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ORIGINAL ARTICLE

A spray-on environmentally friendly degradable mulch material and its high efficiency in controlling above-ground biomass of weeds in greenhouse experiments

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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 obtain a mulch material with the best possible properties. Formulations with different ingredients were prepared and tested for their material properties. The formulations were investigated for potential shrinkage tendency and heat resistance as well as water resistance. Further tests such as resistance to mould infestation and aerobic degradability according to DIN EN ISO 17556 were carried out with the formulation that performed best in the previous tests. Mould resistance was enhanced by adding sodium benzoate. In the laboratory experiment, the CO_2 decomposition rate was about 30% after seven weeks. With the favouritised variant, which was found step by step through the experiments, an outdoor field test was carried out to investigate the durability under natural conditions over the vegetation period. In the field, the mulch material maintained its function for six months. In the greenhouse, the effect of the mulch material on weeds was studied. It was found that the mulch material showed a high efficiency in controlling above-ground 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.

Keywords Mulch film · Biocomposite · Weed control · Renewable Resources · Sustainable agriculture

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 (Kasirajan and Ngouajio 2012). 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% (Sintim and Flury 2017) and global demand for plastic films is expected to increase by a further 59% from 2018 to 2026 (Sintim et al. 2020).

Low density polyethylene (LDPE) films are the most commonly used form of mulch films (Menossi et al. 2021). 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 (Li et al. 2022). After the use, the LDPE films are dirty of soil, organic matter and agro-chemicals (Immirzi et al. 2009). 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

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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 (Santagata et al. 2013). 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 (Pillai et al. 2014), starch (Gáspár et al. 2005; Marques et al. 2006; Bastioli 1998), cellulose (Moeller 2008), polylactic acid (PLA) (Rocca-Smith et al. 2017), polyvinyl alcohol (PVOH) (Kukal and Sarkar 2010) or hydrolysed proteins (Sartore et al. 2013). These materials can contain natural fillers such as cellulose fibres to increase mechanical strength and even coloured pigments to block the transmitted light to inhibit weed growth (Brault et al. 2002). 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 (Sintim and Flury 2017).

Recently, sprayable mulch films containing polysaccharides, proteins or other polymers in water has been developed (Sartore et al. 2013; Johnston et al. 2017; Giaccone et al. 2018; Roeder et al. 2007). Unlike conventional films, the mulch film is formed in situ on field (Avella et al. 2007). Mulch materials containing polymers like sodium alginate, glucomannan, chitosan and cellulose have been described (Sartore et al. 2013). 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 (Zimdahl 2007). For weed control, their germination and growth behaviour as well as their longevity play a crucial role (Long et al. 2015). 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 (Liebman et al. 2001). 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 (Schonbeck 1999). 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 renewable resources. A favouritised formulation with the best possible material properties such as reduction of mould infestation, heat and water resistance was to be found through concatenated tests. The durability of the mulch layer should be determined with a degradability test and a field trial. In addition, the effect of the material on weeds was to be investigated in greenhouse trials.

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 sulphate were obtained from Carl Roth (Karlsruhe, Germany); all chemicals had a purity of 99%. Glycerine was supplied from Distripark (Duisburg, Germany). Cellulose fibres were obtained from J. Rettenmaier & Söhne (Rosenberg, Germany) (CAS 9004–34-6, ARBOCEL BC 100, average fibre length700 μm, average fibre thickness 20 μm). Sawdust was obtained from the institute's own joinery. Before use, the sawdust was sieved through a 100 μm sieve.

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.

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 × 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 was calculated according to the following formula:

$$S = \frac{(d_0 - d_t)}{d_0} \quad (1)$$

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. The difference in mass was calculated according to (1) with mass (m) was used instead of diameter (d).

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. The solution was made from mouldy kitchen waste. The waste was stirred in water at 30 °C for one hour. The solids were then filtered off using a coarse-mesh sieve. 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 mould was present. The investigations were carried out as triplicates.

Biodegradability

Aerobic degradability was investigated in accordance with DIN regulation 17,556 (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) 2019). 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 (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

Table 1 Formulation of the different materials. All values are given in mass-% (weigh-in by total 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 fibre, b sawdust

evolved (ISO 17556:2019) 2019; Modelli et al. 1999). The CO_2 trapping was done in two reaction steps:

$$KOH + CO_2 \rightarrow KHCO_3 \quad (2)$$

$$KHCO_3 + KOH \rightarrow K_2CO_3 + H_2O \quad (3)$$

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

$$K_2CO_3 + HCL \rightarrow KHCO_3 + KCl \quad (4)$$

$$KHCO_3 + HCL \rightarrow KCl + H_2O + CO_2 \quad (5)$$

According to that reaction steps, the volume of HCl between the two equivalence points was used for determining the amount of CO_2 (Kale et al. 2007). The mass of CO_2 was calculated with the following formula (6) (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) 2019; ASTM International Standard Test Method for Determining Aerobic Biodegradation of Plastic Materials Under Controlled Composting Conditions xxxx):

$$m_{CO_2} = \frac{V_{HCl} \cdot c_{HCl} \cdot 44}{1000} \quad (6)$$

In addition, the mulch material (F6) 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) (see Fig. 1). 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. 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. During the first two months, it rained only 3 times (5 L/m^2, 5 L/m^2 and 12 L/m^2). Temperatures were mostly above 20 °C. From June onwards, there were a few additional heat storms that brought precipitation. Temperatures rose above 25–30 °C. Overall, the summer was very dry compared to previous years.

Fig. 1 Application of the mulch material with an air brush for the field trial

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 number of plants were thinned to 2 per pot. The rhizome pieces of *Elymus repens* were each treated with 25 mg 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 minimum or maximum 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 3 km/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 effect on above-ground biomass 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 above-ground dry matter determination was not possible due to the treatment with mulch material, only the below-ground biomass was analysed. It was washed carefully to preserve the fine roots and 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

Descriptive statistics using the arithmetic mean and the standard error were used for the characterisation of the properties of the mulch material. The data of the greenhouse experiments were analysed for normal distribution using a Kolmogorov–Smirnoff test. The results of efficiency of weed control (expressed by the percentage of dead leaf area) violated normality and therefore the nonparametric Kruskal–Wallis ANOVA was used for group comparisons. A post-hoc Dunn test was performed to identify the differing groups. The data of root dry matter was normally distributed, but Levene test showed heterogeneous variances. Thus, Welch ANOVA was used to analyse group differences, followed by a post-hoc Games-Howell test for comparisons between the treatments. All tests for significance were conducted on the $p < 0.05$ level. The Welch ANOVA with post-hoc Games-Howell test was performed using R Studio 2022.02.3, and all other statistical analyses were performed using origin 2021b (OriginLab Corporation, Northampton, USA).

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 (Braunack et al. 2021; Adhikari et al. 2019). 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 (Xu et al. 2005) or for a few hours at higher temperatures in a drying oven (Gao et al. 2022). 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 (Coviello et al. 2007). 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 (Grasdalen et al. 1981; Grasdalen 1983; Grant et al. 1973). 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

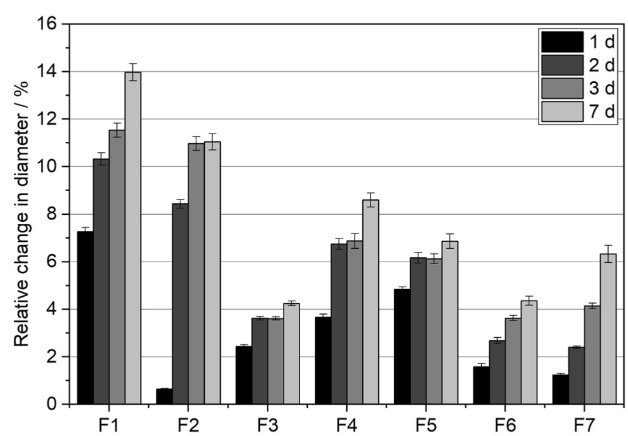

Fig. 2 Properties of the different rapeseed oil/starch formulations with regard to shrinkage behaviour. Error bars show the standard error, and all values shown are the mean values from a triple determination

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% (Averous et al. 2000).

Depending on the region and weather conditions, maximum ground temperatures of 60 °C may occur in rare cases (Kerridge et al. 2013). 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 (Karlsson et al. 2002). F2 and F6 showed the lowest mass losses within 3 h in the drying oven with 4 and 5%, respectively, while F4 and F5 lost more than 10% of their mass as water after 3 h. 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 (Immirzi et al. 2009).

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

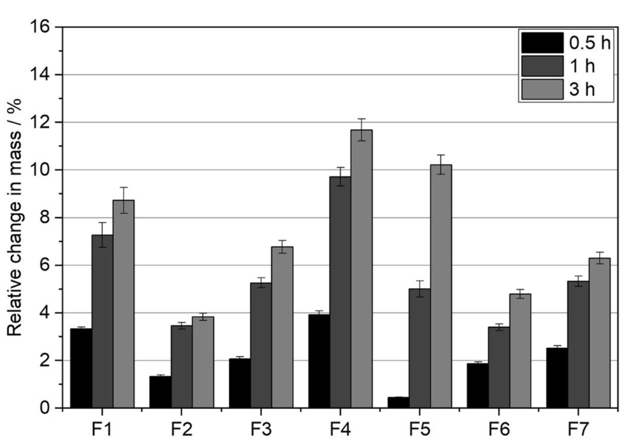

Fig. 3 Properties of the different rapeseed oil/starch formulations with regard to heat resistance. Error bars show the standard error, and all values shown are the mean values from a triple determination

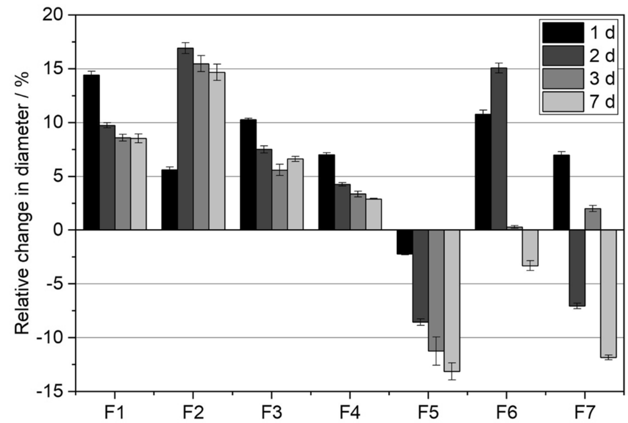

Fig. 4 Properties of the different rapeseed oil/starch formulations with regard to swelling behaviour. Error bars show the standard error, and all values shown are the mean values from a triple determination

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 (Samanta and Ray 2014). 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 (Brul and Coote 1999), propionic acid (Kung et al. 1998), potassium hydroxide (Hinton and Ingram 2006), tannic acid (Abd El-aal and Halaweish 2010), zinc oxide (Pasquet et al. 2015), and sodium benzoate (Shahmohammadi et al. 2016)), 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

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	-	+

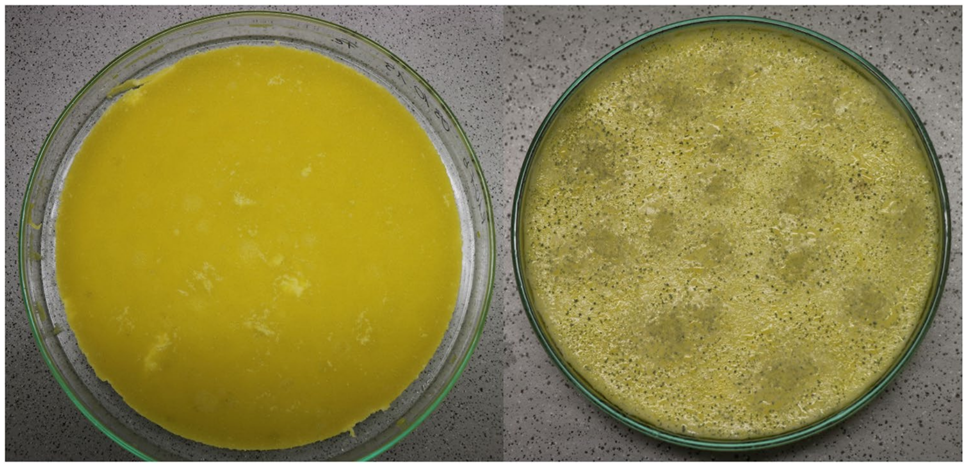

Fig. 5 Comparison of two formulations when testing the tendency of mould growth after 21 days storing in a darkened, humid box at room temperature. The test samples shown differ only in the presence of a preserving agent (left—1% sodium benzoate, right—without preserving agents)

oxide. The test samples were visually evaluated to determine whether mould infestation occurred or not (Table 2).

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% (Lennerz et al. 2015). The main reason for this, however, is that an undesirable aftertaste occurs at sodium benzoate concentrations above 1% (Khayatzadeh et al. 2011).

Based on the test results, F6 with an addition of 1 mass per cent 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 per cent

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 sulphate	1.5	Glycerine	4.5
Cellulose fibres	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 for titration (Modelli et al. 1999).

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

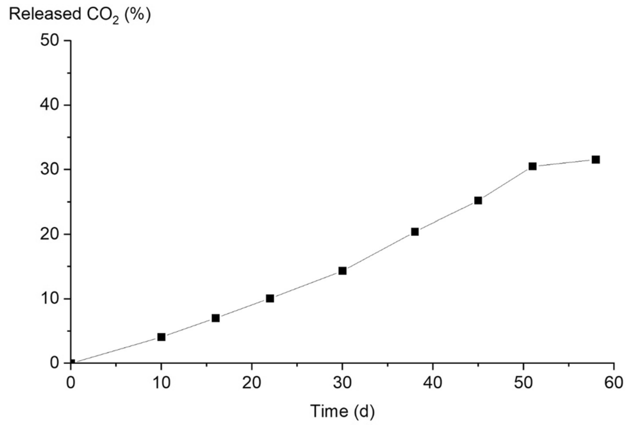

Fig. 6 CO_2 released as a percentage of the theoretical maximum amount of carbon available. The data shown are from a single determination

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 compared to other degradations known in literature. Our data are 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 (Costa et al. 2014). 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. 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. From mid-September it rained more frequently (440 L/m2 in the period of mid-September to end of October) and temperatures dropped to 5–10 °C. The mulch material also became very dark from this point onwards. This colour 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 (Giaccone et al. 2018). 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 (Vox et al. 2013). Biodegradable polymeric materials based on hydrolysed proteins had a durability of almost 9 months (Sartore et al. 2013) and sprayable mulches based on sodium alginate showed a decomposition after 109 days (Immirzi et al. 2009). The mulch material developed in this study is thus in the upper range of durability compared to other sprayable mulch materials.

Greenhouse experiment

The effect of the developed mulch material on three species of weeds (*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

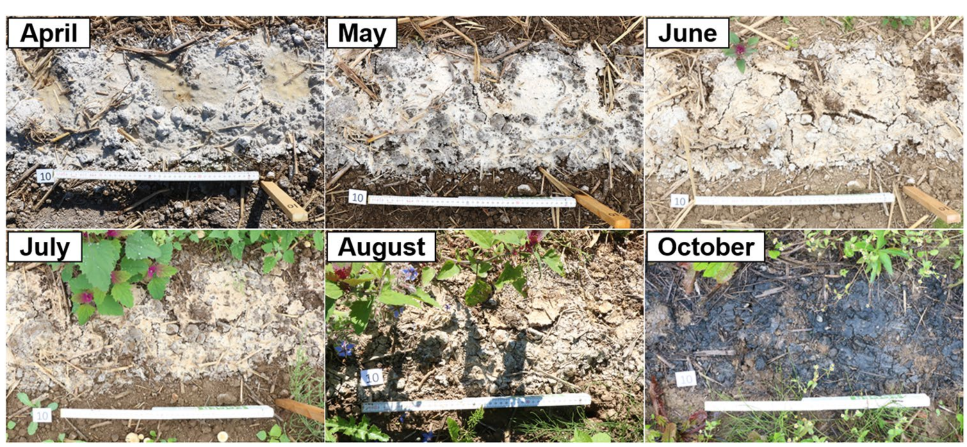

Fig. 7 Appearance of the mulch material (layer thickness 5 mm) during the observation period April to October

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 Dunn test showed no significant difference between the mulch material and glyphosate treatment for these two weeds. The efficacy of the mulch material for *Elymus repens* control was 76% and significantly lower compared to 96% for the glyphosate treatment. 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 (Hodge et al. 2019). 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) (Gloeb et al. 2023). 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 (Zwerger and Arlt 2002) because they have a high vegetative reproduction ability in contrast to annual weeds, like *Amaranthus retroflexsus and Setaria viridis* (Holzner and Glauninger 2005).

The results of root biomass (Fig. 9) varied depending on the weed species. Welch ANOVA showed no significant differences between the treatments for *Amaranthus retroflexus*. Nevertheless, in tendency 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. The differences between the control and the mulch material treatment were not significant. 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

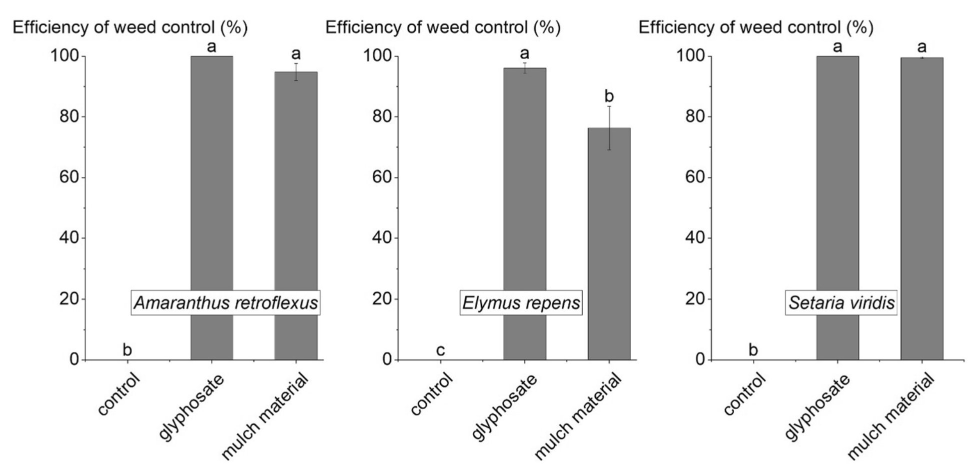

Fig. 8 Efficiency of weed control (mean ± SE) from the visual score of dead leaf area of *Amaranthus retroflexus*, *Elymus repens* and *Setaria viridis* of the treatments control, glyphosate and mulch material 22 days after the application. Different letters over the bars indicate significant differences between means at $p < 0.05$ (Kruskal–Wallis ANOVA, Dunns post-hoc test)

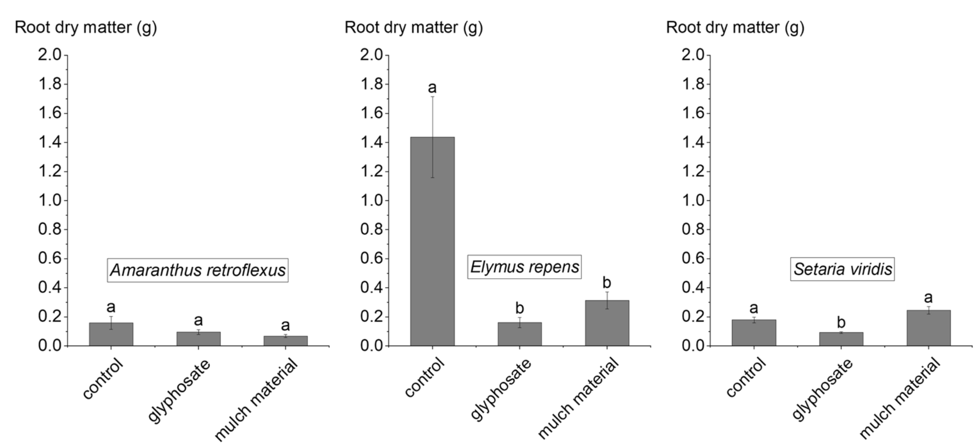

Fig. 9 Root biomass per plant (mean ± SE) of *Amaranthus retroflexus*, *Elymus repens* and *Setaria viridis* of the treatments control, glyphosate and mulch material 22 days after the application. Different letters over the bars indicate significant differences between means at $p < 0.05$ (Welch's ANOVA, Games-Howell post-hoc test)

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 (Li et al. 2023). Therefore, increasing the layer thickness of the material tested in our study could improve the rate of weed control could, especially for *Elymus repens*. Another study showed that the use of hydromulch significantly reduced the number of emerged seedlings of *Amaranthus retroflexus* (Claramunt et al. 2020). 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 (Gloeb et al. 2023). 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 (Giaccone et al. 2018; Hodge et al. 2019; Gloeb et al. 2023; Claramunt et al. 2020; Shen and Zheng 2017). 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 glyphosate. Previous studies have mainly focussed on the application of the mulch material before weed emergence (Giaccone et al. 2018; Braunack et al. 2021; Claramunt et al. 2020; Shen and Zheng 2017; Warnick et al. 2006). Gloeb et al. (2023) showed in his study that the application of mulch material after emergence can also have a good effect (Gloeb et al. 2023). In the trial, the mulch material reduced weed biomass by 84.7%. This value is comparable to the results achieved in this study.

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 degrades quickly due to its easily biodegradable 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 any external substances remaining on the field and accumulating there. 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.

Author 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.

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Data availability 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.

Declarations

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

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