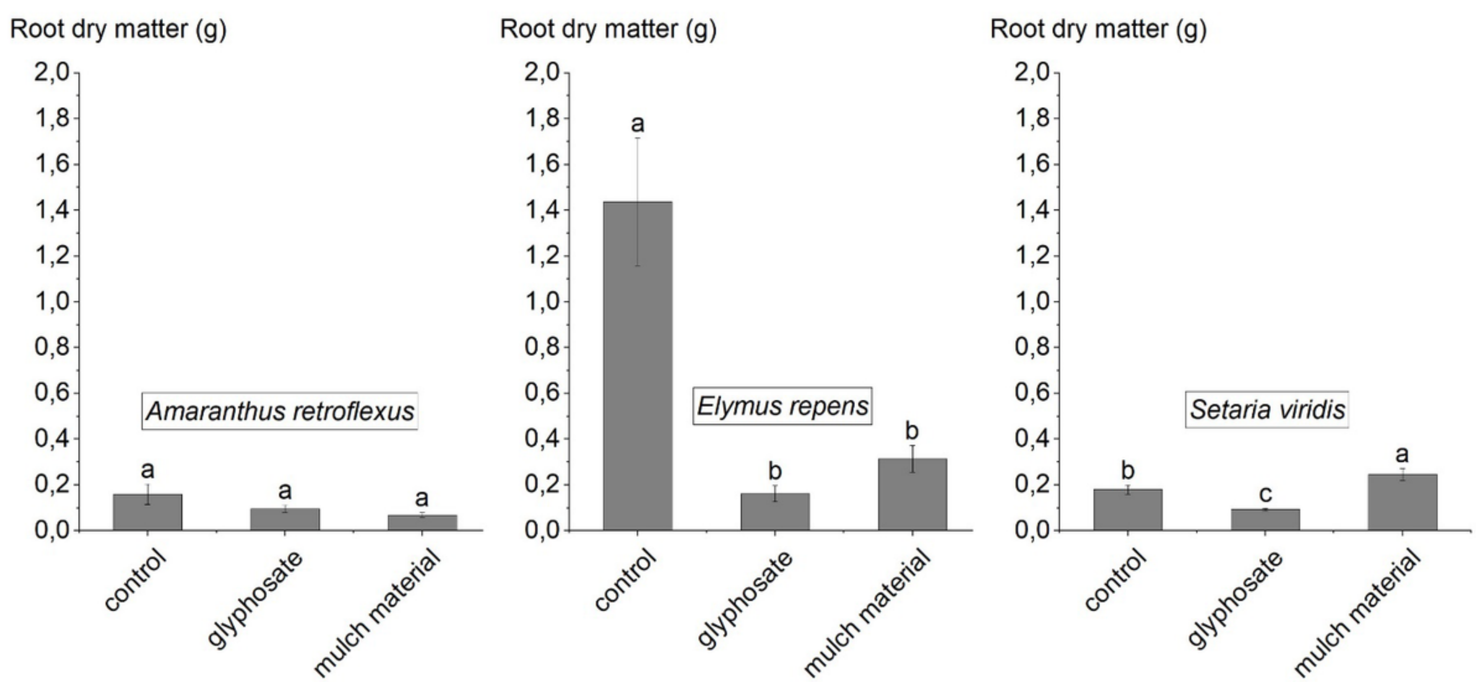

Figure 9

Root biomass (mean ± SE) of *Amaranthus retroflexus*, *Elymus repens* and *Setaria viridis*of the treatments control, glyphosate and mulch material 22 days after the application