

Biodegradation in compost environment of PLA bioplastic containing brown algae biomass

Chadia IHAMOUCHEN^{1*}; Nadia AOUDIA¹; Hocine DJIDJELLI¹; Amar BOUKERROU¹

1: Department of Processes Engineering, Laboratory of Advanced Polymer Materials, University of Bejaia, 06000 Bejaia, Algeria

*Corresponding author email: Chadia.benmerad@univ-bejaia.dz

Received 2 May, 2023 ; Accepted : 27 July 2023; Published: 29 July 2023

Abstract

This work was focused to the study of the biodegradation of poly lactic acid (PLA) alga composites in compost environment over a period of 50 days. To highlight the interaction between the natural reinforcement and the matrix, an in-situ grafting of maleic anhydride directly during the implementation in the extruder, will be consider to act as a compatibilizing agent (PLA-g-MAH) in the PLA/Algae system. The monitoring of the degradation process was evaluated by infrared structural analysis, mass loss and mechanical tensile analysis. The results revealed that the mass change is positive, suggesting that the chain scission phenomenon predominates over the cross-linking phenomenon. The mass loss increases with the loading rate, processing and composting time. The tensile test study revealed a decrease in stress and elongation and an increase in stiffness with the addition of the untreated filler. The treatment resulted in an improvement in mechanical properties. After 50 days in the compost medium, it was found that all the parameters underwent a clear decrease due to the chain scission reactions by enzymatic hydrolysis. For the FTIR results, an increase in the intensity of the O-H absorption band at 3325 cm^{-1} was observed with the untreated load, due to its high OH concentration. With treatment, this decreases, attributed mainly to the decrease in the hydrophilic character of the feed after treatment. After 50 days of composting, we have a decrease of the absorption band located at 1120 cm^{-1} (ν C-O) which corresponds to the hydrolysis of the ester bond. The appearance at 1620 cm^{-1} of a new band corresponds to the ends of carboxylic acid chains (COO) generated by enzymatic hydrolysis, due to microorganisms that consume lactic acid and surface oligomers

Keywords: Biodegradation, Marine algae, Mechanical property, Poly lactic acid,

I. Introduction

Nowadays, plastics are present in the life of each individual; they are use in several applications that it would be very difficult to do without them. Nevertheless, beyond their numerous advantages, they generate voluminous waste, which poses enormous problems related to their treatment at the end of life [1]. For this reason, the development of new concepts called "ecological" or "sustainable" materials from renewable sources have emerged. This category of materials can solve the problems of plastic waste, including their ability to degrade naturally in the environment under the action of living organisms and their low rates of emission of greenhouse gases, and they offer distinct advantages over conventional plastics. These new "green" materials generally have the advantage of degrading in a non-toxic way under environmental conditions, without wasting fossil fuels [2]. This phenomenon known as "biodegradation" consists in the degradation resulting from a biological activity (presence of microorganisms) leading to a

modification of the chemical structure of a material. Generally, this process ends with a phase of bio assimilation, which consists in a mineralization of the intermediates of degradation by the microorganisms and ends in aerobic conditions with the production of simple compounds such as carbon dioxide and water as well as a new biomass [3].

Poly lactic acid (PLA) is one of these bioplastics, from the family of aliphatic polyesters. It is considered among the first renewable polymers capable of competing with conventional polymers in terms of performance and environment, because it is three times less CO₂ emitting and already available on the market [4]. Developed in 1960 and 1970 for biomedical applications because of its high price and its ability to be degrade in physiological conditions. However, with the technological revolutions, the tonnages of its production, which explode, and the prices, which fall, the PLA with integrated several other fields of application than the biomedical such as the automobile transport, the packing, the products of hygiene, the electronic material, etc. PLA comes

from renewable resources such as corn or sugar cane. It is obtained by fermentation of sugar or starch, and then transformed into a monomer: the lactide. The polymerization of the latter makes it possible to obtain PLA [5, 6]. To improve the different properties of this biopolymer, it is mixed with synthetic polymers or by incorporating natural reinforcement, which allows the development of bio composites. In this study, the choice of the reinforcement was made on the brown algae. Algae are living chlorophyllous photosynthetic organisms found in aquatic environments [7]. They vary greatly in shape, colour and size. Some are microscopic, others macroscopic. Their processing has developed massively in recent years, with 25 million tons harvested each year for a market estimated at more than \$6 billion. They are an important source of polysaccharides (carrageenans, alginates, agar...) whose physicochemical, stabilizing and gelling properties are of interest to many industrial sectors [8].

The reinforcement of composite materials by plant fillers is in full expansion of academic and industrial research. Their potential in terms of mechanical and environmental gains is undeniable, even if their sensitivity to humidity remains a barrier [9, 10]. The innovation in this type of material concerns the interaction between these natural fibers and the matrix, which leads to incompatibility problems. For this reason, physical or chemical modifications of the filler are most often used. This work has a double objective; the first is to develop a new material based on a biodegradable PLA matrix and brown algae. To highlight the interaction between the natural reinforcement and the matrix, an in-situ grafting of maleic anhydride directly during the implementation in the extruder, to obtain PLA-g-MA, which will be considered to act as a compatibilizing agent in the PLA/Algae system. The second is the monitoring of physico-chemical properties for a better understanding of the mechanisms involved in the degradation process.

II. Material and methods

II.1. Materials

II.1.1. Poly (lactic acid) (PLA)

The matrix used is the Poly (lactic acid) (PLA) produced by Nature Works LLC (United States), is supplied by the company Nature Plast (France), under the trade name Ingeo "7001D", in the form of granules (figure III.1), specially designed for injection blow molding machines. Its main characteristics are grouped in table 1.

Table 1: Characteristics of the PLA matrix.

Properties	Unit
Appearance	Transparent
Melt index (210 °C, 2.16 Kg)	6 g/10 min

Melting temperature	145-160 °C
Glass transition temperature	55-60 °C
Density	1.24
Number average molar mass	75 000 g.mol ⁻¹

II.1.2. Brown seaweed meal

The load used in this study is the flour of brown algae of the species *Fucus serratus* collected on the beach of Fort-bloqué in Ploemeur, Lorient (France) during January. Scientific name *Fucus serratus*, of color brown olive with the blackish green. This rockweed presents a very flat thallus has divided fronds, with toothed edges, measures in general between 40 and 80 cm length (figure 1).



Figure 1: The species *Fucus serratus* (brown alga)

Before their use, these algae have undergone several pre-treatments, namely: Sorting: Manually in order to eliminate any source of contamination. Washing: The algae are rinsed twice with tap water and then twice with distilled water to remove all kinds of contamination: sand, insects, water-soluble compounds. Drying: The seaweeds underwent a preliminary drying in the open air for three days and then in an oven at 80 °C for 24 hours to evaporate the water. Grinding and sieving: The algae were ground in a laboratory grinder and sieved through a 250µm sieve. Then preserved in hermetically sealed plastic bags.

II.1.3. Other products: Maleic Anhydride (MAH) 99%, and Dicumyl peroxide (DCP) 98% were purchased from Sigma-Aldrich, are used for in situ grafting directly in a brabender on the PLA chain to obtain PLA-g-MAH, which will be considered as a compatibilizing agent in the PLA/alga system. All of PLA and algae powder were dried under vacuum oven at 60°C overnight before use.

II.1.4. Compost

The compost used in the study was recovered from a local company in the region of El-Kseur, Bejaia, Algeria. The main

characteristics of this compost are visualized below in figure 2.



Figure 2: The main characteristics of the compost used

II.2 Methods of elaboration of PLA/algae biocomposites

II.2.1. Formulations

The biopolymer (PLA) and the filler (alga powder) are previously dried at 80° C in an oven for 24 hours, in order to eliminate the water content. The different percentages were weighed, and then mixed manually. In total, seven formulations were prepared, according to the proportions indicated in Table 2.

Table 2: Compositions of the different formulations

Formulations	Noted	PLA	Algae powder	Maleic anhydride (MAH)	Benzoyl peroxide (BOP)
PLA	F0	100	0	0	0
PLA/10% Algae	F10	90	10	0	0
PLA/20% Algae	F20	80	20	0	0
PLA/30% Algae	F30	70	30	0	0
PLA /10% Algae /PLA-g-MAH	F10g	85	10	3	1,5
PLA /20% Algae /PLA-g-MAH	F20g	75	20	3	1,5
PLA /30% Algae /PLA-g-MAH	F30g	65	30	3	1,5

II.2.2. Compression molding

The PLA, PLA/algae formulations with and without compatibilizer are prepared in the molten state in a brabender of model W50 EHT at 185 °C with a rotation speed of 50 rpm for a residence time of 8 min. The mixture is recovered for use in compression molding under the following working conditions: Temperature of 170 °C, under a pressure of 80 KN and during a residence time of 5 min (a preheating of 3 minutes is carried out until a preliminary fusion of the mixture, in order to avoid the presence of air bubbles). Plates of 1 mm thickness are obtained, and then are cut to be used in the various tests.

II.2.3. Biodegradation test

The biodegradability tests were performed in polyethylene bins at room temperature in the composting environment. Rectangular (length 70 mm, width 10 mm, thickness about 1 mm) and square (20 x 20 mm) samples are buried in containers containing 2 to 3 kg of industrial compost. A sample is taken every 25 days over a period of 50 days, with weekly watering with borehole water [11].

II.2.4. Mass variation

The observation of mass variation is simple and effective method. It does not require special instrumentation, and is widely used for the determination of the biodegradability of polymers in the solid state. Samples are weighed before burial in the compost to record the initial mass (m_0). After collection, the samples are wiped, dried in an oven at 60 °C for 2h, and then weighed to obtain the average mass (m_t). The mass loss is calculated by the equation (1) :

$$\Delta m \% = \frac{m_0 - m_t}{m_0} \cdot 100 \dots\dots\dots (1)$$

With: Δm : Variation in mass

m_t : Mass of the sample after burial.

m_0 : Initial mass of the sample before burial

II.2.5. Fourier Transform infrared analysis

Spectroscopy in general is a method of analysis based on the study of interactions between matter and electromagnetic radiation. The Fourier Transform Infrared (FTIR) is a very effective method for identifying organic and inorganic molecules from their vibrational properties (deformation, elongation). It allows studying the structural modifications of polymers resulting from chemical treatments, degradation or aging of various origins.

The FTIR spectra of the different samples were recorded in absorbance mode using a SHIMADZU FTIR-8400 S model infrared spectrophotometer, with a resolution of 4 cm⁻¹ in the range 400-4000 cm⁻¹ with a number of scans of 32. The analysis is performed on PLA/Algae composite films.

II.2.6 Tensile test

The tensile test consists in determining the deformation of the specimen under the application of a load with a defined speed. This test makes it possible to determine the modulus of elasticity E (MPa) or Young's modulus, the stress at break (σ) and the elongation at break (ϵ). The tensile test was conducted at the research unit of the University of Boumerdes at room temperature on a traction machine brand "Zwick type 8306" controlled by software. The speed of traction was kept constant at 5 mm /min. On average, three tests were carried out for each formulation.

III. Results and discussion

III.1 Mass loss

The figure 3 shows the variation in mass of the PLA/algae composites as a function of the composting time. It can be seen that the variation is positive (loss of mass), which suggests that the phenomenon of chain scission predominates over the phenomenon of cross-linking [12]. We can also note that the longer the biodegradation time, the greater the loss of mass is for all the formulations developed.

✓ The results obtained reveal that PLA reaches a lower degree of disintegration, with mass losses of 0.25% and 4% after 25 and 50 days. This low biodegradation reveals the difficulty that microorganisms find to attack this material.

✓ On the other hand, the composites loaded with the untreated seaweed powder, they present a higher biodegradation compared to the virgin PLA, due in particular to their natural origin that contributes to their biodegradation more easily. This increase increases with the loading rate and the composting time. As an example, at 25 days, 4, 11 and 16% were recorded, for the formulations F10, F20 and F30 respectively and after 50 days, the loss of mass reached 11, 14 and 23% for the same formulations.

✓ With the treatment, the mass loss decreases compared to the untreated composites, this is probably due to the presence of the PLA-g-MAH compatibilizing agent, since the latter contains several hydrophilic sequences on the main chain that can be easily accessible sites by microorganisms or their secretion products.

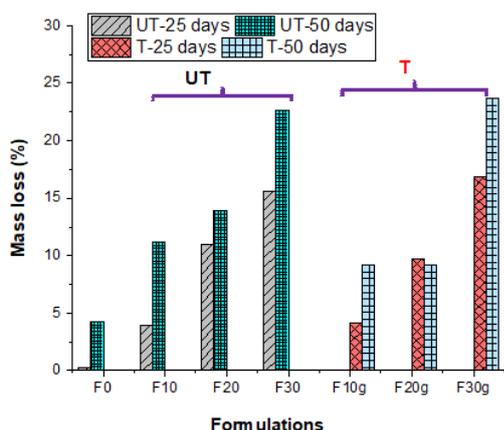


Figure 3: Evolution of mass loss of treated and untreated composites before and after 50 days in compost.

III.2 Fourier transform infrared analysis (FTIR)

III.2.1. Effect of the load

The figure 4 shows the FTIR spectrum of virgin PLA.

The spectrum of PLA reveals the presence of several absorption bands [13, 14]:

- Two peaks centred at 3503 and 2970 cm^{-1} correspond to the region of the hydroperoxide groups, attributed to the elongation vibrations of the -CH groups.
- A broad and intense band centred at 1734 cm^{-1} , corresponding to the absorption of the C=O carbonyl groups of the esters present in PLA.
- A series of broad absorption bands centred at 1300 and 1465 cm^{-1} , attributed to the -CH₃ groups present in the form of a mixture of vibrations, symmetrical and asymmetrical deformations.
- A series of bands at 1118 and 1020 cm^{-1} corresponding to the elongation vibrations of C-O groups.
- A peak at 866 cm^{-1} is attributed to the elongation vibrations of C-C
- we could also note on the spectrum, that there was a rather spread out peak, centered at 3500 cm^{-1} which is typical of the presence of hydroxyl groups -OH, in our case they are the ends of chains.

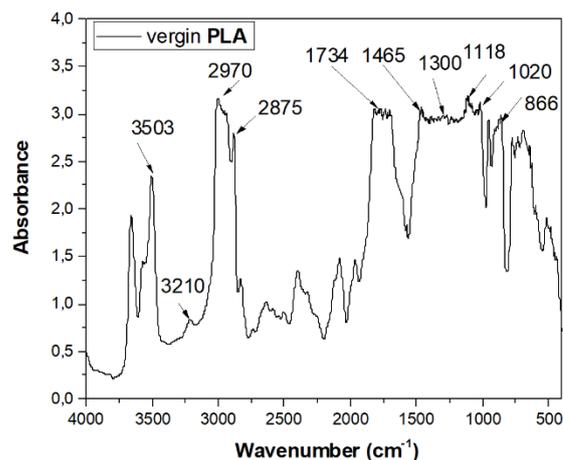


Figure 4: FTIR spectrum of virgin PLA.

The FTIR spectra of the PLA/algae composites are shown in Figure 5. The same peaks appear as for PLA, but with different intensities. As an example, an increase in intensity is recorded for the absorption band recorded at 3325 cm^{-1} that corresponds to the stretching vibration of the OH bond of the absorbed water, which reflects the hydrophilic character of the charge. Moreover, in the peaks at 1620 cm^{-1} , which correspond to the carboxylic groups COO, whose contribution comes from the alginates contained in the brown algae [15].

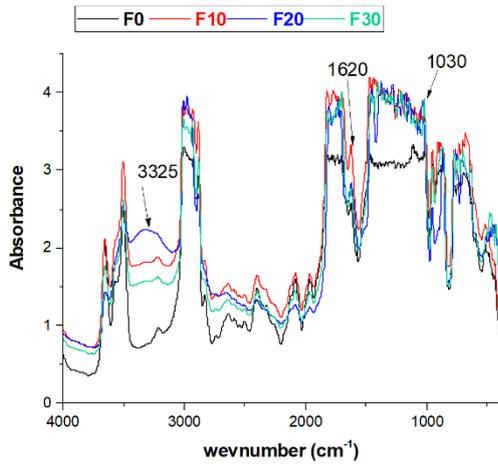


Figure 5: FTIR spectrum of PLA/algae composites

III.2.2. Treatment effect

The compatibilizing agent PLA-g-MAH, was used to improve the interfacial adhesion between the filler and the matrix, by creating bonds that did not exist until then and lowering the hydrophilic character of the natural filler used, and to highlight this treatment, the FTIR spectra of the composites untreated and treated with PLA-g-MAH are shown in Figure 6.

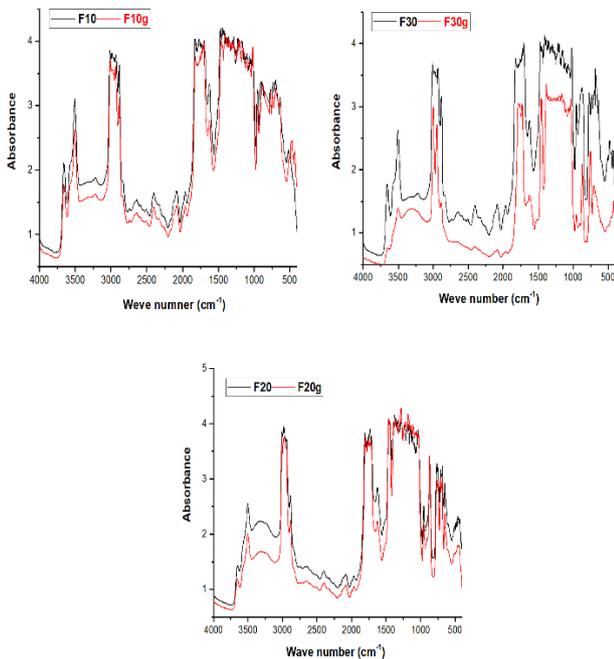


Figure 6: FTIR spectra of untreated and treated composites

Effectively, we notice that the treated composites F10g, F230g and F30g show an absorption band that is located in the region 3500 and 3000 cm^{-1} , and which corresponds to the elongation

vibrations of the hydroxyl groups (-OH), for which we register a decrease in its intensity compared to the untreated composites. This decrease is mainly attributed to the decrease of the hydrophilic character of the filler after the treatment with PLA-g-MAH.

III.2.3. Aging effect

The pristine PLA samples, recovered after 50 days in compost media, were analysed by FTIR and the results are shown in Figure 7. The superposition of the PLA spectra at 0 day and 50 days highlights the decrease of an absorption band at 1120 cm^{-1} and the appearance of a new band at 1620 cm^{-1} .

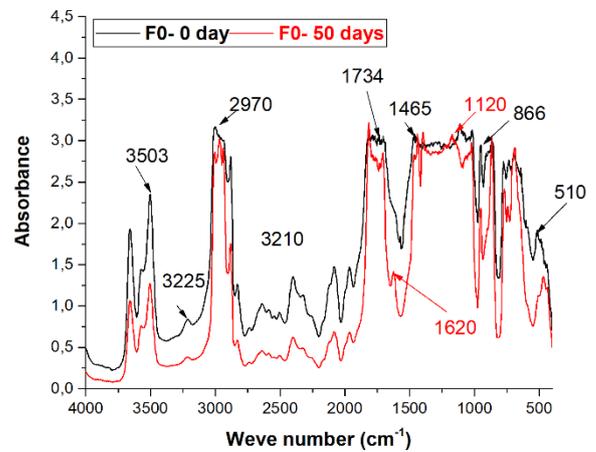


Figure 7: FTIR spectrum of PLA before and after 50 days in compost

According to the literature [16], the decrease of the absorption band located at 1120 cm^{-1} (vibration of the CO groups) would correspond to the hydrolysis of the ester bond. The appearance of a new absorption band at 1620 cm^{-1} corresponds to the ends of carboxylic acid chains generated by enzymatic hydrolysis. The formation of carboxylate ions at the ends of the chains would be due to the microorganisms consuming the lactic acid and the surface oligomers.

During the degradation process, the concentration of COO^- is increased by the presence of carboxyl groups resulting from the hydrolysis mechanism of the ester functions. With each hydrolyzed ester bond, a new carboxylic acid chain end is formed, and this catalyzes the hydrolysis reaction of the remaining ester bonds. The concentration of the concentration of carboxyl groups increases as the process proceeds, accelerating the degradation.

The spectra of the PLA/algae composites are shown in Figure.8.

The same observation is made for the treated and untreated PLA/algae composites, The spectra highlight the decrease of the absorption band at 1120 cm^{-1} . The decrease of the

absorption band located at 1120 cm^{-1} (vibration of the CO groups) would correspond to the hydrolysis of the ester bond.

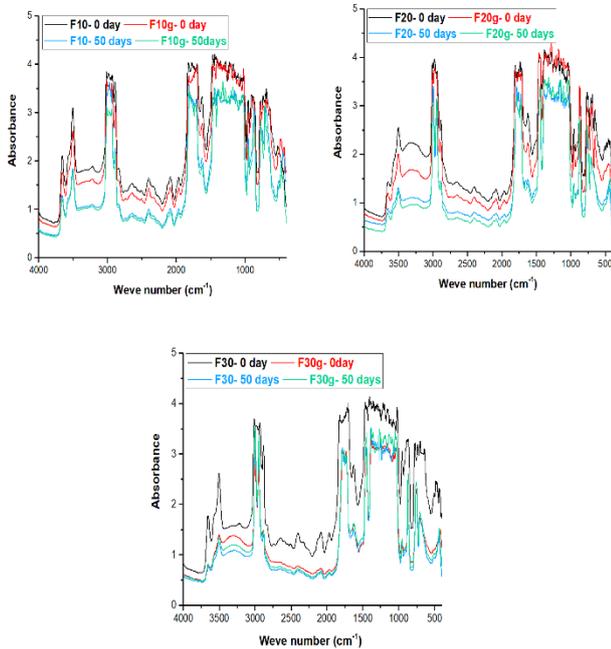


Figure 8: FTIR spectra of treated and untreated composites before and after 50 days in compost

III.3 Tensile test

III.3.1. Tensile strength

The evolution of the stress at break of the PLA/algae composites after 50 days in compost medium was represented in figure 9.

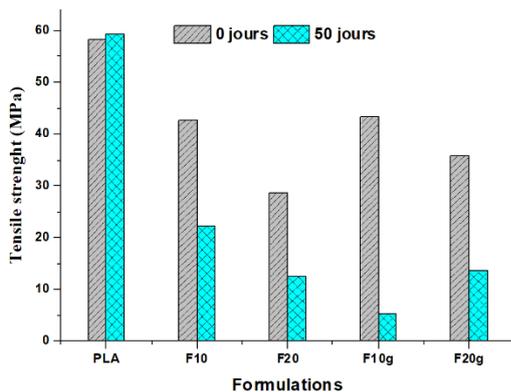


Figure 9: Evolution of the stress at break of PLA/Alga composites before and after composting

- It can be seen that the tensile strength of the composites decreases with the introduction of the algal filler and this decrease was accentuated with the increase of the filler rate; it reaches almost half the value of PLA for 30 % wt. of filler going from 58.8 MPa to 30 MPa. This decrease is

mainly attributed to the poor dispersion of the filler, forming agglomerates, which induces a decrease in the bonding strength between the matrix and the filler and consequently the failure of the stress propagation [17, 18].

- The addition of 5% PLA-g-MAH slightly improved the strength values of the formulations, indicating better stress transfer from the matrix to the filler in the presence of the compatibilizer.
- After 50 days in the compost medium, it can be seen that the stress at break for the PLA matrix was not influenced too much, increasing from 58 to 59 MPa. On the other hand, a clear decrease of the stress is recorded for the untreated and treated composites. It should be noted that the F30 and F30g formulations were not tested, as the specimens were found broken in the composting bins, during sampling after 50 days.

III.3.2. Elongation at break

The evolution of elongation at break of untreated and treated composites as a function of composting time is shown in Figure 10.

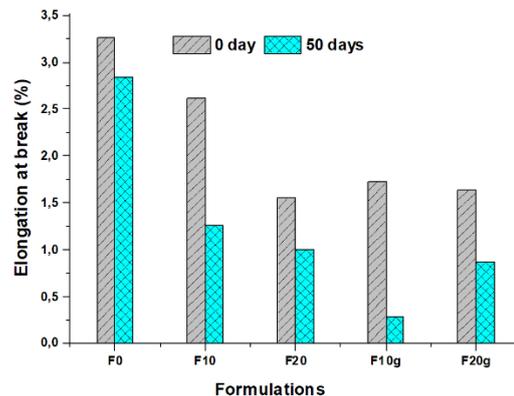


Figure 10: Evolution of elongation at break of PLA/Algae composites before and after composting

- The elongation at break of the composites decreases with the increase of the algae powder content, reaching a minimum value (1%) at 30% by weight of filler. This decrease is attributed to the increased stiffness provided by the filler, which reduces the plasticity range of the matrix and thus limits its deformation and flow, which is a common characteristic of reinforced thermoplastic composites.
- The addition of PLA-g-MAH further reduces the elongation at break for the 10% filled composites, but slightly increases for the 20% filled composites. This increase is due to the accounting agent acting as a plasticizer.
- After 50 days in the compost, we notice that the trend of all the formulations is characterized by a significant decrease in the elongation at break. The decrease in elongation at break of PLA and F10 and F20 composites was estimated at 12.89;

51.73 and 35% respectively. The same finding for the F10g and F20g formulations estimated at 83.73 and 46.62%. This sudden decrease in deformation with the time of composting is due to the reactions of scission of the chains, increasing the density of molecules links between the crystalline phases, and consequently decrease in deformation [19].

III.3.3. Young's modulus

The histograms in figure 11 show the evolution of the Young's modulus of the different samples as a function of the composting time.

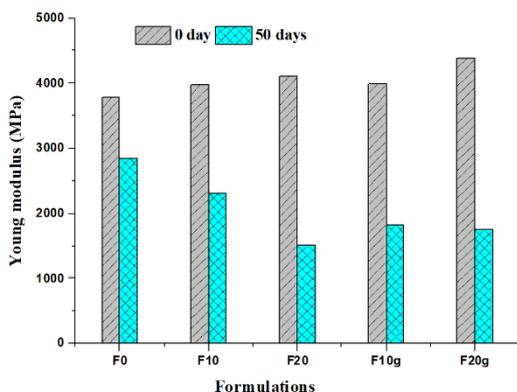


Figure 11: Evolution of the Young's modulus of PLA/Alga composites before and after composting

- The addition of the algae powder results in an increase in Young's modulus, suggesting a microstructural change within the polymer. With a 26% improvement with the addition of 30% algae powder, which is due to the increase in the rigid nature of the filler [20, 21]
- Young's modulus values are higher for composites compatibilized with PLA-g-MA than non-compatibilized composites; this can be explained by the correlation between the improvement of interfacial adhesion between matrix and filler in the presence of compatibilizer, and the increase in tensile modulus.
- The modulus decreases as a function of composting time regardless of the composition of the sample. This decrease is due to the phenomenon of chain splitting, where the cut chain fragments have more freedom and more movement [22; 23].

IV. Conclusions

This work, relates to the study of the biodegradation of biocomposites poly (lactic acid) reinforced by the powder of brown alga (PLA/Alga) in a compost medium over a period of 6 months, but because of lack of time, we carried out just two samples after 25 and 50 days and the study is still in progress. At the end of this study, the results obtained allowed us to draw the following conclusions:

The mass variation is positive, which suggests that the chain scission phenomenon predominates over the cross-linking phenomenon. The loss of mass increases with the loading rate, the treatment and the composting time.

The tensile test study revealed a decrease in stress and elongation and an increase in stiffness with the addition of the untreated filler. The treatment resulted in an improvement in mechanical properties. After 50 days in the compost medium, it was found that all the parameters underwent a clear decrease due to chain scission reactions by enzymatic hydrolysis. For the FTIR results, an increase in the intensity of the O-H absorption band at 3325 cm^{-1} was observed with the untreated load, due to its high OH concentration. With treatment, the latter decreases, attributed mainly to the decrease in the hydrophilic character of the feedstock after treatment. After 50 days of composting, we have a decrease of the absorption band located at 1120 cm^{-1} (ν C-O) which corresponds to the hydrolysis of the ester bond. The appearance at 1620 cm^{-1} of a new band which corresponds to the ends of carboxylic acid chains (COO) generated by an enzymatic hydrolysis, due to microorganisms which consume lactic acid and surface oligomers. Following the spectral analysis carried out by FTIR, the spectrum showed that the introduction of the agent Maleic Anhydride (MAH) in the PLA/Alga composites reduces in a remarkable way the hydroxyl groups, since the latter contains several hydrophilic sequences on the main chain that can be sites easily accessible by the microorganisms or by their secretion products.

The main conclusions of the study may be presented in a short Conclusions section, which may stand alone or form a subsection of a Discussion or Results and Discussion section.

References

- [1] Emma M.N. Polman, Gert-Jan M. Gruter, John R. Parsons, Albert Tietema. Comparison of the aerobic biodegradation of biopolymers and the corresponding bioplastics: A review. *Science of the Total Environment* 753, 141953, 2021. <https://doi.org/10.1016/j.scitotenv.2020.141953>
- [2] J.-G. Rosenboom, R. Langer, G. Traverso, Bioplastics for a circular economy, *Nat. Rev. Mater.* 7 117–137, 2022. <https://doi.org/10.1038/s41578-021-00407-8>
- [3] S. K. Awasthi, M. Kumar, V. Kumar, S. Sarsaiya, P.Anerao, P. Ghosh, L.Singh, H. Liu, Z. Zhang, M. Kumar Awasthi. A comprehensive review on recent advancements in biodegradation and sustainable management of biopolymers. *Environmental Pollution* 307, 119600, 2022. <https://doi.org/10.1016/j.envpol.2022.119600>

- [4] A. Le Duigou, A. Bourmaud, C. Baley, In-situ evaluation of flax fibre degradation during water ageing. *Industrial Crops and Products*, 70, 204-210, 2015. <https://doi.org/10.1016/j.indcrop.2015.03.049>
- [5]: D. Garlotta, A literature review of poly (lactic acid). *Journal of Polymers and the Environment*, 9(2), 63-84, 2001. <https://doi.org/10.1023/A:1020200822435>
- [6] A. Karimah, M. R. Ridho, S. S. Munawar, D. Sudarwoko Adi, Ismadi, R. Damayanti, B. Subiyanto, W. Fatriasari, A. Fudholi. A review on natural fibers for development of eco-friendly bio-composite: characteristics, and utilizations. *Journal of materials research and technology*; 13: 2442 -2458, 2021. <https://doi.org/10.1016/j.jmrt.2021.06.014>
- [7] Ullah K, Ahmad M, Sofia Sharma VK, Lu P, Harvey A, Zafar M, et al. Assessing the potential of algal biomass opportunities for bioenergy industry: a review. *Fuel*; 143, 414–23, 2015. <https://doi.org/10.1016/j.fuel.2014.10.064>
- [8] H.P.S. Abdul Khalil, C.K. Saurabh, Y.Y. Tye, T.K. Lai, A.M. EasaaE Rosamah, M.R.N. Fazita, M.I. Syakir, A.S. Adnan, H.M. Fizree, N.A.S. Aprilia, A. Banerjee. Seaweed based sustainable films and composites for food and pharmaceutical applications: A review. *Renew. Sust. Energy Rev.* 77 353–362, 2017. <https://doi.org/10.1016/j.rser.2017.04.025>
- [9] L. Kerni, S. Singh, A. Patnaik, N. Kumar, A review on natural fiber reinforced composites, *Mater. Today Proc.* 28 1616–1621, 2020. <https://doi.org/10.1016/j.matpr.2020.04.851>
- [10] M. Gupta, R. Srivastava, Mechanical properties of hybrid fibers-reinforced polymer composite: a review, *Polym.-Plast. Technol. Eng.* 55 (6) 626–642, 2016. <https://doi.org/10.1080/03602559.2015.1098694>
- [11] Shi, H., Wang, X.C., Li, Q., Jiang, S., Degradation of typical antibiotics during human feces aerobic composting under different temperatures. *Environ. Sci. Pollut. Res. Int.* 23 (15), 15076–15087, 2016. <https://doi.org/10.1007/s11356-016-6664-7>
- [12] R. Kumar, M. K. Yakubu, R. D. Anandjiwala. Biodegradation of flax fiber reinforced poly lactic acid. *eXPRESS Polymer Letters* Vol.4, No.7 423–430, 2010. <https://doi.org/10.3144/expresspolymlett.2010.53>
- [13] T.Gerard, T Budtova.. Morphology and molten-state rheology of polylactide and polyhydroxyalkanoate blends. *European polymer journal*, 48(6), 1110-1117, 2012. <https://doi.org/10.1016/j.eurpolymj.2012.03.015>
- [14] A.Rapacz-Kmita, E. Stodolak-Zych, M. Dudek, B. Szaraniec, A. Rozycka, M. Mosialek, L. Mandecka-Kamien., Degradation of nanoclay-filled polylactide composites. *Physicochemical Problems of Mineral Processing*, 49(1), 91-99, 2013. <http://dx.doi.org/10.5277/ppmp130109>
- [15] J. Jayaraj, A. Wan, M. Rahman, Z. K. Punja, Seaweed extract reduces foliar fungal diseases on carrot. *Crop Protection*, 27(10), 1360-1366, 2008. <https://doi.org/10.1016/j.cropro.2008.05.005>
- [16] H. P. Zhang, J. M. Ruan, Z. C. Zhou, Y. J. Li. Preparation of monomer of degradable biomaterial poly (L-lactide). *Journal of Central South University of Technology*, 12(3), 246-250, 2005. <https://doi.org/10.1007/s11771-005-0136-4>
- [17] C. Hellio, D. De La Broise, L. Dufosse, Y. Le Gal, N. Bourgoignon, Inhibition of marine bacteria by extracts of macroalgae: potential use for environmentally friendly antifouling paints. *Marine environmental research*, 52(3), 231-247, 2001. [https://doi.org/10.1016/S0141-1136\(01\)00092-7](https://doi.org/10.1016/S0141-1136(01)00092-7)
- [18]: Y. H. Kim, J. H Kim, H. J. Jin, S. Y. Lee. Antimicrobial activity of ethanol extracts of *Laminaria japonica* against oral microorganisms. *Anaerobe*, 21, 34-38, 2013. <https://doi.org/10.1016/j.anaerobe.2013.03.012>
- [19] Tao Yu, Ning Jiang, Yan Li. Study on short ramie fiber/poly(lactic acid) composites compatibilized by maleic anhydride. *Composites Part A: Applied Science and Manufacturing*. 64, 139-146, 2014. <https://doi.org/10.1016/j.compositesa.2014.05.008>
- [20] T. Budtova, M. Bulota. PLA/algae composites: Morphology and mechanical properties. *Composites: Part A* 73, 109 -115, 2015. <https://doi.org/10.1016/j.compositesa.2015.03.001>
- [21] T. Bulota M, Budtova . Valorisation of macroalgae industrial by-product as filler in thermoplastic polymer composites *Composites Part A: Applied Science and Manufacturing* Vol 90, 271-277, 2016. <https://doi.org/10.1016/j.compositesa.2016.07.010>
- [22] Judith Sarasa, Jose M. Gracia, Carlos Javierre. Study of the bio-disintegration of a bioplastic material waste. *Bioresource Technology* 100 3764–3768, 2009. <https://doi.org/10.1016/j.biortech.2008.11.049>
- [23]: S. K Saha, H. TsujiHydrolytic. Degradation of Amorphous Films of l-Lactide Copolymers with Glycolide and d-Lactide. *Macromolecular materials and engineering*, 291(4), 357-368, 2006. <https://doi.org/10.1002/mame.200500386>