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Algae-Based Bioplastics

HOW TO PRODUCE PLASTIC FROM ALGAE AND TESTS OF BIO-DEGRADATION

Plastic polymers present a fundamental environmental problem, which needs to be addressed urgently. The work performed herein, reports the use of alginate for selfproduction of algae-based plastic and addresses issues of bio-degradation. After a period of 12 weeks, clear signs of the degradation process in two different environments (forest floor / salt water) were evident. In any case, significant in-depth research is still necessary to progress this approach.

DIE JUNGFORSCHERIN

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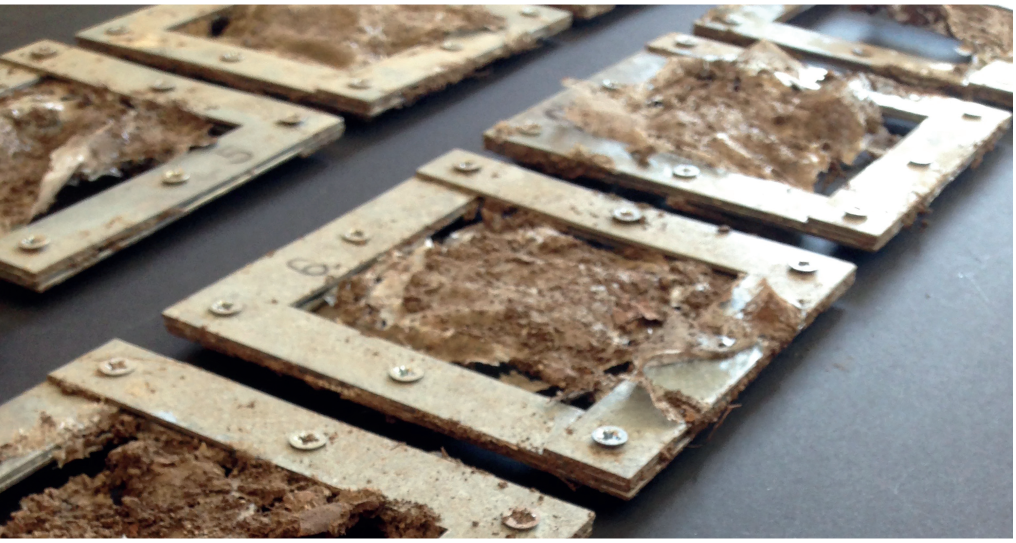

Algae-Based Bioplastics

HOW TO PRODUCE PLASTIC FROM ALGAE AND TESTS OF BIO-DEGRADATION

1. Introduction

One of the biggest issues today is environmental pollution. Plastics are an indispensable part of our everyday life and plastic debris contributes significantly to marine pollution. Three quarters of marine debris is plastic. Estimates indicate that between 4.8 million and 12.7 million tons of plastic waste ends up in the oceans every year ([5] to [9]). A consequence of this pollution is the formation of trash islands. The largest of them, the "Great Pacific garbage patch", has an area of more than 3 million square kilometres and is located between Hawaii and North America. This corresponds approximately to the area of Central Europe [2]. The amount of surface debris is only a small portion of the total waste. More than 70 percent of the debris sinks to the ocean floor and approximately 15 percent of this plastic debris is washed ashore. Beaches on uninhabited islands are therefore covered in rubbish ([5] to [7]). The durability of plastic represents the main issue. The decomposition of plastic products can take up to 450 years and even then may not be entirely completed. [4]. Table 1 provides an overview of various plastic products and their decomposition time.

Tab. 1: Products and Decomposition Time

Product	Decomposition Time
Fishing line	▪ 600 years
Disposable nappies	▪ 450 years
Plastic bottles	▪ 450 years
Polystyrene cups	▪ 50 years
Plastic bags	▪ 10–20 years

The incorrect disposal of plastic waste is the primary cause of marine plastic pollution [6]. In 2010, the 20 countries with the highest pollution rate accounted for 83 percent of all incorrectly treated plastic waste [9]. China, Indonesia, Thailand, Vietnam and the Philippines are the primary sources of plastic waste. An estimated 80 percent of the waste originated on land and the remaining 20 percent came from fishing and illegally disposed ship-generated waste [10]. The shocking fact is that forecasts predict that by 2050 the total number of plastic particles may exceed the number of fish. [12].

1.1 Effects of Plastic Debris on Wildlife

The number of dead seabirds with plastic in their stomach is continuously increasing because the birds confuse pieces of plastic with food.

Animals choke on plastic particles, die from constipation or starve because their stomach cannot ingest proper food anymore. Scientists found plastic parts in the stomachs of 93 percent of fulmars that they examined. Along with the sea birds, marine mammals, reptiles and fish are also affected. Moreover, animals die in agony because they are regularly trapped in rubbish or abandoned fishing nets [11].

1.2 Microplastics

On the one hand, even smaller plastic particles are produced by the ongoing decomposition of plastic sometimes

doi: 10.7795/320.201906

lasting for centuries. This ultimately leads to micro-particles that are smaller than one millimetre. On the other hand, plastic microbeads are now deliberately added to cosmetics, toothpastes and detergents. Microbeads can end up in our bodies as a result of eating fish and/or shellfish that have ingested microbeads. The consequences have not yet been adequately researched. [11].

A further negative aspect of microplastics is that they act as a "poison magnet", favouring the adhesion of lipophilic substances. This means that toxins frequently accumulate on the surface of the microbeads. These toxins can enter the food chain and subsequently be absorbed into the human body [5, 7, 13].

1.3 Countermeasures

Given that the plastic trash islands are in international waters, no nation will ultimately take responsibility and relevant agreements are ineffective. A possible solution would be to replace conventional plastics with biodegradable ones and thereby counteract the microplastics issue. The aim of this paper is to contribute to the solution of the plastic waste problem following this replacement approach.

1.4 Bioplastics

An in-depth discussion of this subject has been omitted from this abridged version in order to meet the requirements.

There are three primary reasons to produce plastic from renewable resources instead of oil:

- Oil is a limited available resource.
- The combustion of fossil fuels contributes to climate change through the release of carbon dioxide.
- The environmental problem of plastic pollution could be reduced through the use of this special plastic.

According to Dr Thielen [1, p. 76], "from a purely technical perspective, 90 percent of all plastics could be converted from fossil to renewable sources. In the short and medium term, however, this conversion will not be possible due to economic obstacles, for example, and the lack of short-term biomass". (Unofficial translation)

1.4.1 Market Situation

In 2016, bioplastics accounted for approximately 1 percent of the world's plastic production of 300 million tons. Due to the increasing demand and improved production processes, this market is growing by 20 – 100 percent annually [1, 19].

1.4.2 Areas of Application

Due to their special properties, bioplastics cannot be used in all areas. They are predominantly produced for disposable use. Table 2 provides an application of Bioplastics provides an overview of some of the application areas.

1.4.3 Algae-Based Bioplastics

Normally, corn or potato starch is currently used for the production of bioplastics. Bioplastics based on algae are a relatively new development. There are four processes of algae presently (2016) used as a raw material for the production of bioplastics:

- So-called hybrid plastics contain a certain proportion of algae; the remaining part of the plastic is oil-based.
- For cellulose-based plastics, the cellulose present in the algae cell walls is used for bioplastics production.
- The bacterial fermentation of algal biomass produces lactic acid, which can be used for the production of bioplastics.
- Ethanol can be obtained from algae, which can be used later, for example, by "cracking" as biofuel

Tab. 2: Application of Bioplastics

Application Area	Example
Horticulture	▪ plant pots, floral foam inserts, peat bags, binding material, etc.
Agriculture	▪ protective plastic, mulching film, twine, etc.
Medical Technology	▪ surgical material, sutures, screws, capsules, implants, etc.
Packaging	▪ loose fill, film, blister pack, hollow core packing, trays, cups, sacks, bags, etc.
Consumer Goods	▪ hygiene products, rubbish bags, handicraft materials, etc.
Gastronomy and Catering	▪ tableware, cutlery, straws, drinking cups, etc.

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and for plastic production.

It is possible to make these four types of algae-based plastic, however, they are often much more expensive than conventional plastics derived from oil [14].

There are already companies (2016) that produce bioplastics based on algae. Examples are Petro Sun [15], Cereplast [16], Soarplast (Algix) [17], and the Soley Biotechnology Institute [18]. Algopack [26] produced by Frenchman Rémy Lukas must also be mentioned. It should be noted however, that despite thorough internet research, no evidence of bioplastics based on sodium alginate was found.

1.5 Alginate Field Study

In order to generate the biomass required for the production of plastics, one can also revert to algae starch, the so-called alginate (Figure 1). One advantage of using this raw material is that it is not necessary to depend on agricultural land to grow feedstocks for the production of bioplastics. It was for this reason that I decided to use alginate as the raw material for my self-made bioplastics.

1.5.1 Alginate Production

Brown algae are the primary source of alginate. Their cell walls consist of alginate and cellulose. The cellulose stabilises the cell walls and the alginate combined with the water forms a gelatinous mass in the cell walls which intensifies their strength enabling the brown algae to withstand severe physical stresses, such as ocean currents. The proportion of alginate in the dry matter is between 15 % and 40 %. The larger species of brown algae are preferred for alginate production. Brown algae are among the fastest growing plants in the world. Some species can grow up to 30 cm a day which makes them predestined starch providers. Specially adapted ships are used to harvest the algae fields. Algae washed ashore are also used and approximately 9,500 tons of brown algae are gathered annually in Ireland, for example [28]. Once harvested, the brown algae are cleaned and dried. They are then thoroughly washed and ground to generate a dry powder from which the alginate is ultimately recovered through various extraction and filtration processes [29]. Worldwide more than 40,000 tons of alginate are produced annually. The main producers are the United Kingdom, the United States, Norway, France, Canada, China and Japan [28].

1.5.2 Occurrence

Brown algae belonging to the laminariales species form so-called kelp forests. These are found in relatively shallow waters, as the plants require light to carry out photosynthesis. In addition, this type of brown algae prefers cooler water temperatures of up to a maximum of 20 °C [27].

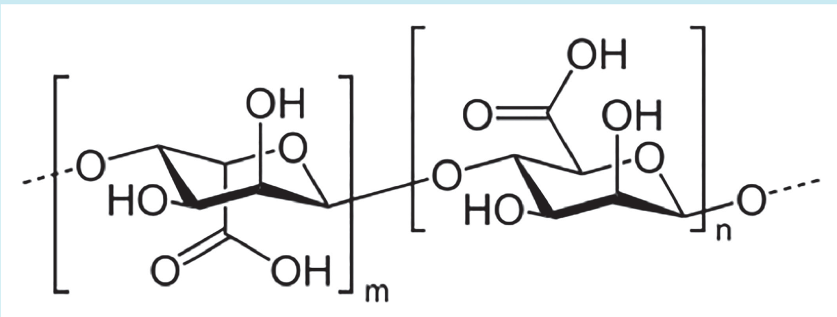

Fig. 1: Structure of Algnic acid (Alginate)

1.5.3 Polysaccharides and Decomposition

Alginates belong to the so-called polysaccharides (multiple sugars) and are assigned to the same group as starch or cellulose. Polysaccharides are complex carbohydrates comprising a number of sugar molecules. These are broken down by amylase, an enzyme that catalyses the hydrolysis of starch into sugars. The decomposition process generates dextrins and maltose which are then decomposed by other enzymes to form low molecular weight glucose.

Amylase is an enzyme that is produced by the bacterial strains *lactobacillus amylovorus* and *arthrobacter* [29].

2. Material and Methods

The situation presented in the introduction highlights that it is urgently necessary to find solutions for the environmental issues generated by plastics.

The aim of the practical part of my work was therefore to produce a completely biodegradable plastic film and verify its degradability in two different environments: forest floor and the Mediterranean Sea.

2.1 Preparation of Alginate Films

An important component of bioplastics is starch. If starch from algae is used, this has the advantage that no foodstuffs are misused for the production of bioplastics. Based on this concept, a formula for the production of bioplastics using corn starch was continually modified in a separate series of experiments until it was finally possible to produce a film based on algae starch and to define a formula for production.

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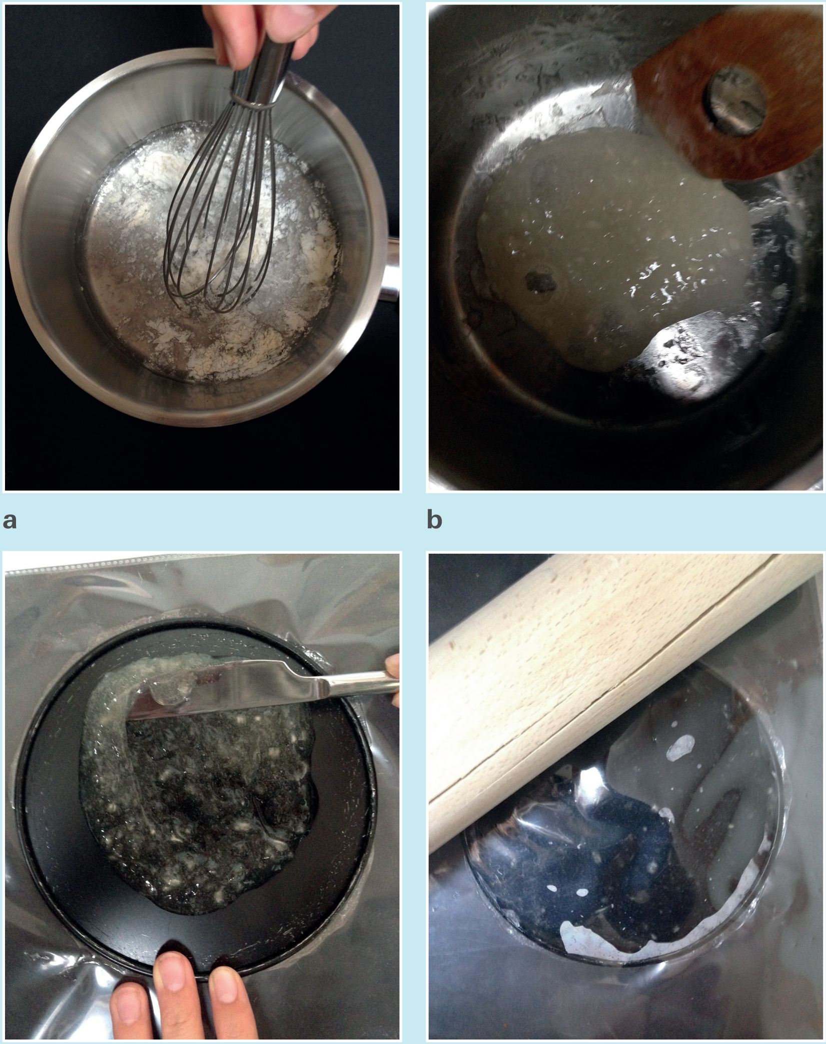
The reactants are 70 g distilled water, 5.25 g sodium alginate and 4.375 g glycerine (85 percent). The steps for preparation the alginate films are (Figure 2): Mix the exact amount of the reactants in a cold state with a whisk, then heat slowly the resulting mass on the stove. Stir the mixture thoroughly with a wooden spoon throughout the heating process and when the mixture begins to bubble, continue to heat for approximately one more minute. Place the mass on the base of a round baking tin and cover the mixture with a plastic film and distribute evenly. Then remove the plastic film and allow the mixture to dry for three days on the base of the baking tin. Once drying is complete, use a knife to remove the finished film from the baking tin.

All of the films used for the degradation tests were produced using this procedure. The result of that series of experiments was a circular self-made plastic-film with an area of approximately 132 cm^2 and a thickness of 0.2 to 0.3 mm. However, the thickness is not entirely determinable since there are small air bubbles in the foil. Additionally, the film is quite flexible and does not break easily. The self-made foil is partially transparent.

Exact measurements determining e.g. tensile strength, heat resistance or flexibility could not be taken since it exceed the dimensions of a student project.



a b c d

Fig 2: Preparing the alginate film: a) mixing reactants b) heating c) spreading mixture d) smoothing with rolling pin

2.2 Degradation Tests

In the second part of the fieldwork, the self-made films of equal size (132 cm^2) and thickness (0.2–0.3 mm) were tested for their degradability in the forest floor and the Mediterranean Sea. The duration of the degradation test was set at twelve weeks, based on the EU standard for the disintegration of material to compost.

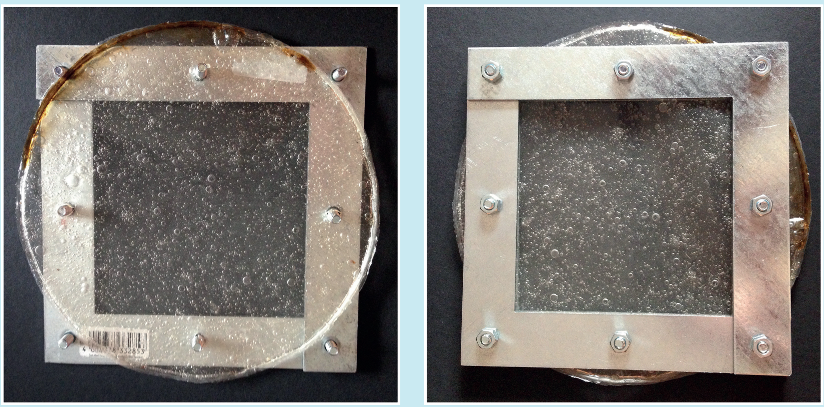


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Fig. 3: Preparing the sample for degradation test a) film is pierced over screws b) finished sample

2.2.1 Degradation Test in Forest Floor

doi: 10.7795/320.201906

The samples, which were buried in the forest floor (altitude : 1000 m, depth: 20 cm) for the decomposition test, were clamped in steel frames (Figure 3) in order not to lose them in the soil. The final surface of each sample in the metal frame was 64 cm^2. A total of eight samples were buried in the forest floor (Figure 4). A sample was retrieved every two weeks. After twelve weeks, three samples were retrieved together. The samples were dried and carefully cleaned. All samples were photographed and weighed. The degree of decomposition of each sample was analysed in detail using the available images.

2.3 Degradation Test in the Mediterranean Sea

The three samples deployed in the Mediterranean Sea (coastal region of Elba) were placed between two polymer lattices to avoid rusting of the frame (Figure 5). Every four weeks one sample was collected. After collecting the samples were only air-dried. All samples were photographed and weighed. The degree of decomposition of each sample was analysed in detail using the available images.

3. Results

Figure 6 and 7 show the progress of the

Fig. 5: Metal mesh with samples attached to it in the Mediterranean Sea

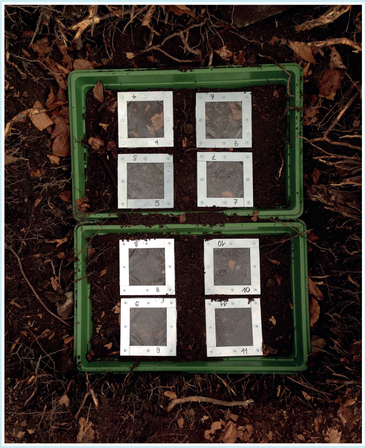

Fig. 4: Setting up sample on forest floor (depth of the hole 20 cm)

Fig 6: The samples after decomposition in Mediterranean Sea for 4 weeks (Probe 1), 8 weeks (Probe 2) and 12 weeks (Probe 3)

doi: 10.7795/320.201906

degradation process. It is noticeable that the mass of the film decreases and the individual pieces get smaller. Additionally, the film gets thinner the longer the sample was exploit.

The result can be summarized as follows:

The series of tests proves that it is possible to produce a plastic film from sodium alginate, distilled water and glycerine. The self-made films fulfill their purpose for the biodegradability tests.

The self-made films show clear signs of degradation in the sea and the forest floor after twelve weeks. As expected, the self-made sodium alginate-based plastic film, similar to other biodegradable starch-based plastics, is biodegradable.

The degradation process of the samples

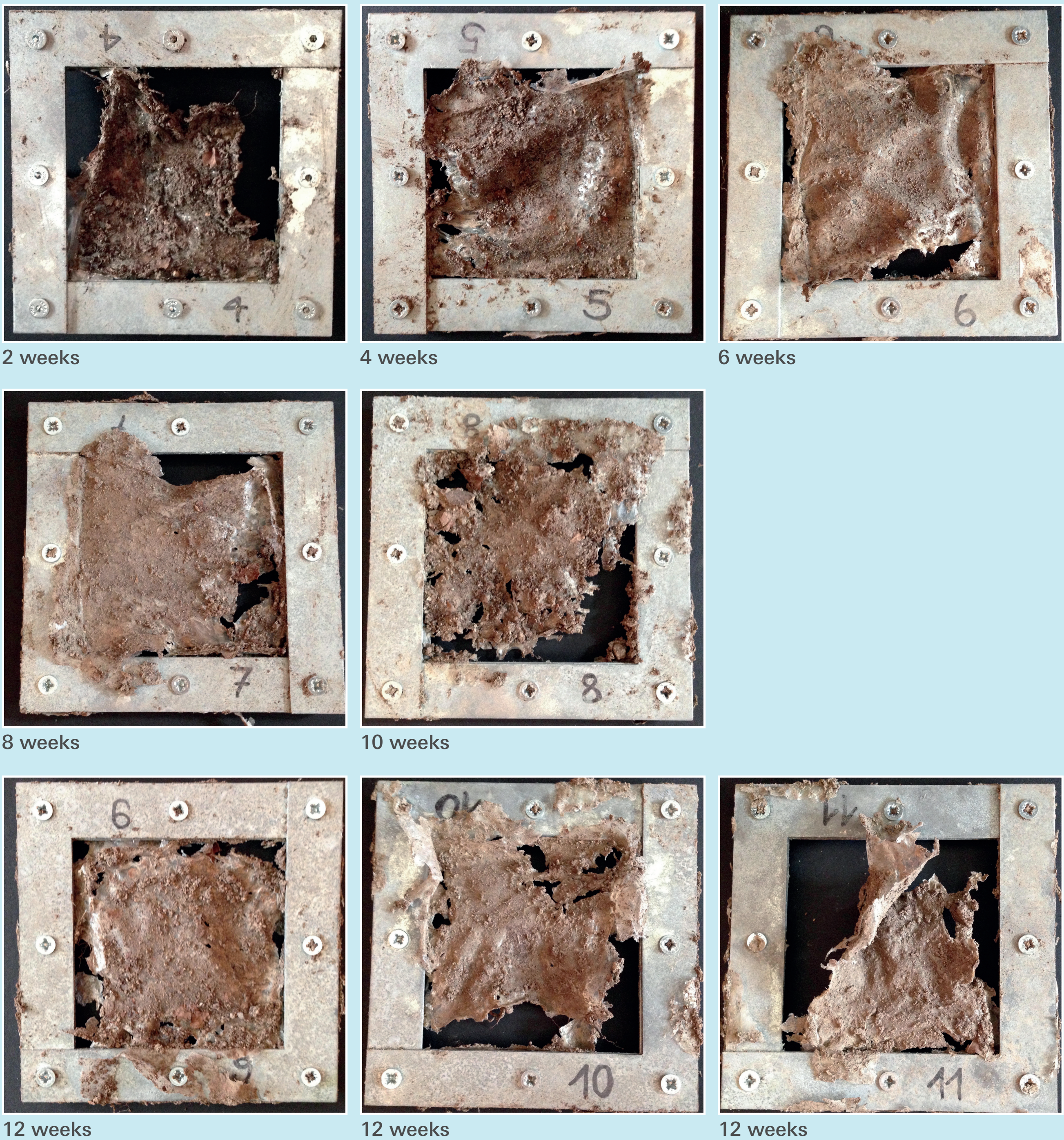

Fig. 7: The samples after decomposition in the forest floor

placed in the sea is faster than that of the samples buried in the forest floor.

4. Discussion

4.1 Temperature

If my degradation tests are compared with the requirements of the EU standard for the biodegradability of bioplastics, the temperature difference during the degradation process is considerable. In industrial composting, the average temperatures are around 50 °C [20]. The average forest floor temperatures at the chosen altitude were between 10 °C and 12 °C in the months of April to June [20]. In the Mediterranean Sea, the average water temperature during the decomposition tests was around 20 °C [25]. At lower temperatures, less favourable conditions inhibit the propagation of many of the bacteria which produce the enzymes responsible for the decomposition of bioplastics [22].

4.2 Different Environments

The impression of the faster decomposition process in the sea could be enhanced by the fact that small particles which separated from the samples were not retained by the polymer lattices into which the samples were clamped during the experiment. In addition, the following factors must be taken into account when considering the decomposition process in the sea as opposed to that in the forest floor: higher temperature of sea water compared to that of the forest floor, mechanical abrasion from the waves, hydrophilicity of the film.

The significance of the weight comparison of the samples is limited, because non-removable soil residues (soil samples), the loss of minute particles (sea) or the algae growth (sea) distort the measurement results.

4.3 Advantages of Self-Made Film

The self-produced film is completely biodegradable. Furthermore there is no misuse of foodstuffs in acquiring the starch necessary to produce the film. In addition to that no fertiliser or pesticide treatment of the starch source (algae) is necessary. This also eliminates any adverse side effects of fertiliser and pesticide treatment.

4.4 Disadvantages of Self-Made Film

The air pockets in the self-made film would have to be eliminated. Another problem is the film's hydrophilicity, a disadvantage which is problematic in certain areas of application. Lastly, the cost of the self-made film is currently far too high. It is worth mentioning that some features of the film are still unknown since further testing is still to be done.

4.5 Potential Applications of Self-Made Film

The present technique of adding water-repellent, biodegradable polymers such as polyester [22] to starch-based bioplastics to reduce their hydrophilicity could also be possible with my film. Based on this technique, an algae starch-based film could also be used in applications similar to those of starch blends, such as horticulture (e. g. plant pots), packaging (e. g. yogurt containers and drinking cups) or hygiene products (e. g. diaper films) [24].

4.6 Outlook

Bioplastics have a great potential. In 2016, bioplastics accounted for about 1 percent of the 300 million tons of plastic produced worldwide [29]. According to current estimates by European Bioplastics, the production capacity for bioplastics in 2019 will be four times greater than the capacity in 2014. The concept of algae-based bioplastic production could serve to further expand this market and increase the share of global plastics production. More disturbing, however, is the foreseen increase in the production of bio-based plastics which are not biodegradable. It is estimated that by 2019, 80 percent of the total bioplastics production of 7.8 million tons will be non-biodegradable [29]. The problem of oil as a limited resource would be partially solved, but the problem of degradation would remain. This is one reason for intensifying research into (algae) starch-based bioplastics. Given today's perspective, it cannot be assumed that bioplastics will entirely replace conventional plastics, especially when the lower maximum usability temperature of bioplastics, compared to that of oil-based plastics, limits their application. High-performance non-biodegradable plastics will still have to be reverted to for the production of technically demanding parts where durability and heat resistance are primary properties [3, p. 143].

5. Conclusion

The use of biodegradable plastics could effectively address the issue of plastic pollution described in this paper, especially in water bodies. The development possibilities for algae-based bioplastics are far from exhausted. They could, however, play a major role in the future bioplastics production since various deficiencies within conventional bioplastics can be eliminated [14].

The statements above have been substantiated by producing my own algae-based bioplastic film and conducting degradability tests in a forest floor and the Mediterranean Sea. It is still a long way until my idea becomes a finished product for everyday use and will certainly require further experimentation and an improved manufacturing process. My goal, however, is to make a small contribution to the struggle against marine pollution. I have achieved that and who knows, maybe in 50 years alginate-based bioplastics will be in

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daily use.

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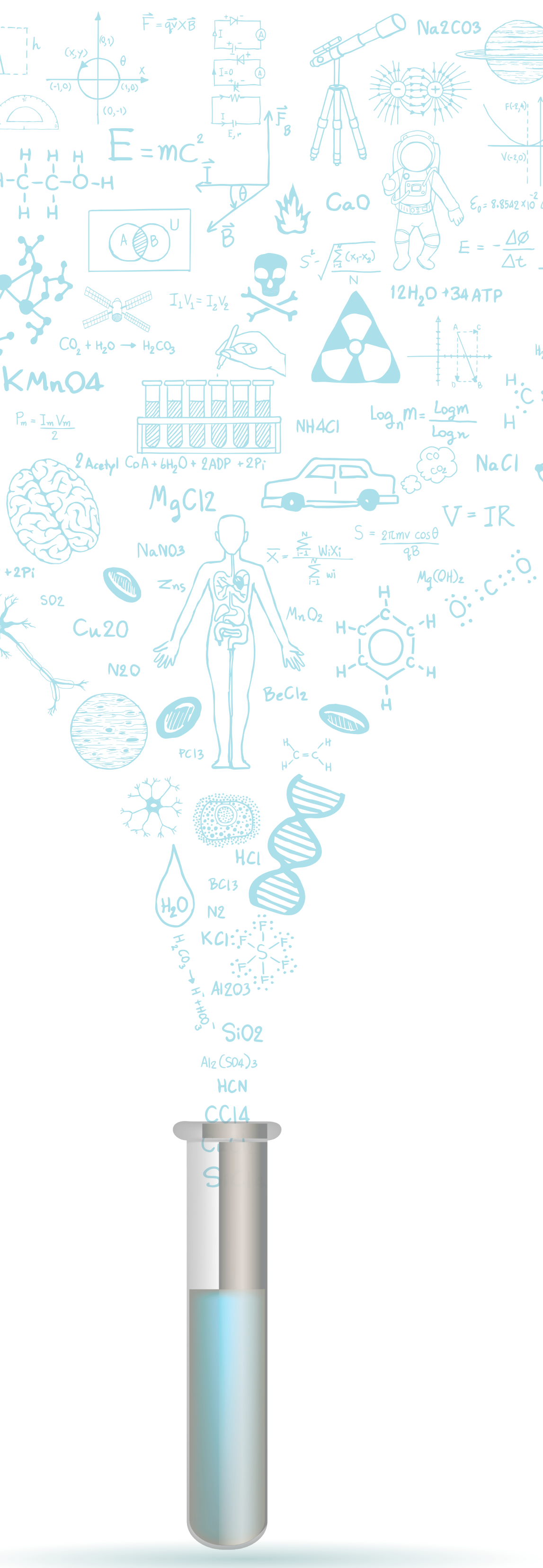

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