SOME ASPECTS OF EXTRACTION AND APPLICATION OF SEAWEED *FURCELLARIA LUMBRICALIS* CARRAGEENAN IN PRODUCTION OF RECYCLED PAPER

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Abstract. The present paper focuses on seaweed (macroalgae) detritus as a potential feedstock for recycled paper material production, since significant quantities of seaweed residues are available in the research site – Kurzeme coast (Western Latvia). This study aims to adapt the method for paper manufacturing from red seaweed *Furcellaria lumbricalis*. Binding agents manipulate properties of the paper material. *Furcellaria lumbricalis* material has been gathered on Kurzeme coast in Liepaja city and brought to the Liepaja University for carrageenan substances isolation/separation and further use in papermaking. The samples were thoroughly washed with tap water, then boiled for 3 hours and hot filtered into cold isopropanol to get the binding material. After adding the binder material to the recycled paper material, paper strength tests were performed. Paper with algae binder is 9% less resistant than recycled paper with added PVA glue, but 40% stronger than recycled paper without any added binders. The results of the experimental study demonstrate that the method adapted for seaweed treatment is appropriate for low-input paper manufacturing. It shows that local natural resources can be used in production of paper, without the addition of binder chemicals. Still, the research results should be considered as preliminary ones. Further studies are necessary to develop compatible paper material and extract pulp from *Furcellaria lumbricalis*. Obtaining pulp from algae, at first they need a chemical treatment with alkali- NaOH, followed by bleaching with H_2O_2 and acid hydrolysis – H_2SO_4, eventually producing cellulose.

Keywords: *Furcellaria lumbricalis,* carrageenan, recycled paper.

Introduction

According to statistical data, in the developed countries of the world, one person consumes about 80 kg of paper every year, almost half of the paper consumed is paper packaging. In Latvia, paper in municipal waste is 64 033 tons of the total amount of municipal waste 800 413 tons in 2019 [1]. In comparison, this means that every inhabitant of Latvia consumes as much paper during the year as is obtained from one tree. Recycling is the return of used materials for use as a modified material. To successfully perform one or the other material recycling method, sorting of used materials and assessment of the condition of the sorted materials are of paramount importance. By opportunity, recycled materials can be divided into three groups, these groups are summarized in Table 1.

Table 1

Recyclability of various materials

Material is recyclable		
Easy	**Medium**	**Hard**
Paper	Ceramics	Laminates
Glass	Concrete	Reinforced composites
Metals	Reinforced concrete	Coatings
Plastic		

From the group of easily recyclables, materials are returned in practically as the same materials. Plastics are most often made up as various composite materials.

Ceramics, concrete, and reinforced concrete cannot be recycled directly. Metal fittings are mechanically separated from used reinforced concrete structures and recycled as metal. Concrete and ceramics are crushed or grounded. The obtained dispersion materials are usually used as aggregates to produce various composites – asphalt concrete, etc. Rational recycling of laminates, reinforced polymer composites and coatings is practically impossible.

Right now, plant-based composites have many benefits and are worth exploring. Natural fibres are mainly obtained from lignin, pectin waxes, hemicellulose, and cellulose [2]. Common plant-based fibres are flax, cotton, jute, hemp, sisal, palm, bagasse, ramie, and processed speciality fibres [3]. Natural fibres being used as reinforcement in composite materials tend to display good mechanical properties, thereby gaining a lot of attention in recent years. They are known to be fully biodegradable, renewable, environmentally friendly, cheap, available in abundance and have a low density [4].

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The synthesis of an environmentally friendly bio composite using organic waste is an inexpensive easy way. Currently, composite materials are made from organic waste such as: wheat straw -paper-coconut composite, wheat straw-coconut fibre composite, corncob-coconut composite [5] and there are various attempts to make new composites of all kinds of organic waste including seaweeds [6]. Macroalgae detritus can be potential feedstock for recycled paper composite material production as the binding agent using extract from *Furcellaria lumbricalis*.

Marine algae can be considered as alternatives due to a vast and cheap source of potential biopolymers and composites [7].

Furcellaria lumbricalis – algae are washed on coast by spring and autumn storms on the shores of the Baltic Sea, in the seaside of Liepaja and Ventspils, mainly red algae – *furcellaria lumbricalis* on the shores of the Baltic Sea along the Latvian border (497 km) washed on coastline every year (mostly in the autumn) one hundred thousand tons of seaweed. Algae are washed out of the sea most in Pape, Liepaja, Uzava, Pavilosta, Sakas, Ventspils, Mersrags, Roņurags, Kaugurciems, Ainazi and Salacgriva. *Furcellaria lumbricalis* decomposes quickly and is as valuable as manure [8].

The municipal administration of Liepaja recognizes it as a disturbance, according to approximate estimates, 3717 m^3 of algae waste material has been transported from the Liepāja coast (only from public beach territory alone) per year and removal costs are 24795 EUR [9].

As the authors mentioned before, reinforced composites have a hard recycling ability and furthermore, producing new composite material from seaweed, biodegradability needs to be taken in consideration.

Landfills or composting plants end up with large quantities of materials containing organic polymers: wood, paper, plastics, etc.

When such products end up in waste, it would be desirable for them to be able to biodegrade rapidly. This would reduce the amount of waste in landfills or speed up the decomposition process. Biodegradation of polymers is a sufficiently complex set of chemical reactions. The processors are microorganisms, mainly aerobic bacteria. In essence, micro-organisms use the products of its transformation as nutrients when microorganisms encounter the polymer.

The microorganism secretes enzymes - biomolecules, most often they are proteins that are absorbed on the surface of the polymer product, accelerate the cleavage reactions of the polymer macromolecules. Cleavage results in small molecules of water-soluble products that, when dissolved in the environment, are assimilated into the cells of the micro-organism. The fission process also produces small molecules that are released into the environment: carbon dioxide, water, and methane. The polymer material is lost because of these reactions. Erosion of the polymer surface occurs, the specific surface area increases, which accelerates the biodegradation process. Biodegradability is determined by the structure of the polymer macromolecules. A small range of polymers degrades quickly enough [10]. Natural polymers that decompose rapidly are polysaccharides – cellulose; proteins-gelatine, casein, silk, wool; polyesters – polyhydroxyalkanoates and others – lignin, natural rubber.

Carrageenan is a family of natural linear sulphated polysaccharides that are extracted from red edible seaweeds. In this paper, the further described paper-seaweed composite is considered as a biodegradable material, because, as mentioned above, red seaweed *Furcellaria Lumbricalis* detritus consists of polysaccharides, small amounts of proteins and traces of lipids [11]. Recycled paper what is used in production of composite seaweed-paper, the material microscopic photo is shown in Figure 1, consists of cellulose, which is obtained from wood, paper materials in general are biodegradable materials, if not laminates and plastic materials added.

Materials and Methods

The preparation of paper pulp takes place in the paper recycling laboratory of the Liepaja University. The pulp is made from recycled office paper collected from the offices of the Liepaja University. During the pre-processing process, the paper is shredded in a paper shredder and placed in storage carton boxes for further use. The paper pulp making process requires shredded paper in 4x35 mm particles in the paper shredder *Fellowes Powershred 53C*.

Red seaweed *Furcellaria lumbricalis* detritus was harvested in October 2021 from the coastal area of Liepaja municipality public beach. After collection, the algal biomass with sand impurities is transported to the laboratory for the first process treatment of the algae – drying and removal of impurities. It is important to remove the sand, as the sand damages the running gear and blades of the equipment used – blender Russell Hobbs Illumina Jug Blender, 1.5 L, 850 W.

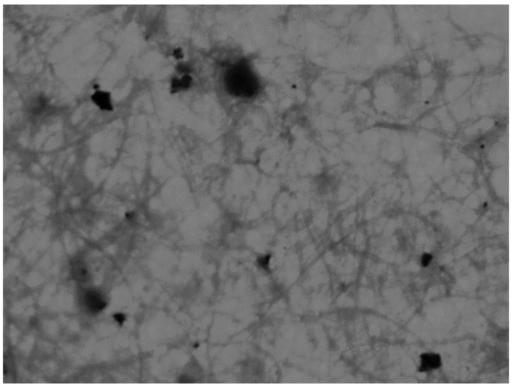

Fig. 1. **Composite seaweed-paper OM image by 720 nm, unedited, grayscale**

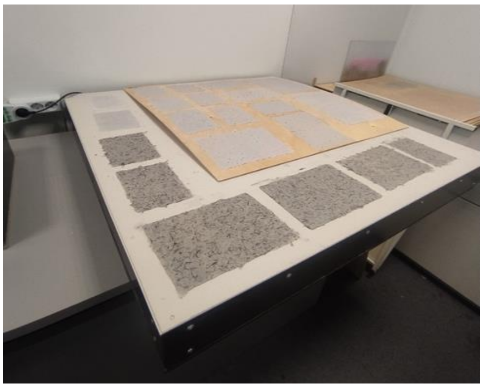

Fig. 2. **Composite seaweed-paper in drying process**

Extraction of carrageenan of red algae, for further use as a binding material, takes place in the Liepaja University environmental chemistry laboratory. For the current experiment we needed to take 450 g cleaned red algae *Furcellaria lumbricalis*, boil 3 litres of water for 3 h in an aluminium pot on *MCS 77 hotplate stirrer*. A gel-like mass is formed which can be stored in the refrigerator for more than 1 week, if not used immediately during the manufacturing process. 40 ml of cold (7 ºC) isopropanol (99.9% V/V) can be used for extraction. Distilled water must be used for purification; alkaline solutions of KOH or NaOH of various concentrations may be added at the boiling point. The hot extract can be filtered through a porous gauze filter in cold (6 ºC) isopropanol (99.9% V/V) to precipitate polysaccharides. The carrageenan precipitate must be separated from the mixture of alcohol and water by filtration through a porous gauze filter. The isolated polysaccharide mixture must be dried to constant weight in an oven (80 ºC, 1 day) and then ground for later use, which can be continued immediately after isolating the polysaccharide. In the current experiment, carrageenan is used as a binder in production of seaweed paper composites immediately after extraction.

After extraction of carrageenan, it is necessary to prepare pulp of the recycled paper. Seaweed paper composite requires 150 grams of pre-shredded used office paper. Blend the paper with 1 litre of water and add 172 g of extracted carrageenan. After preparing the pulp, it is necessary to create sheets of paper in the paper making sieves. The resulting sheets of paper are placed on a paper dryer, see Figure 2, and dried for 2 hours at 45 ºC. Carrageenan can be used as a binder [12] in production of paper composites and crushed dried algae can be added, if the paper is used for decorative purposes. For this article seaweed-paper is only with carrageenan as a binding material to replace chemical binders, such as polyvinyl acetate.

After recycled paper material was dried, the paper strength tests were performed.

Results and discussion

Strength tests were performed with 4 different paper types- regular office paper, recycled paper without any binding agent added, recycled paper with added carrageenan, recycled paper with added polyvinyl acetate binding agent. Each paper type was tested 10 times. All paper type samples were divided in strips. The strip dimensions 100 mm x 10mm. The paper strips are attached to a laboratory support stand with clips, the weight added to each test strip. When the paper breaks to withstand the weight, a fixation is made with the result in grams. The used scales *Kern FGE5K-3S d*, the weighing range from 1g to 5000 g, accuracy ± 2**%**. The test results are shown in Table 2.

The properties of carrageenan allow them to dissolve in water, form highly viscous solutions and remain stable over a wide pH range. They are used in a variety of commercial applications such as gelling, thickening, and stabilising agents, especially in food products and sauces. In addition, carrageenans are used in experimental medicine, pharmaceutical formulations, cosmetics, and industrial applications.

Table 2

Strength test results

Tests	Weight capacity in grams, accuracy ± 2%			
	Regular fine grade office paper	**Recycled paper without binding agent**	**Recycled paper with added carrageenan**	**Recycled paper with added polyvinyl acetate**
1.	3888	2360	2370	2709
2.	4760	2310	2365	3850
3.	4191	2663	3575	3156
4.	4189	2362	3180	4123
5.	3981	2160	3478	3258
6.	3765	2263	3231	3201
7.	4182	2257	3232	3203
8.	3872	2260	3759	3200
9.	5644	2214	3553	5284
10.	5928	2087	3540	3348
Average	**4440**	**2294**	**3228**	**3533**

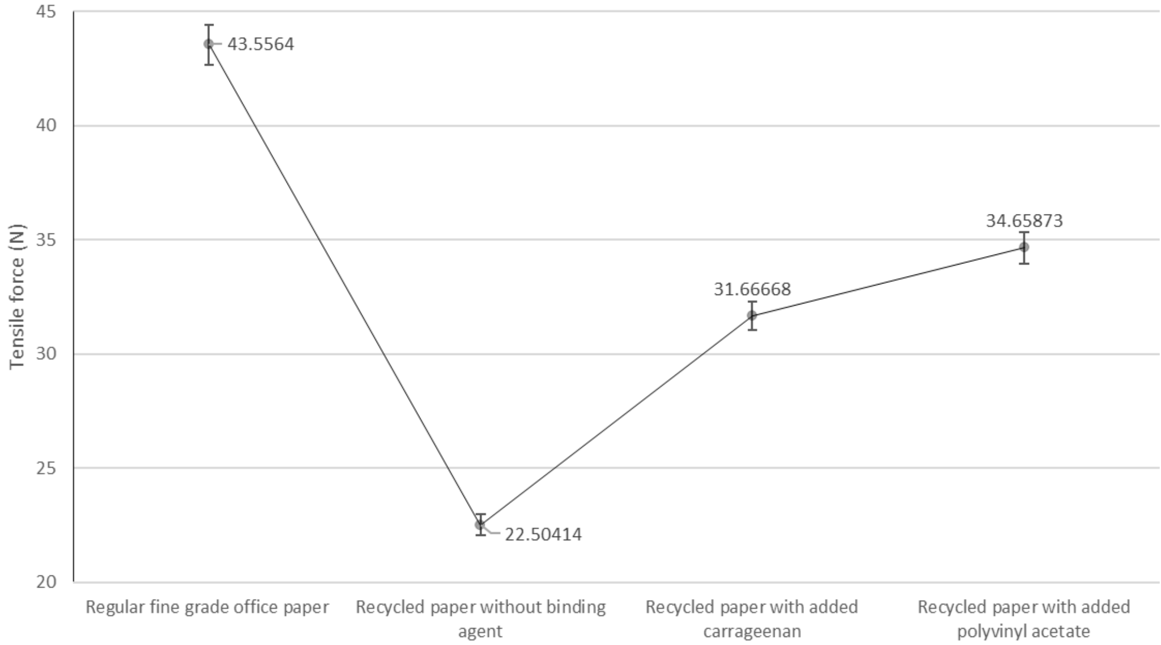

Fig. 3. **Tests results of tensile strength of paper example**

According to the test results, paper with algae binder is 9% less resistant than recycled paper with added PVA glue, but 40% stronger than recycled paper without any added binders. Regular fine grade office paper was tested for comparison with industrial manufactured paper. The results show that the carrageenan binder can be used in production of paper to replace chemical inorganic compounds. The use of carrageenan in production of composite materials would lead to more environmentally friendly composite materials in terms of biodegradation. As mentioned above, carrageenan is used in the food industry and pharmacy, but currently used only in production of bioplastics based on carrageenan derived from red algae [11]. The use of seaweed extraction of carrageenan would reduce the management costs for local authorities, which must deal with collection and transport of biomass to landfills.

Conclusions

1. Carrageenan from red algae *Furcellaria lumbricalis* can be used as a binder for paper recycling.
2. The method adapted for seaweed treatment is appropriate for low-input paper manufacturing.

3. Further research requires mechanical, chemical, water resistance and biodegradation tests of materials and binders from *Furcellaria lumbricalis*.
4. To replace the use of wood for cellulose production, further research should focus on extraction of cellulose from *Furcellaria lumbricalis*.
5. Biomass leached from the Baltic seashore can be a resource rather than bio-waste.
6. The use of seaweed reduces the management costs for local authorities, which must deal with collection and transport of biomass to landfills.

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Author contributions

Conceptualization and methodology, S.O. and U.Z.; investigation, S.O. and U.Z.; writing – original draft preparation, writing – review and editing, S.O., U.Z. visualization, U.Z. and S.O.; project administration and funding acquisition, U.Z. All authors have read and agreed to the published version of the manuscript.

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