DEGRADATION STUDY OF POLYLACTIC ACID, SPIRULINA AND ALGINATE COMPOSITES IN COSMETIC APPLICATION

MOHAMMAD SHAHRIZAD PAIRON[1], FATHILAH ALI[1*], HAZLEEN ANUAR[2]

[1] *Department of Biotechnology Engineering, Kulliyyah of Engineering, International Islamic University. Malaysia (IIUM), Jalan Gombak, 53100 Kuala Lumpur, Malaysia.*
[2]*Department of Manufacturing and Materials Engineering, Kulliyyah of Engineering, International Islamic University Malaysia, Kuala Lumpur, Malaysia*

**Corresponding author: fathilah@iium.edu.my*

ABSTRACT: Plastic composites are suitable materials in the production of a cosmetic patch. It could be used as a matrix to hold the fiber in the composites. The fiber used in the cosmetic patch is an active ingredient that has a good reaction with the skin. However, the plastic material gives irritation and allergic when contacting the skin. Hence, the usage of biodegradable plastic such as Polylactic acid (PLA) replacing the conventional plastic in the plastic composites of the cosmetic patch. PLA has a slow degradation rate, therefore the natural fiber (spirulina and alginate) were used to increase the degradation rate of PLA. The objectives of this project were to study the degradation of the PLA composites and to characterize the surface morphology and surface properties of the degraded PLA composites. The selection of the best PLA composites is by the highest Young's Modulus and Elongation at break value. The samples were then left for microbial degradation. The microbial degradation results showed that the spirulina enhanced PLA composite degradation. However, microbial degradation was not the best degradation method since the disturbance of alginate as a binding agent in the soil give an inconsistent result. Scanned Electron Microscopy (SEM) images showed that the fiber initiates the degradation in the PLA composites.

KEYWORDS: *Polylactic Acid (PLA), Alginate, Spirulina, Polymer Degradation, Polymer composites.*

1. INTRODUCTION

Conventional plastic had been used widely in our daily applications. Plastic is a flexible material type where it can easily mold into various shapes. The commercialized production of plastic had been increasing since 1950 and it was estimated to reach 330 million metric tonnes in 2016 [1]. From the rate of growth, the usage and the production of conventional plastic tend to double in the upcoming 20 years [1]. This was because the usage of plastic usually brings benefits at a lower cost at the marketplace than other types of material. Single-use plastic is a term for packaging plastic that is only used once before being thrown and also called as disposable plastic. The landfill is not the end life of plastic. In the environment, plastic will persist up to 1000 years without being decomposed by sunlight or microorganisms. Plastic waste recycling was one of the alternatives being used for plastic waste disposal. However, only 16% of the plastic waste had been recycled and only 2% of them can be efficiently recycled [2]. Moreover, the recycling process of plastic waste had to be taken up to 600 years [2].

For this reason, some steps had been taken to replace conventional plastic with different types of materials such as paper or metal and avoided single-use plastic usage or production with low durability plastic-type. Other than that, biodegradable plastic could replaced the usage of conventional single-use plastic [3]. Polylactic acid (PLA) was one of the biodegradable plastics used widely nowadays. It was discovered by Wallace Carothers in 1932 and Cargill Inc. was the first industry to commercialize it [4]. PLA is the most preferable type among the biodegradable polymers as it has almost the similar properties of conventional plastic used in packaging. In addition, its application was not only limited to packaging, but also been used in medical implants, 3D printing, and also cosmetic patches.

The polymer is one of the main ingredients in the cosmetic patch and acts as a thickener. Thickener affects the rheological profile of the formulation and also influences the application of the product, water sensitivity of the formulation, and delivery of the active ingredients [5]. PLA is a suitable material to be used in a cosmetic patch because its chemical structure and its degraded compounds such as water and carbon dioxide are not toxic or carcinogenic [6]. In conjunction with that, replacing conventional plastic with biodegradable plastic gives a beneficial outcome because conventional plastic gives reactivity when making contact with the skin and causing irritation [7] while biodegradable plastic does not.

To improve the capability of PLA in the cosmetic patch, PLA-based polymer composites were introduced. Polymer composites consist of two different materials, matrix, and fillers. Matrix is a major phase that supports the position of filler/fiber [3]. Filler/fiber such as metal or ceramic, mix with matrix and improve properties to the composites. Spirulina was tested for eight weeks and it showed improvement in antioxidant property on the human skin [8]. Other than that, alginate also acts as a thickener, useful for hand gel and lotions [9]. This proved the capability of spirulina and alginate in the cosmetic industry.

The matrix used in this research was PLA while spirulina extract and alginate were used for cosmetic purposes. All of these materials are biodegradable and can be consumed by the microorganism that makes the composites fully biodegradable and environmentally friendly products. This research aimed to study the degradation of polylactic acid composites in cosmetic used with spirulina and alginate as fibers.

2. MATERIALS AND METHOD

2.1. Materials

PLA granules were supplied from NatureWorks (USA) with grade Ingeo 3251D with average molecular weight of 148000 g/mol. Spirulina extract or Phycocyanin powder purchased from Xi'an Quanto Biotech Co., Ltd (China). Alginate powder was purchased from Take it Global company. Chloroform was purchased from HmbG chemicals (analytical grades, Germany) and used as it is. The soil was bought from a nursery at Sungai Chinchin.

2.2. Preparation of PLA and PLA/Spi/Alg composites

The choloroform had been used as a solvent to dissolved the PLA granules. Before using the PLA granules, they should be kept in a pre-heated oven at 60℃ for 24 hours [10]. 7g of PLA granules was added into 100ml chloroform at room temperature and kept stirred untill dissolved. Based on Sungkapreecha et al. [11] with modification, the PLA concentration used in this experiment was 7, 10, 13, 15, 17, 20, and 23 w/v%.

Based on Huang et al. [12] with modification, three different fiber compositions had been prepared. First was a balanced composition between the spirulina and alginate (5:5). The second fiber composition was high spirulina ratio (9:1) and the third was high alginate ratio (1:9). The fiber ratio with a total of 1g mixed with 40ml distilled water and stirred until the components dissolve completely. Solvent casting technique by layers was used in the preparation of PLA composites film. The first layer of the film was PLA with various PLA concentrations (7. 10, 13, 15, 17, 20, and 23% w/v) and left to dry. The second layer from spirulina and alginate blending was cast on top of the PLA film and left to dry. As the PLA composites dried, the blue color of the spirulina had become faded. PLA films were used as a reference for PLA composites in degradation. The PLA composites with spirulina only and with alginate only also had been prepared from the best PLA concentration in mechanical test as reference to this study.

3. CHARACTERIZATION

3.1. Mechanical test

Young's Modulus (MPa) and Elongation at break (%) of the PLA composites had been obtained by using Universal Testing Machine (UTM) (Shimadzu, AGS-X, Japan). Samples were prepared according to ASTM D-882 type-V with crosshead speed 5mm/min, load cell of 5 kN, and 30 mm gauge length. The samples were cut into the size of (60x10) mm and the test was repeated 5 times for an average value. The best mechanical properties with high Young's Modulus and Elongation at break proceeded for the degradation study.

3.2. Weight loss

The sample was cut into a size of 20 mm width and 20 mm in height [13][14]. After the film was cut into its size, the PLA composites samples dried in the oven of 35℃ for 24 hours. Different from PLA samples, where the oven temperature used was 40℃. After dried, the sample buried under the soil at room temperature, labeled and the moisture of the soil had to be maintained at 25%. The sample must be weighed before being put into degradation environment. This step had indicate the initial weight, W_i of the sample. After a month, the sample had been weighed again, W_n and the weight loss through the period had been calculated. The PLA composites sample was heated in the oven at 35℃ to remove the moisture untill achieve constant weight. For the reference sample, PLA was heated at 40℃ to remove the moisture untill achieve constant weight. The percentage weight loss calculated as in Eq. (1).

$$Percentage\ weight\ loss\ (\%) = \frac{W_n - W_i}{W_i} \cdot 100\% \quad (1)$$

3.3. Morphology test

The sample was characterized after 6 months of microbial degradation. The samples were prepared with a dimension of (10x10) mm. The apparatus used in completing the test was Scanned electron microscopy (JEOL, JSM-5600, UK) and was observed at 500 magnifications at 8kV accelerating voltage. The samples were coated with palladium sputter before scanning.

4. RESULT AND DISCUSSION

4.1. Preparation of sample

In Table 1, 8 samples were selected from the total number of 21 samples needed to be prepared. As the ratio of alginate was reduced, the homogeneity of the sample was reduced. Not equally distributed fiber would affect the degradation rate and was removed from the selected sample. As the PLA concentration increased, the layers of the PLA composites tended to separate. Difference hydrophobicity of the matrix (PLA) and fibers (spirulina and alginate) caused the separation of the PLA composites layers. However, this effect had low impact at low concentration of PLA. The separated PLA composites films were also removed because these samples could not behave as a composites for the degradation study.

Table 1: PLA composites sample

PLA concentration	Spi:Alg (9:1)	Spi:Alg (5:5)	Spi:Alg (1:9)
PLA7	NA	PLA7S5A5	PLA7S1A9
PLA10	NA	PLA10S5A5	PLA10S1A9
PLA13	NA	PLA13S5A5	PLA13S1A9
PLA15	NA	PLA15S5A5	PLA15S1A9
PLA17	NA	NA	NA
PLA20	NA	NA	NA
PLA23	NA	NA	NA

4.2. Mechanical test

4.2.1. Young's Modulus

From Fig. 1(a), as the PLA concentration increases, the value of Young's Modulus increases too. The highest value gained at PLA concentration of 13w/v% for PLAS1A9 (0.20 MPa) and PLAS5A5 (0.48 MPa). Proved by the study of Qiu et al. [15], where the high number of modulus indicated the brittleness of the samples caused by the low ductility of PLA. Apart from that, high Young's Modulus also represented the strength of the materials. However, at the 15w/v% PLA concentration had low Young's Modulus compared to 13w/v%. This was because the matrix and fiber began to act individually in the composites. This resulted in the separation of the matrix and fiber layer at the end of the test. Apart from that, although alginate could provide brittle properties [16], the increase of alginate ratio had decreased Young's Modulus value. This was because the increased of alginate had increased the film thickness. According to Chang et al. [17], the thickness of polymer film increased the Young's Modulus of the materials. However, until at a certain thickness, Young's Modulus value began to drops.

4.2.2. Elongation at break

From Fig. 1(b), when the PLA concentration increased, the elongation at break of the sample was increased too. This was because, as the PLA concentration increased, the film thickness increased proportionally. The increament of film thickness caused the internal stress in the PLA composites resulting in the increasing of the elasticity of the PLA composites. The highest value gained at PLA concentration of 13w/v% for PLAS1A9 (9.875%) and PLAS5A5 (6.2%). A similar mechanism happens by alginate content in the sample, where the film thickness increases when the alginate content increases. This results

in the high elongation at break of PLAS1A9 compared to PLAS5A5. Same with the Young's Modulus, the elongation at break of PLA concentration at 15w/v% was lower than PLA concentration 13w/v% based on the individual behavior of the composites layer. The best elongation at break value and Young's Modulus value of PLA concentration for the composites was 13w/v%. Based on Miletic et al. [18], the selection of good mechanical properties of cosmetics was based on high maximum stress and high elongation at break. The best elongation at break value and Young's Modulus value of PLA concentration for the composites were 13w/v%. Therefore, 13w/v% PLA concentration had been used for degradation study.

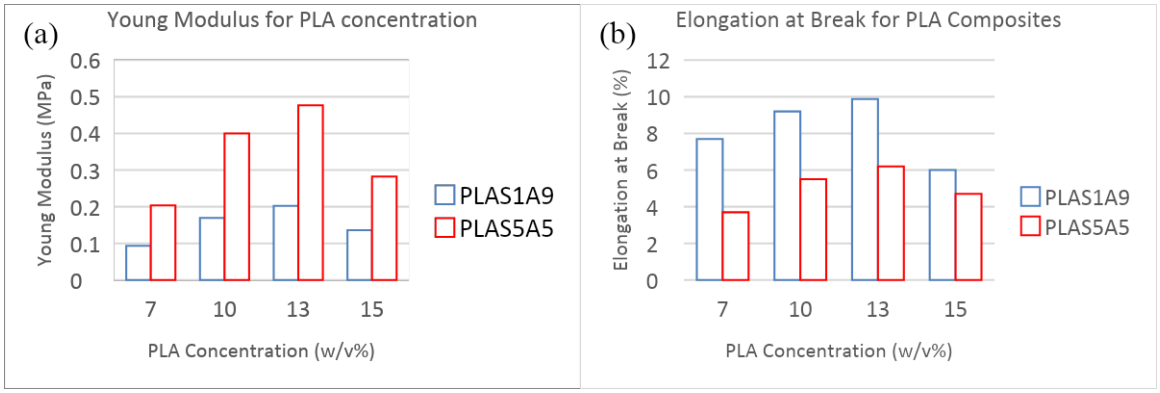

Fig. 1. The comparison of PLA composites in (a) Young's Modulus and (b) Elongation at break.

4.3. Weight loss

For the comparison of degradation between PLA and PLA composites, the PLA concentration had been kept constant at 13% w/v. From Fig. 2, the data displayed by weight percentage versus time. It was observed PLA composite's degradation rate was higher compared to PLA. The result revealed that natural fiber from the composites was vulnerable to the degradation of the PLA. This was because the carbon contains in the fiber was higher than PLA. After 7 months, PLA composites with a balance fiber ratio (PLAS5A5) had the highest weight loss. Between the fibers ratio, it could be concluded that spirulina enhances the degradation rate compared to alginate. 16.67% of the weight had loss when the ratio of spirulina was higher in the composites (PLAS5A5). Meanwhile, PLAS1A9 with low spirulina ratio only loss 6.25% of its weight after 7 months. This could be understood by spirulina extraction consist of several natural compounds with high carbon contents. However, the PLA composites with the presence of a low ratio of spirulina (PLAS1A9) had a low degradation rate compared to PLA composites without spirulina (PLAA). The degradation of PLAS1A9 also leveled off after 2 months of degradation. This showed some errors in the degradation of the PLA composites.

We observed the error in degradation weight loss was caused by the irremovable soil that sticks to the sample. The soil attached on the sample could not be removed by tap water, since the properties of the fiber within the composites were soluble in water. The cleaning method only swept with dry tissue towards the surface of the film as mentioned by Deepa et al. [14]. Different from hydrolytic degradation, microbial degradation used water to enhance microbial activity in the soil without any effect of water on the samples. It had been observed that the higher the alginate concentration, the more soil attachment toward the sample. The alginate was the source of error in this degradation study. This could be justified by the experiment of Cheng et al. [19], where sodium alginate had been used as a binding agent to close up the porosity of the sand with the help form calcium ion (Ca^{2+}).

Sodium alginate had been used with a mixture of microorganisms and organic carbon. From this microbial degradation, soil microorganism tended to react with sodium alginate and the organic carbon (PLA). The calcium ion (Ca^{2+}) could be found as a mineral in the soil.

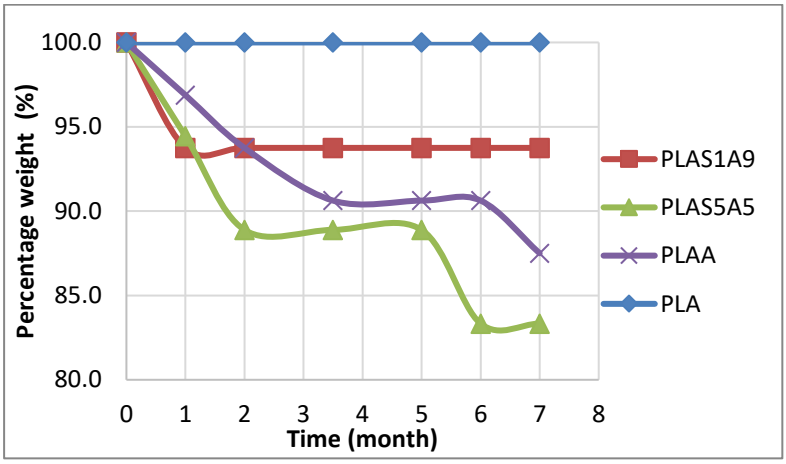

Fig. 2. Percentage weight of PLA and PLA composites by microbial degradation

4.4. Morphology test

SEM was carried out to observe the surface morphology of the cross section of PLAS1A9, PLAS5A5, and PLAA,. The samples were taken for SEM analysis before degradation and after 6 months of microbial degradation. The PLA composites film tended to be separated between the matrix and fiber when coated with palladium under the pressure of 8kPa. From the SEM images in Fig. 3, PLA layer had a strong and thick structure indicated that it was the matrix of the composites. The fiber layer of the composites had a thin and flexible structure. The addition of alginate had increased the fiber layer. After the degradation period, the structure of PLA had no major changed while the structure of the fiber was ruptured. The ruptured structure indicated the spot where the microbial attack on the fiber. The microbial degradation started from the fiber (spirulina and alginate) of the composites.

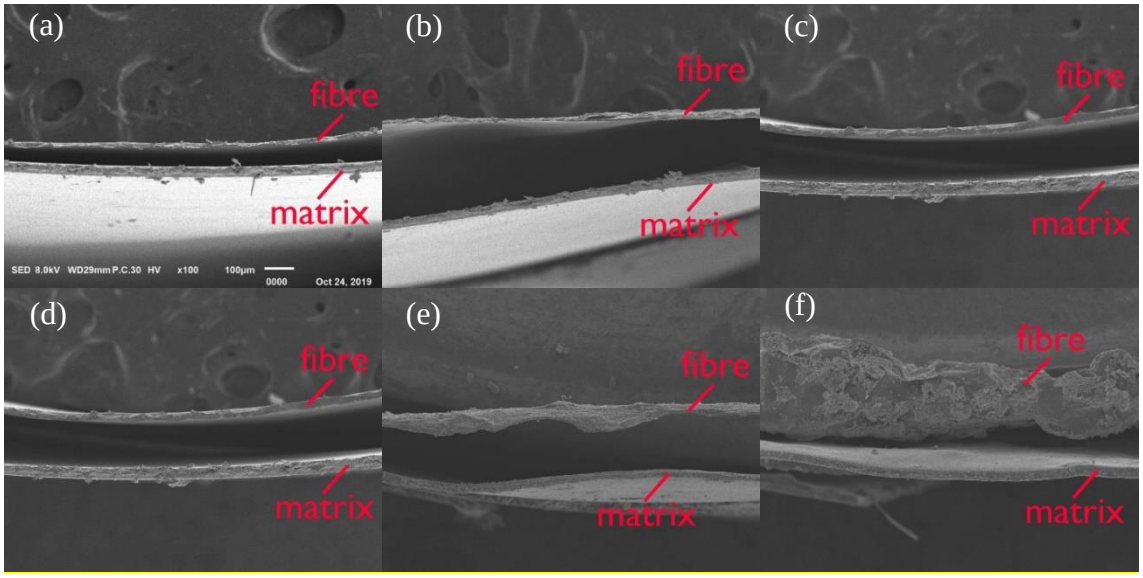

Fig. 3. SEM micrograph of cross section of (a)PLAS1A9 (b)PLAS5A5 and (c)PLAA before the degradation. Cross section off (d)PLAS1A9 (e)PLAS5A5 and (f)PLAA after the degradation.

5. CONCLUSION

In conclusion of this study, the objective of the experiment had been achieved which was to study the degradation behaviour of PLA composites with the characterization on the surface morphology. The mechanical test showed that the PLA composites were best at 13w/v% PLA concentration and this concentation continued with degradation study. From the results, Young's Modulus for PLA13S5A5 was 0.48MPa meanwhile PLA13S1A9 was 0.20MPa, and elongation at break for PLA13S5A5 was 6.2% meanwhile PLA13S1A9 was 9.875%. The increasing of the film thickness by alginate had decreased the stiffness and increased the elasticity of the composites. In microbial degradation showed that spirulina had enhanced the degradation of the PLA. 16.67% of the weight had loss from the PLAS5A5 composites after 7 months. However, the data could not be justified since the influence of alginate as a binding agent that attaches the soil to the surface of the samples affected the weight of the degraded sample. The SEM showed the surface rupture at the side of the fiber in the degraded samples and prove the degradation of PLA composites began with fiber.

ACKNOWLEDGEMENT

The authors thank International Islamic University Malaysia (IIUM) and Kulliyyah of Engineering for the support. This work is funded under the IIUM Research Acculturation Grant Scheme (IRAGS) 2018 (IIUM/504/RES/G/14/3/3/2) from International Islamic University Malaysia.

REFERENCES

[1] Lebreton, L., & Andrady, A. (2019). Future scenarios of global plastic waste generation and disposal. *Palgrave Communications*, *5*(6) 1–11. https://doi.org/10.1057/s41599-018-0212-7

[2] Hidayat, Y. A., Kiranamahsa, S., & Zamal, M. A. (2019). A study of plastic waste management effectiveness in Indonesia industries. *AIMS Energy, 7*(3), 350–370. https://doi.org/10.3934/energy.2019.3.350

[3] Moharam, R., & Almaqtari, M. (2014). The Impact of Plastic Bags on the Environment: A Field Survey of the City Of Sana'a And The Surrounding Areas, Yemen. *International Journal of Engineering Research and Reviews*, *2*(4), 61–69.

[4] Balkcom, M., Welt, B., & Berger, K. (2002). Notes from the Packaging Laboratory : Polylactic Acid -- An Exciting New Packaging Material 1. *University of Florida*, 1–5.

[5] Patil, A., & Ferritto, M. S. (2013). Polymers for Personal Care and Cosmetics : Overview. In A. Patil & M. S. Ferritto (Eds.), *Polymers for Personal Care and Cosmetics* (pp. 3–11). American Chemical Society.

[6] Jaya, A., Kunhanna, B., Ramachandra, K., Shivarama, B., & Glorious, A. (2019). Spectral, morphological, and optical studies on bischalcone doped polylactic acid (PLA) thin films as luminescent and UV radiation blocking materials. *Optical Materials, 90*, 145–151. https://doi.org/10.1016/j.optmat.2019.02.028

[7] Ammala, A. (2013). Biodegradable Polymers as Encapsulation Materials for Cosmetics and Personal Care Markets. *International Journal of Cosmetic Science*, *35*, 113–124. https://doi.org/10.1111/ics.12017

[8] Darvin, M. E., Jung, S., Schanzer, S., Richter, H., Kurth, E., Thiede, G., Meinke, M. C., & Lademann, J. (2015). Influence of the Systemic Application of Blue–Green Spirulina platensis Algae on the Cutaneous Carotenoids and Elastic Fibers in Vivo. *Cosmetics*, *2*, 302–312. https://doi.org/10.3390/cosmetics2030302

[9] Pereira, L. (2018). Seaweeds as Source of Bioactive Substances and Skin Care Theraphy-Cosmeceuticals, Algotheraphy, and Thalassotherapy. *Cosmetics*, *5*(4), 68. https://doi.org/10.3390/cosmetics5040068

[10] Rhim, J. W., Mohanty, A. K., Singh, S. P., & Ng, P. K. W. (2006). Effect of the processing methods on the performance of polylactide films: Thermocompression versus solvent casting. *Journal of Applied Polymer Science*, *101*(6), 3736–3742. https://doi.org/10.1002/app.23403

[11] Sungkapreecha, C., Beily, M. J., Kressler, J., Focke, W. W., & Androsch, R. (2018). Phase behavior of the polymer/drug system PLA/DEET: Effect of PLA molar mass on subambient liquid-liquid phase separation. *Thermochimica Acta*, *660*, 77–81. https://doi.org/10.1016/j.tca.2017.12.021

[12] Huang, J., Cui, C., Yan, G., Huang, J., & Zhang, M. (2016). A Study on Degradation of Composite Material PBS / PCL. *Polymers & Polymer Composites, 24*(2), 143–148. https://doi.org/10.1177/096739111602400209

[13] Tan, Z., Yi, Y., Wang, H., Zhou, W., Yang, Y., & Wang, C. (2016). Physical and Degradable Properties of Mulching Films Prepared from Natural Fibers and Biodegradable Polymers. *Applied Sciences 6*(5) 147. https://doi.org/10.3390/app6050147

[14] Deepa, B., Abraham, E., Pothan, L. A., Cordeiro, N., Faria, M., & Thomas, S. (2016). Biodegradable Nanocomposite Films Based on Sodium Alginate and Cellulose Nanofibrils. *Materials*, *9*(50), 1–11. https://doi.org/10.3390/ma9010050

[15] Qiu, T. Y., Song, M., & Zhao, L. G. (2016). Testing, characterization, and modelling of mechanical behaviour of poly (lactic-acid) and poly (butylene succinate) blends. *Mechanics of Advanced Materials and Modern Processes*, *2*(7). https://doi.org/10.1186/s40759-016-0014-9

[16] Aarstad, O., Heggset, E. B., Pedersen, I. S., Bjørnøy, S. H., Syverud, K., & Strand, B. L. (2017). Mechanical Properties of Composite Hydrogels of Alginate and Cellulose Nanofibrils. *Polymers, 9*(8), 378. https://doi.org/10.3390/polym9080378

[17] Chang, J., Toga, K. B., Paulsen, J. D., Menon, N., & Russell, T. P. (2018). Thickness Dependence of the Young's Modulus of Polymer Thin Films. *Macromolecules*, *51*(17), 6764–6770. https://doi.org/10.1021/acs.macromol.8b00602

[18] Miletic, A., Pavlic, B., Ristic, I., Zekovic, Z., & Pilic, B. (2019). Encapsulation of Fatty Oils into Electrospun Nanofibers for Cosmetic Products with Antioxidant Activity. *Applied Science*, *9*(15), 2955. https://doi.org/10.3390/app9152955

[19] Cheng, L. (2018). In-situ microbially induced Ca2+-alginate polymeric sealant for seepage control in porous materials. *Microbial Technology*, *12*(2), 324–333. https://doi.org/10.1111/1751-7915.13315