CHEMICAL ENGINEERING TRANSACTIONS

VOL. 60, 2017

A publication of AIDIC
The Italian Association of Chemical Engineering
Online at www.aidic.it/cet

Guest Editors: Luca Di Palma, Elisabetta Petrucci, Marco Stoller

ISBN 978-88-95608- 50-1; **ISSN** 2283-9216

DOI: 10.3303/CET1760020

Degradability and Sustainability of Nanocomposites Based on Polylactic Acid and Chitin Nano Fibrils

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Plastic food packaging materials currently in use are hardly recyclable and very often post consume plastic packaging is directed to incineration or landfill. Use of bio-recyclable plastic will have positive effect on environment, and is gaining importance in particular for the production of active packaging, where a longer shelf-life of the packed food, coupled with improved sustainability can justify the higher cost of biodegradable polymers versus current petro based polymers used in packaging. Among other biodegradable polymers polylactic acid (PLA) has attracted researcher and industries attention for the production of plastic food packaging. In the present contribute we report a study to evaluate the degradability in compost of some representative examples of materials prepared with PLA and chitin nano-fibrils (NC). Since blending a biodegradable polymer with an active compound might hinder the compost ability of the materials produced, it is important to perform test of degradability on innovative materials even if based on biobased and biodegradable components. As well the production of bio-based, biodegradable materials when based on innovative processes, may present several steps that may have a negative effect on sustainability being not optimised in yield, energy consumption and proper valorization of each stream generated in the process. A life cycle assessment study is very important to spot the critical steps in the process and propose corrective actions in the production cycle in order to make the final material more sustainable. The materials based on PLA and NC passed the test of disintegration in compost, evidencing no toxicity on germination of cress seeds. The process of production of NC fibrils, was mostly affected by the high consume of water, and use of chemicals thus plans for recovery and re-use of the water based buffer will improve the sustainability of the process. The bio-nanocomposites based on PLA and NC have a positive environmental effect due to being based on natural resources and having compost ability as possible end of life scenario.

1. Introduction

The utilization of "bio-polymers" for the production of "bio-plastic" has became worldwide an assessed priority with the aim of reducing dependence from petro sources, and handle the concern for disposal of waste generated from not degradable plastics [Seggiani 2015, 2016].
Plastic food packaging materials currently in use are hardly recyclable and very often post consume plastic packaging are directed to incineration or landfill. Use of bio-recyclable plastic will have positive effect on environment, and is gaining importance in particular for the production of active packaging, where a longer shelf-life of the packed food, coupled with improved sustainability can justify the higher cost of biodegradable polymers versus current petro based polymers used in packaging. Thus during the latter period, evaluation of the advantages resulting from decreased food losses as a consequence of improved food packaging use has emerged [Williams 2011].
Asia Pacific is the largest market of the chitin and chitosan in terms of consumption. In a report of 2015, it was estimated that every year, some 6 million to 8 million tons of waste crab, shrimp and lobster shells are produced globally, about 1.5 million ton in Southeast Asia alone. In developing countries, waste shells are often just dumped in landfill or in the sea. In developed countries, disposal can be costly — up to US$150 per

Please cite this article as: Cinelli P., Coltelli M.B., Mallegni N., Morganti P., Lazzeri A., 2017, Degradability and sustainability of nanocomposites based on polylactic acid and chitin nano fibrils, Chemical Engineering Transactions, 60, 115-120 DOI: 10.3303/CET1760020

ton in Australia, for example [Yan 2015]. Thus one of the aim of the present study was finding an environmentally sustainable pathway for valid commercial use for chitin derived by-products of food industries, such as shrimp shells, that currently are mainly discarded. Chitin is a natural polymer used for production of edible polymer and as thickener with antioxidant and anti microbial properties [Shahidi 1999]. Chitin Nano fibrils are an innovative material that might be suitable to act as part of new economical and ecological food packaging concepts. Thus MAVI Sud has developed and patent a technology for the production of NC fibrils that were used in the present study [Morganti 2007, Morganti 2012].

At the same time replacing synthetic polymers currently used in packaging applications with biodegradable polymers, in order to obtain final product for which bio-recycling is a possible option, will improve the environmental performance.

The materials studied were addressing the development and assessment of a complete biodegradable packaging solution by using Polylactic acid (PLA) based materials for the production of rigid packaging and flexible films. PLA is produced from renewable resources, as well as chitosan and chitin allows valorising shrimp shell wastes. The possibility to improve packaging functionality by the chitin nano (NC) fibrils based formulations with particular reference on improving storage time of the packed food and of the packaging itself (shoppers), as well as time of shelf life of food are also benefits for environmental sustainability.

Since blending a biodegradable polymer with an active compound might hinder the compost ability of the materials produced, it is important to perform test of degradability on innovative materials even if based on biobased and biodegradable components (Cinelli 2014). A biodegradable plastic is defined as a degradable plastic in which the degradation process results in lower-molecular weight fragments produced by the action of naturally occurring microorganism such as bacteria, fungi, algae. Biodegradation must be carried out in a medium that, on one hand, is close to the natural medium (such as soil or compost), and on the other hand, allows the researcher to recover the metabolites and residues. In the present study degradability in compost was evaluated by standard disintegration tests following Standard ISO 20200-2004.

The environmental impact of the PLA/NC based materials was studied by Life Cycle Analysis (LCA) from cradle to grave including the preparation of the NC and of masterbatches based on NC, plasticizer and water as well as the use of these formulations for the production of flexible films and of rigid packaging, respectively by extrusion and then blow moulding or injection moulding of the extruded pellets. The main goal of this study was to evaluate the environmental performance of PLA/NC based materials, to identify environmental hot-spots, and propose improvement options for the production process through the LCA feedback (ecodesign).

2. Experimental

PLA used was 2003D from Natureworks. The NC production is usually made my MAVI on industrial scale at 2% by weight NC in water suspension, while considering the feedback of LCA analysis, for the production of materials by extrusion it was decided, to produce a suspension concentrated at 20% by weight that was used to produce a masterbatch with polyethylene glycol (PEG) 400, from Aldrich, by spry drying. A representative formula selected for investigation of degradability and environmental impact was based on PLA 88%, PEG400 10%, NC 2% by weight. Materials for degradation test in compost were produced with the following procedure: PLA was dried at 60 °C and 133 Pa for 2 days, then mixed with the NC/PEG400 masterbatch and, then processed with a MiniLab II Haake™Rheomex CTW5 conical twin-screw extruder (Thermo Scientific Haake GmbH, Karlsruhe, Germany). Mixing was conducted at 170°C with a screw speed of 100 rpm. Films were produced by compression molding in a CARVER press at 180°C with a pressure of 10 bars, with 200 μm thickness. Films consisting of just PLA were prepared with the same procedure and used as reference material (PLA).

Biodegradation tests are performed in aerobic conditions to simulate degradation in the upper layer of soil.

The method of disintegration, determines the degree of disintegration of test materials on a laboratory scale under conditions simulating an intensive aerobic composting process as reported in the Standard ISO 20200-2004. The solid matrix used consists of a synthetic solid waste inoculated with mature compost taken from a commercial composting plant. Pieces of the plastic test material are composted with this prepared solid matrix. The degree of disintegration is determined after a composting cycle, by sieving the final matrix through a 2 mm sieve in order to recover the non-disintegrated residues. The reduction in mass of the test sample is considered as disintegrated material and used to calculate the degree of disintegration. Test is run in triplicate. Each composting reactor was a polypropylene box of 7 litre capacity, that was placed in air-circulation oven maintained at a constant temperature of (58 ± 2) °C for a minimum period of 45 days and a maximum of 90 days. In each reactor were introduced 1300 g of synthetic solid waste and 4.5 g of samples cut is small pieces (25x25 mm). The synthetic solid waste was regularly mixed and balanced for water content as described in ISO 20200-2004. The degree of disintegration is determined after a composting cycle, by sieving the final

matrix through a 2 mm sieve in order to recover the non-disintegrated residues. The reduction in mass of the test sample is considered as disintegrated material and used to calculate the degree of disintegration.
Phyto-toxicity of the compost on plant growth is evaluated by the “Germination test on Garden Cress (*Lepidum Sativum*)”. The test has the aim to assess that in compost produced in the presence of sample, which are degraded in it, there is not phyto-toxicity induced by the degradation of the samples.

Table 1. Composition of the synthetic solid waste, and analysis of the compost

Material	Dry mass (%)	Analysis	Compost
Sawdust	40	Dry weight (%w/w)	53.3
Rabbit-feed	30	Volatile solids at 550° C (%w/w)	26.5
Ripe compost	10	Carbon content (%w/w)	29.5
Corn starch	10	Nitrogen content (%w/w)	1.9
Saccharose	5	Ratio C/N	15.5
Cornseed oil	4		
Urea	1		
Total	100		

Thus the compost produced without any sample in it (control) is compared with the compost where respectively the films based on PLA and PLA/NC have been degraded. Petri dishes with 100 mm diameter were used, in each of them a piece of filter paper is placed (Whatman N°1 diameter 90 mm). The Petri dishes were prepared in 5 replicates for each sample and 5 replicate containing 2 ml of demineralised water as positive control. 5 g of compost were suspended in 20 ml of water for 4 hours under mild stirring. Then water suspension was separated by centrifuge and the liquid part collected. The liquid extract was added in the Petri dishes (2 ml for each dish). In each dish they were placed 10 seeds of garden cress and kept for 48 h at 28 °C. After this time the dishes are collected and it is registered the number of germinated seeds and the length of the root
The PLA/NC/PEG pellets represented a masterbatch suitable to be used for production of rigid or flexible packaging, by eventually mixing with natural fibres or rubbery biodegradable polymers, and were extruded even on industrial scale extruders.
Life Cycle Assessment (LCA) study was performed with a SimaPro7.3.3, software. Primary data used in the LCA studies refer to 2011-2014. Secondary data from ecoinvent v2. database cover a period between 2004 and 2010.
The collection, evaluation and discussion of the data have been performed in line with the ILCD “International Reference Life Cycle Data System” Handbook and ISO standards (ISO 14040, 14044). The ILCD impact assessment method has been applied to calculate the environmental impacts of the products under study; this method includes 16 midpoint indicators covering a broad range of environmental issues, not only the potential emissions of Green House Gases (GHG). In order to provide a complete overview of the impact of the materials developed the calculation was also done with the method “Recipe”.
In LCA study the results of the environmental assessment for the materials addressed are calculated “cradle-to-grave”, excluding the use phase. Regarding waste management, the main key options were studied, i.e. recycling, with a percentage to incineration or landfill. The percentages were selected based on European averages. Infrastructures have been excluded from the LCA, except in the case of database processes already containing infrastructures.

3. Results

During the test, the synthetic waste became compost, i.e. the composting process occurred. The composting reaction was monitored by inspecting the composting matter when mixing and adding water. During the composting process, it was possible to detect a precise succession of specific odours. Within the first two or three days, the synthetic waste has an acidic odour, which gradually decays into an ammoniacal odour from day 5 to day 10, lasting approximately 10 days. Finally, no particular odour, or an earth-like one, was detected. The visual appearance of the composting matter changed during the first two weeks. Mycelia which grow on the composting matter was visible during the first week. The colour of the synthetic waste, which is initially light yellow (Figure 1) because of the high sawdust concentration, turned brown within 10 days.
After about 10 days all the samples started to degrade, showing a darker colour. There was not evident difference in the degradation of samples based on PLA and PLA/NC. An image of the degradation of these samples after 30 days from the beginning of the test is reported as well in Figure1.

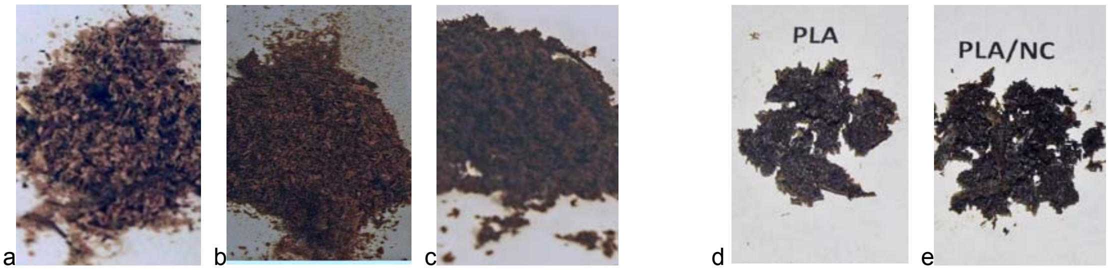

Figure 1. Initial synthetic compost (a), compost after maturation for respectively 30 days (b) and 90 days (c); PLA (d) and PLA/NC degraded after 30 days of burial.

After 90 days it was very difficult to detect debris in the compost. All the samples achieved the disintegration in ISO standard since in all the replicates the amount of sample retrieved was lower than 10% of the starting material ranging between 2-7%.

The quality of the compost for all the tested samples, in terms of volatile solids, pH, carbon-nitrogen content etc was in agreement with values required by the normative. In the Petri dishes with water the germination of Garden cress was over 90% (average value 99%), thus the test is considered valid, since the seeds were of sufficient good quality. Both the compost where PLA was degraded than the one where PLA/NC was degraded met the standard requirements with respectively 88% and 86% germination index. Thus no toxicity was recorded in the compost and no significant effect due to the degradation of these samples and in particular at the presence of 2% of NC in the samples.

In the LCA study the functional unit were respectively one Kg of nano chitin fibrils, and one Kg of pellets based on PLA/NC/PEG400. The net scheme of production of 1 Kg of NC and of one Kg of PLA/NC/PEG400 pellets is reported in Figure 2.

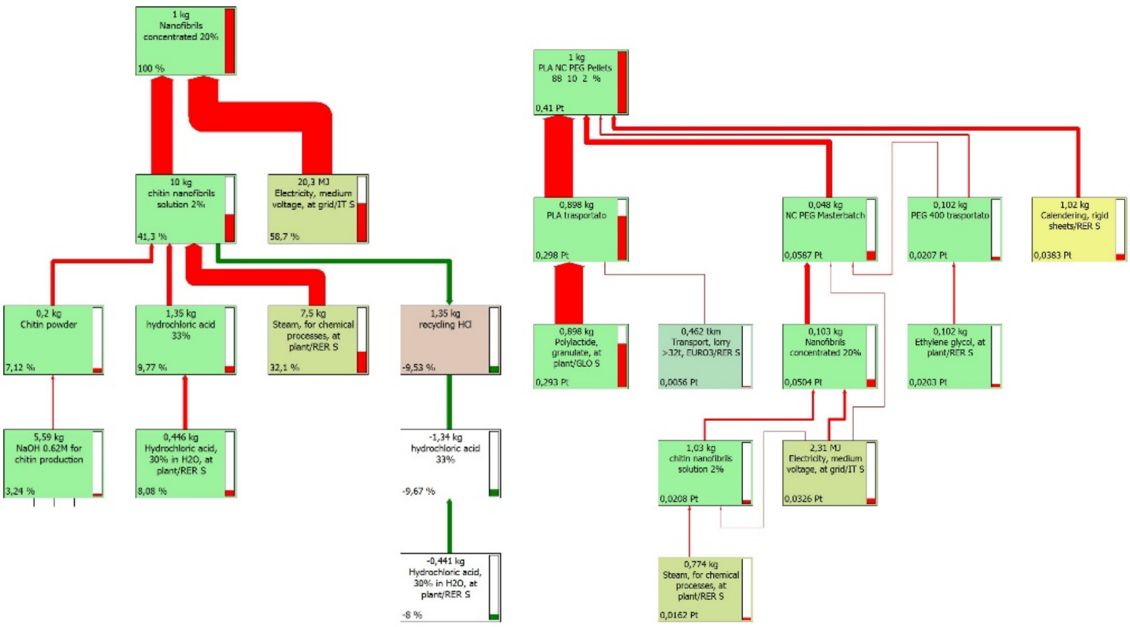

Figure 2. Net scheme of production of PLA/NC/PEG400 pellets

In general, when available, we used the real value, for example for transport and energy consumption, otherwise all calculations referred to the average location of each activity in the supply and value chain.

As reported in Figure 2, the energy associated to drying of the water suspension, starting from 2% by weight, consistently affect all the evaluation. The main suggestion for this process was to adjust the production of NC water suspension optimising the concentration of NC in water, eventually with the addition of specific additives supporting the nano dispersion of NC in concentrated water solution. With this approach NC water suspensions were produced with concentration over 20% by weight, as well it was possible to produce

master-batch of NC and plasticizer by spray drying method reducing significantly the energy consume and impact of water consume and disposal.
The Analysis of production of 1 Kg of NC at 20% by weight with ILCD+ method and, analysis of production of 1 Kg of PLA/NC/PEG pellets with Recipe method are reported in Figure 3.

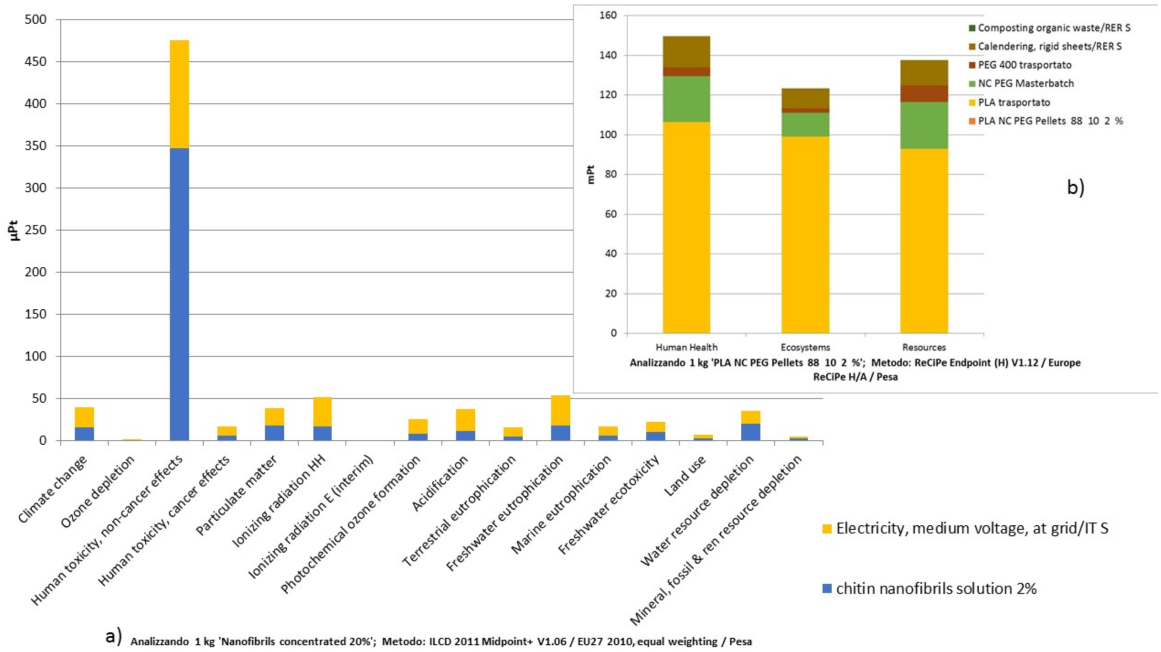

Figure 3. Analysis of production of 1 Kg of NC at 20% by weight with ILCD+ method and, analysis of production of 1 Kg of PLA/NC/PEG pellets with Recipe method

In the production of the masterbatch most of the impact is associated to PLA use, being 88% of the compound, and on land use for its production and transportation from USA to Italy, where compounding was made. The use of PLA produced in Europe, would significantly improve the sustainability of the materials produced.
The main focus of this study was the use of bio-based resources versus the use of fossil resources (PLA, chitin, vs PE) and the carbon footprint and emissions deriving by the disposal of the materials (bio-recycling vs landfill-incineration). Therefore we focused on the use of renewable and non renewable resources, the C balance and emissions, thus particular attention was given to values of Climate change and Fossil depletion. In these terms the materials based on PLA/NC are very sustainable since most of the impact for them is connected to the land use, for PLA, production, transportation and processing to pellets, that would have the same impact as processing of petro derived polymers. Compostability of the present materials, versus landfill or incineration is indeed a benefit, even if not reflected consistently in the LCA studies. Thus in the current LCA evaluations also the recovery of energy as incineration is reported as a benefit in the LCA results, by the way we should consider that the bio recycling is strongly supported by EC policies and is going to be the preferred option.
Thus, we could conclude that the renewable sources of all the components of the material as well as the compostability as possible end of life scenario represent a significant benefit for the environment, supported by the possibility to produce the materials with conventional extruder used for processing of commodities plastics.

4. Conclusions

Samples PLA/NC/PEG were buried in synthetic compost. They underwent significant degradation just after 30 days, and reached the requirements from the normative in the time frame of the test (90 days). The degradation of the samples did not affect the compost quality for its use as fertilizer in open field as attested by test on seed germination. The analysis of the compost outlined a good balance of constituents. Thus we can conclude that the presence of chitin nano fibrils is not affecting the degradation of compostable commercial materials such as those based on PLA, and it is not affecting the quality of the compost.

The LCA study was aimed at suggesting improvements for the production of NC based materials in terms of sustainability and future marketing. From the analysis it is evidenced the need to focus on optimisation on the use of chemicals (HCl, NaOH), increase their recycling, optimise the use of water and when possible recycle it. It is then suggested to consider the direct production of chitin nano fibrils at concentration higher than 2%. The LCA analysis outlined the benefit for the environment for PLA/NC/PEG products mainly related to the renewable sources of most the components used (Chitin, chitosan, PLA, glycerol) as well as the compostability of the product developed. These represent a benefit for the environment. The possibility to produce in industrial scale without modifying the extruders present in the facilities also represented an important achievement for industrialization of these materials. The improved performance of PLA/NC/PEG products versus the commercial counter parts was not enough quantified to be introduced in this study. By the way the possibility of re-using, or using for longer time shoppers, packaging films, or extended shelf life of packed goods such as perishable food (meat, fish etc) would further significantly improve the LCA results in terms of sustainability.

Acknowledgments

The EC contribution granted in the FP7 Project SME-2012-1, n-CHITOPACK Sustainable technologies for the production of biodegradable materials based on natural chitin-nanofibrils derived by waste of fish industry, to produce food grade packaging, GA 315233, is acknowledged. We acknowledge CERMEC SpA Consorzio Ecologia e Risorse di Massa e Carrara for providing the compost inoculum for degradation test.

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