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Electrospun-based biopolymers: Trends and applications

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15th International Symposium on Bioplastics, Biocomposites and Biorefining
Guelph, Canada

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- INTRODUCTION
- APPLICATION I: ALGAL COMPOSITE NANOFIBERS
- APPLICATION II: POLYHYDROXYALKANOATES
- APPLICATION III: DRUG CONTROLLED RELEASE
- CONCLUSIONS

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ELECTROSPINNING

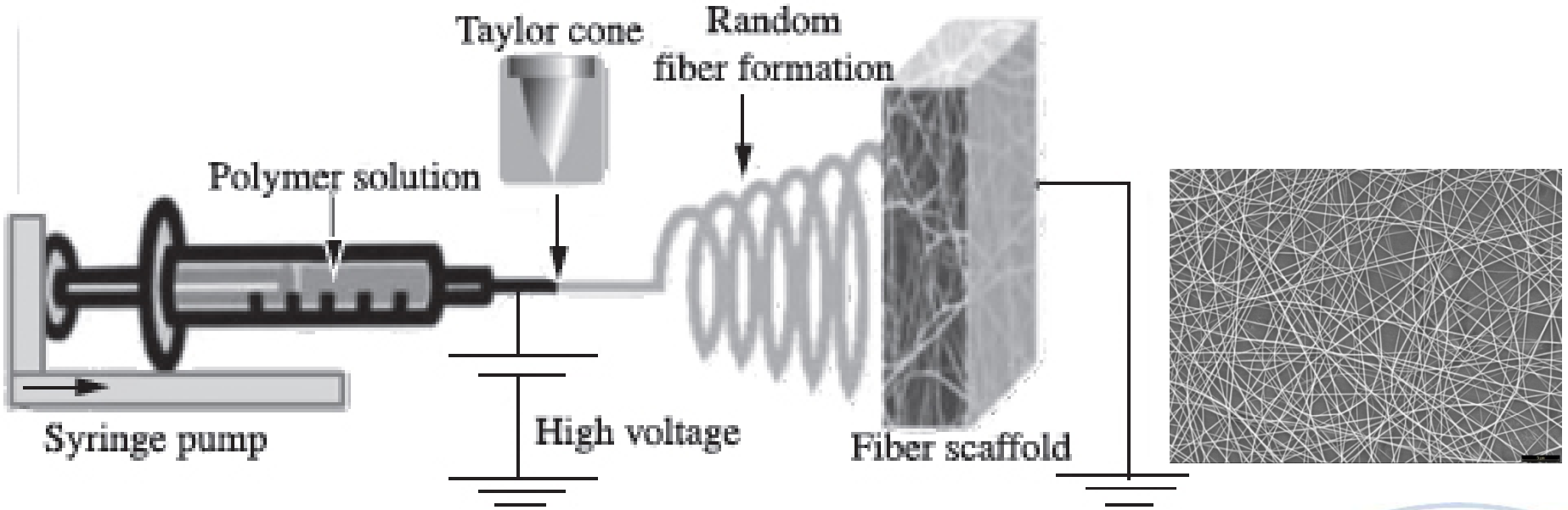
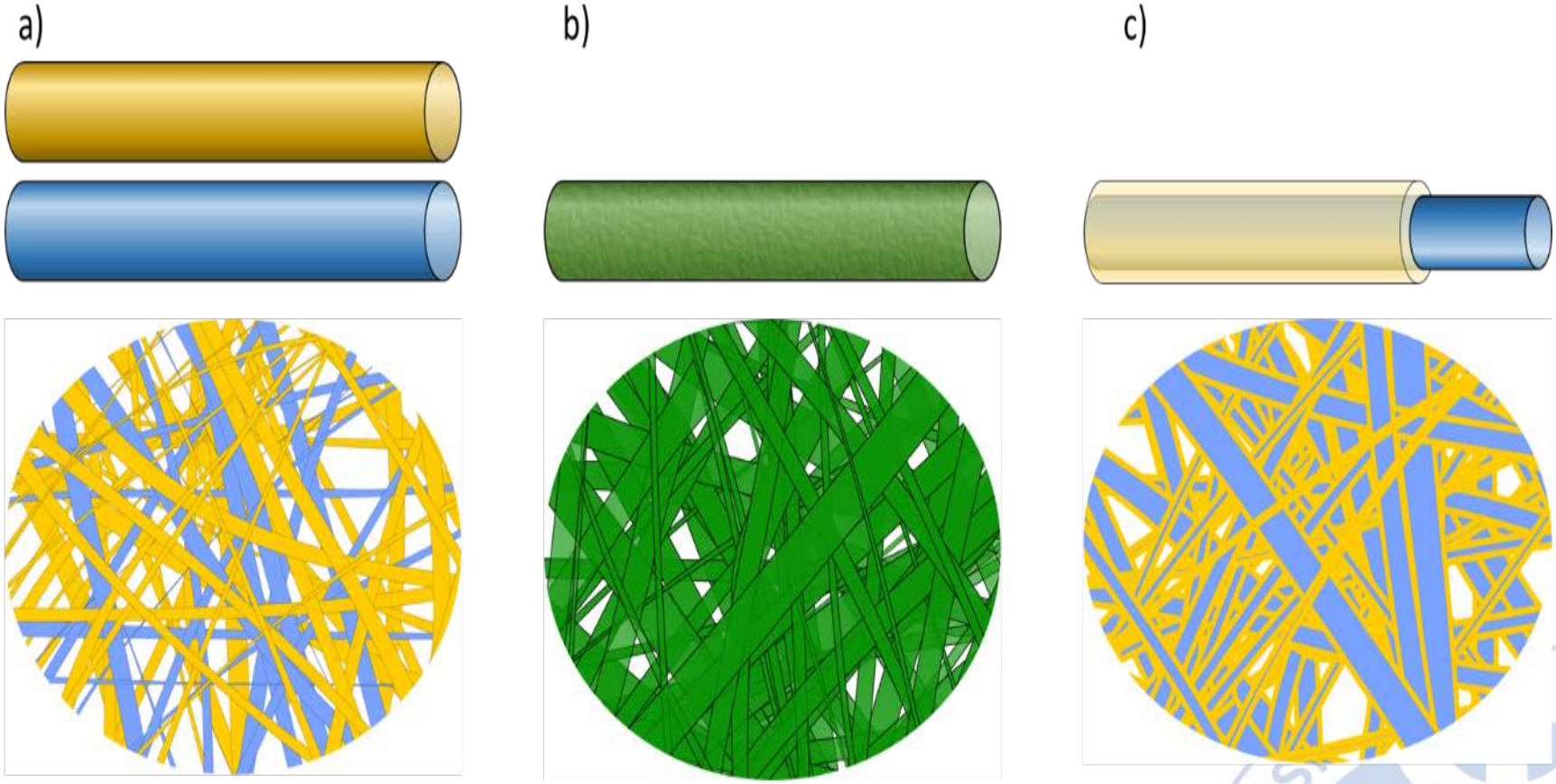


Figure 1. Electrospinning setup.

Dhandayuthapani et al., 2011.

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SCHEMATIC REPRESENTATION OF POLYMERS DISTRIBUTION IN THE FIBERS



a) Combination of fibers of different polymers, b) Polymers-blend in the fibers and c) Coaxial-fibers (or core-shell).

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ELECTROSPINNING



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ALGAL COMPOSITE NANOFIBERS

J Polym Environ (2013) 21:944–951
DOI 10.1007/s10924-013-0609-8

ORIGINAL PAPER

Characterization and Applic
Microalgal Biomass Genera

Claudio Toro · Murali M. Reddy · Rodrig
Mariella Rivas · Manjusri Misra · Amar

Published online: 12 July 2013
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Abstract This research paper pr
about the relevance of third gene
ucts diversification. This diversi
through the utilization of re
(RMB) after oil extraction
analyses the use of RMB a
posite production by means
composition, the thermal
content of RMB. Thermogra
processing window of the RMB for
tion and its dependence on its purity, especially

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Research Article
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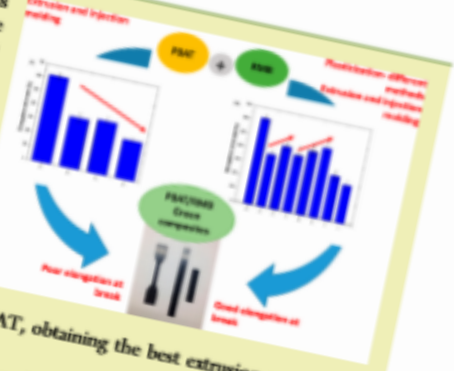
Green Composites from Residual Microalgae Biomass and Poly(butylene adipate-co-terephthalate): Processing and Plasticization

Simonet Torres,[*,†,‡,⊥] Rodrigo Navia,[‡,§] Rachel Campbell Murdy,[⊥] Peter Cooke,[∥] Manjusri Misra,[⊥,⊗] and Amar K. Mohanty[⊥,⊗]

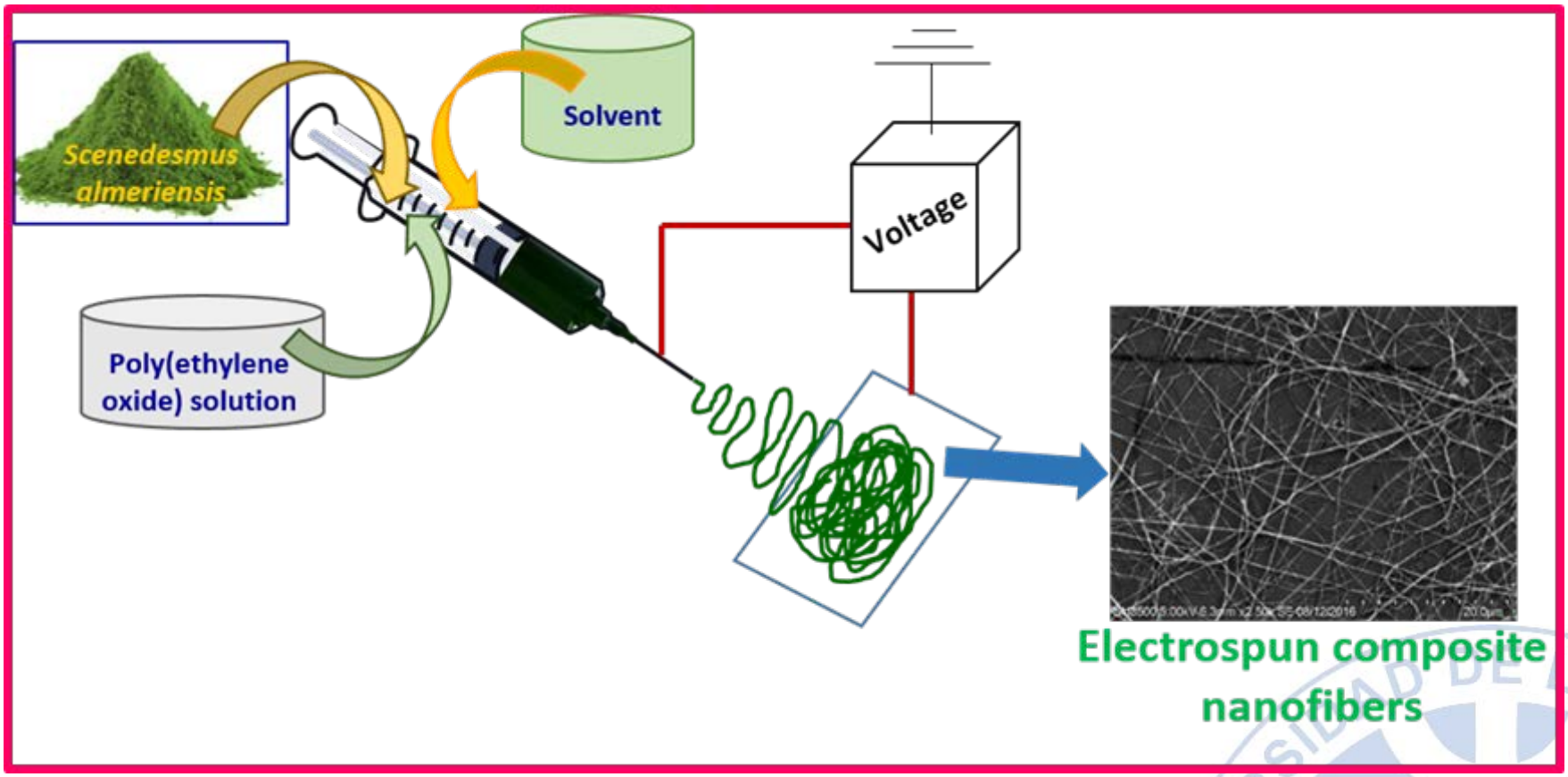
[†]Desert Bioenergy S.A., Av. Presidente Kennedy 5146, Las Condes, Santiago 7550000, Chile
[‡]Departamento de Ingeniería Química y Núcleo Científico Tecnológico en Biorecursos, Universidad de La Frontera, Casilla 54-D, Temuco 4811230, Chile
[§]Centre for Biotechnology and Bioengineering, Universidad de La Frontera, Casilla 54-D, Temuco 4811230, Chile
[⊥]Bioproducts Discovery and Development Centre, Department of Plant Agriculture, University of Guelph, Crop Science Building, Guelph, Ontario N1G 2W1, Canada
[∥]Core University Research Resources Laboratory, New Mexico State University, 945 College Drive, Skeen Hall, Las Cruces, New Mexico 88003, United States
[⊗]School of Engineering, University of Guelph, Thornbrough Building, Guelph, Ontario N1G 2W1, Canada

ABSTRACT: Innovative biocomposites from residual microalgae biomass (RMB), a byproduct of biodiesel production, and PBAT (poly(butylene adipate-co-terephthalate)) have been prepared in this study. RMB was characterized by Fourier transform infrared spectroscopy (FT-IR) and its thermal stability was determined. Subsequently, RMB and PBAT biocomposites were prepared by extrusion and injection molding. Incorporation of 10, 20 and 30% RMB in the biocomposites was studied. The biocomposites were characterized using FT-IR and thermogravimetric analysis, and their mechanical properties were compared, including tensile, flexural and impact strength. The effect of RMB on the morphology of the polymer matrix was analyzed by scanning electron microscopy and confocal laser scanning microscopy. RMB plasticization was performed with glycerol and urea, comparing different proportions of glycerol and urea. The studies show that it is possible to use RMB in the manufacture of biocomposites with PBAT, obtaining the best extrusion results with 20% RMB. Optimal result was achieved with 30% glycerol and 7.5 phr of urea.

KEYWORDS: *Biocomposites, microalgae biomass, biodiesel, poly(butylene adipate-co-terephthalate)*



ALGAL COMPOSITE NANOFIBERS



Sankaranarayanan et al. (2018)

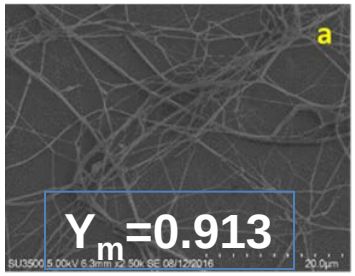
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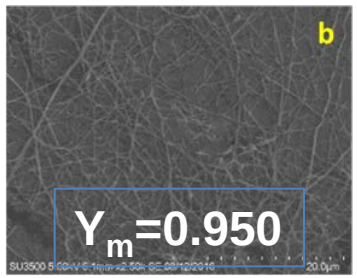
ALGAL COMPOSITE NANOFIBERS

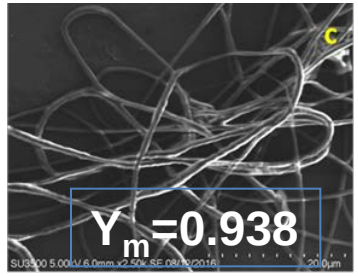
Dielectric constants and dipole moments of the solvents used

Solvent	Dielectric constant (ε)	Dipole moment (D)
Acetone	20.7	2.88
Methanol	33.0	1.70
Chloroform	4.8	1.15
Ethanol	24.3	1.69
Water	80.0	1.85

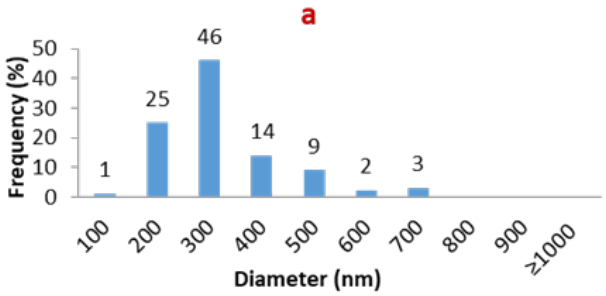
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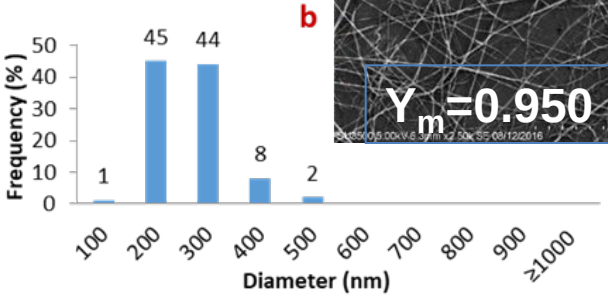


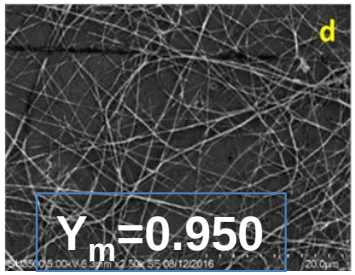


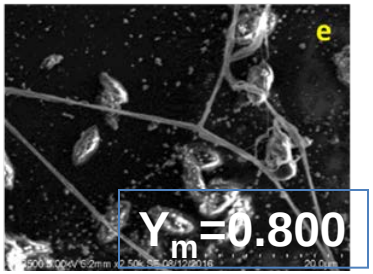
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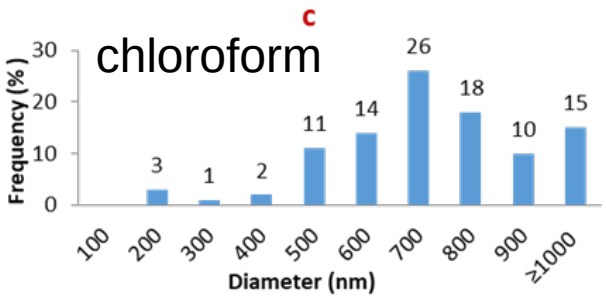


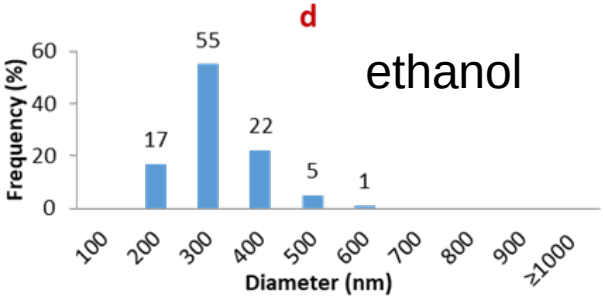
methanol

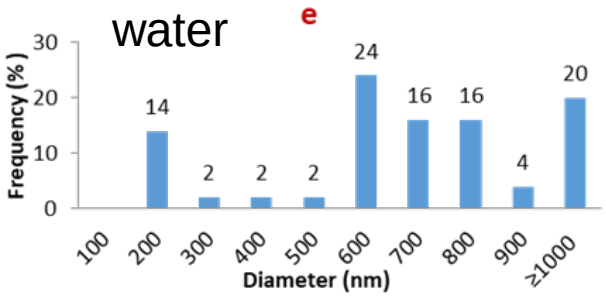








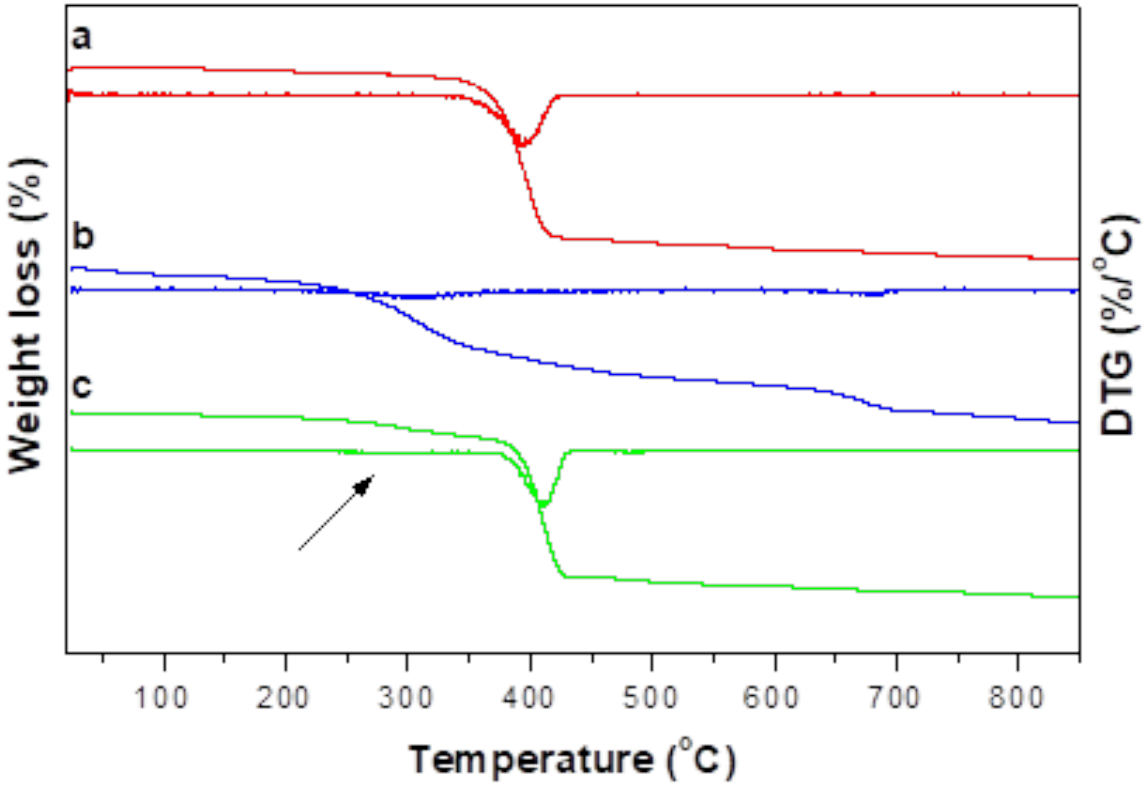




Lipids extraction occurs when using non-polar solvents which may act as viscosity controller

Dielectric constants of solvents are having huge influence in fibers formation

ALGAL COMPOSITE NANOFIBERS



TGA-DTG profiles of (a) PEO, (b) SA, (c) composite nanofibers

Sample code	C (%)	H (%)	N (%)	O (%)	Total (%)
PEO	55.5	8.1	0.1	36.7	100
SA	36.5	5.3	6.0	52.2	100
Composite nanofibers	51.8	7.4	1.0	39.8	100

Elemental composition of PEO, SA and composite nanofibers.
[a]Sulphur content was not detected. O content was calculated by difference to 100 considering C, H, N values.

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ALGAL COMPOSITE NANOFIBERS

Composites Communications 10 (2018) 18–24

Contents lists available at ScienceDirect

Composites Communicatio

journal homepage: www.elsevie

Dielectric constant of solvents (and dipole moments) have great impact on morphology and diameter in microalgal composite nanofibers

The influences of solvents on the el… *Scenedesmus almeriensis* and poly(ethylene … ation of composite nanofibers

Sivashunmugam Sankara… …nosilla[a], Francisca Acevedo[a,b], Rodrigo Navia[a,c,d]

[a] Scientific and Technolo… …d de La Frontera, Av. Francisco Salazar 01145, Temuco 4780000, Chile
[b] Department of Be… …e La Frontera, Av. Francisco Salazar 01145, Temuco 4780000, Chile
[c] Department … …and Sciences, Universidad de La Frontera, Av. Francisco Salazar 01145, Temuco 4780000, Chile
[d] Centre … …Universidad de La Frontera, Av. Francisco Salazar 01145, Temuco 4780000, Chile

…ensis
…e oxide)
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…mposite nanofibers

ABSTRACT

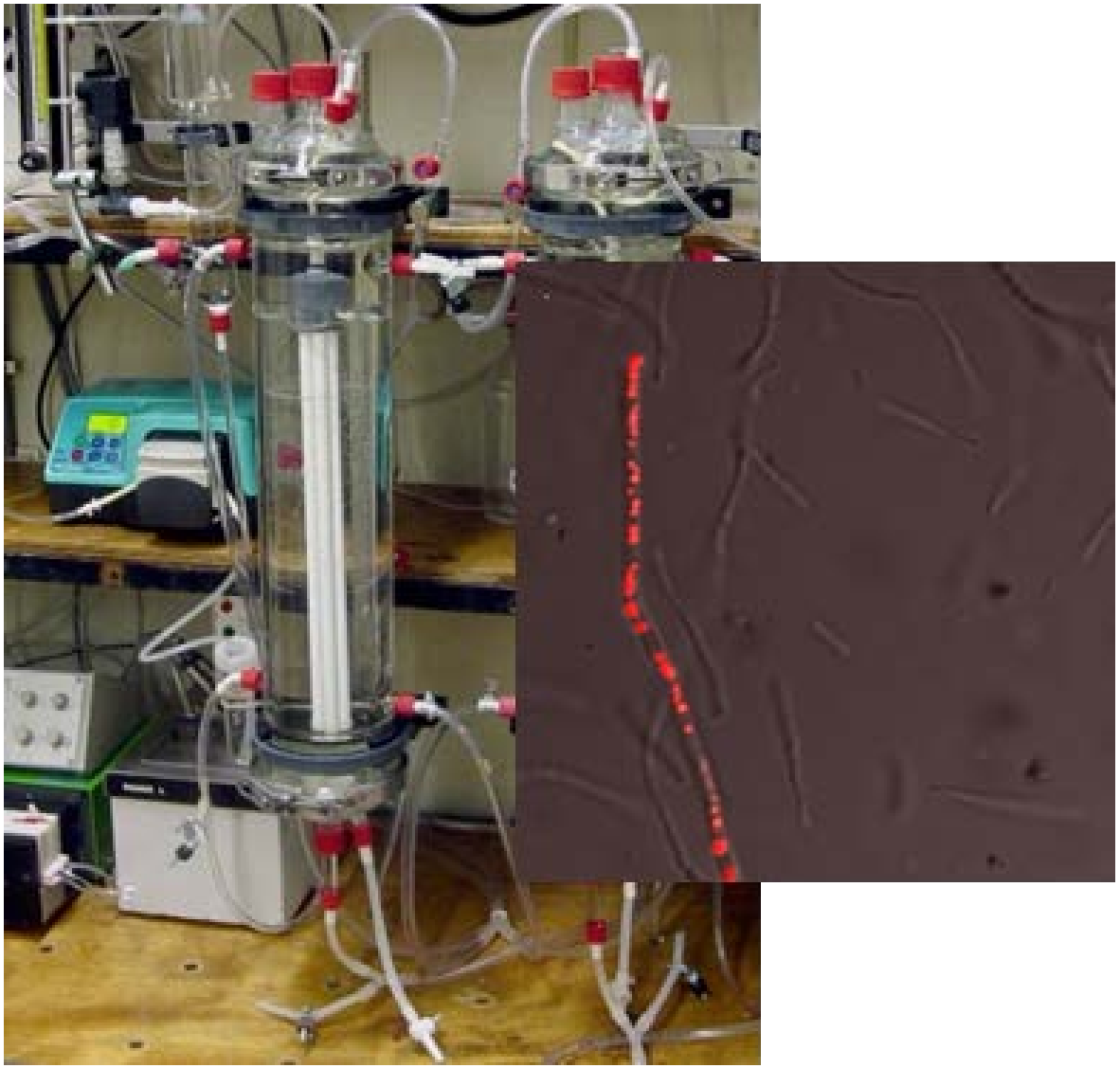
Preparation of composite nanofibers by using whole microalgal biomass (*Scenedesmus almeriensis*) with poly (ethylene oxide) by electrospinning process was explored in presence of different solvents. Diameter and morphology index of the nanofibers were determined by using scanning electron microscopy (SEM) analysis. Out of the solvents examined, ethanol, methanol and acetone resulted in better formation of more dense uniform structured composite nanofibers with diameter < 300 nm. Further studies using ethanol as solvent revealed that 10 wt% of biomass with respect to polymer source is suitable for the preparation of composite nanofibers under our studied conditions. The electrospun process was scaled up to 5 times and the SEM results showed on the one hand the formation of beads along with nanofibers and in addition a lower morphology index. Various characterization techniques supported the formation of composite nanofibers from whole *Scenedesmus almeriensis* and poly(ethylene oxide).

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POLYHYDROXYALKANOATES

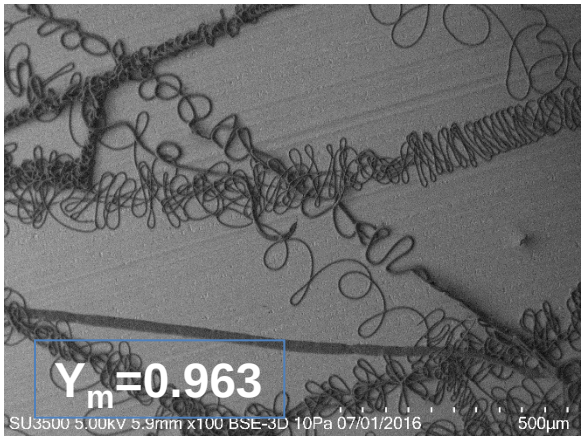


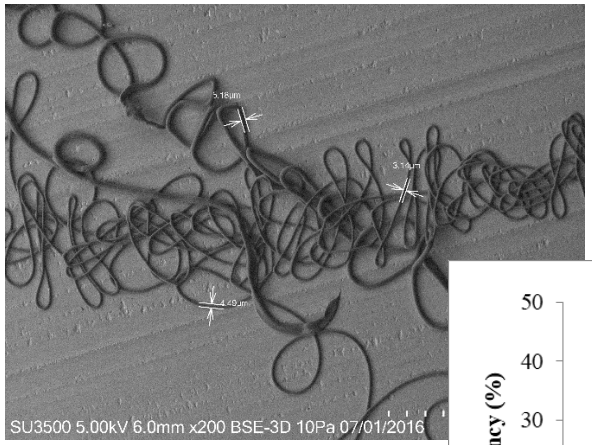
Burkholderia xenovorans strain LB400 produces Polyhydroxybutirate (PHB)

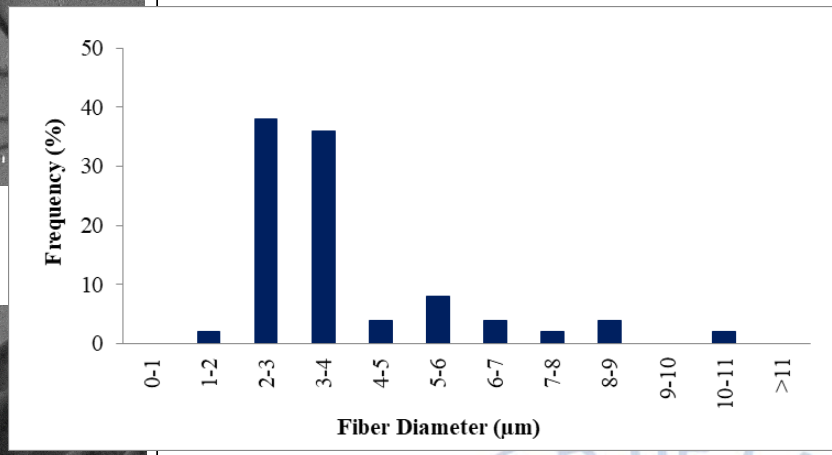
Grown in minimal medium using xylose and mannitol as the sole carbon sources

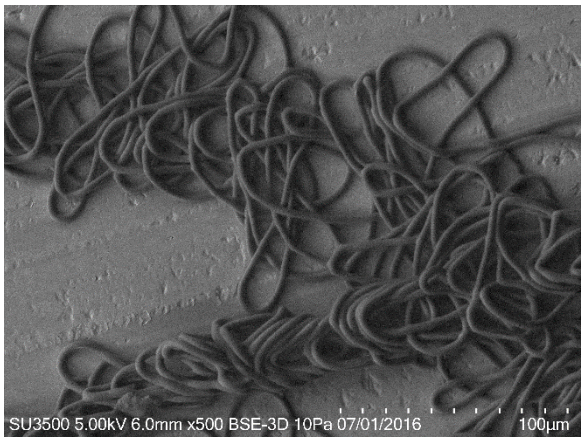
PHB was extracted with chloroform

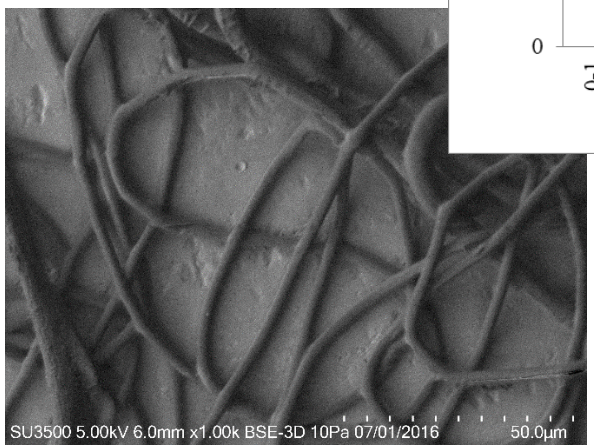
POLYHYDROXYALKANOATES







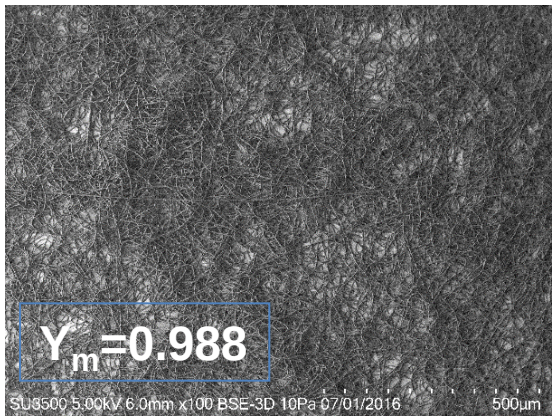


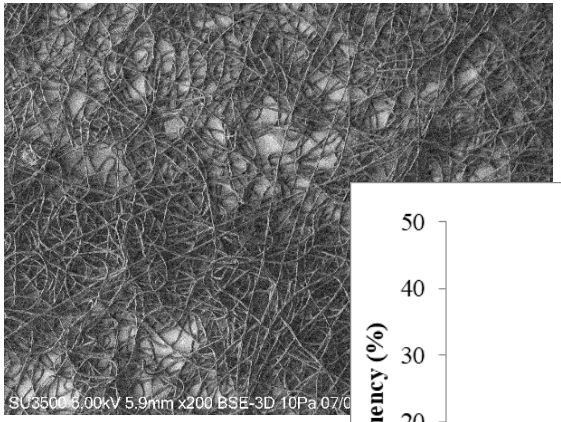


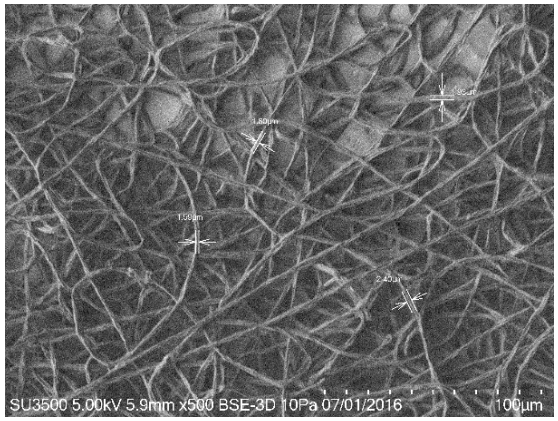
PHB microfibers produced by strain LB400 from xylose

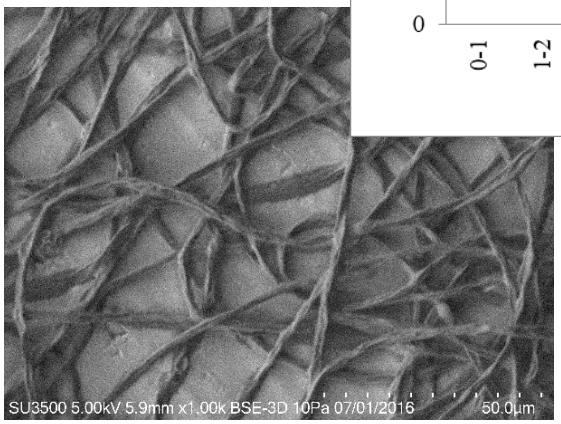
POLYHYDROXYALKANOATES

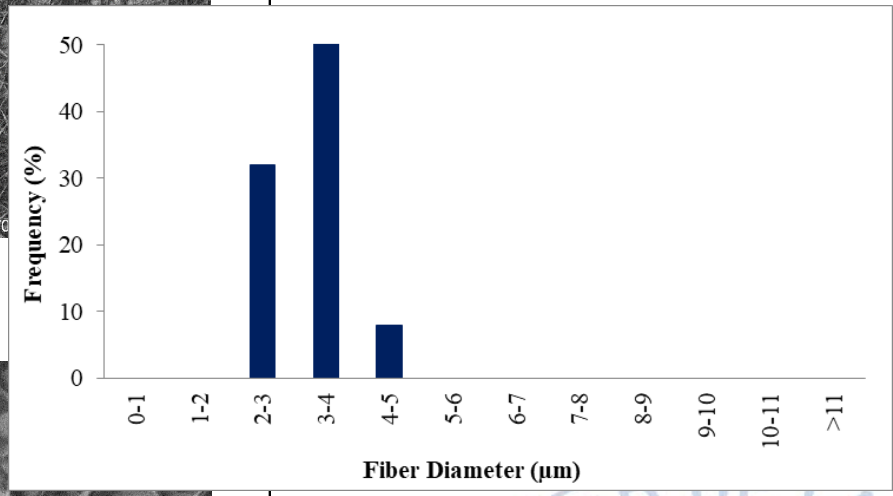
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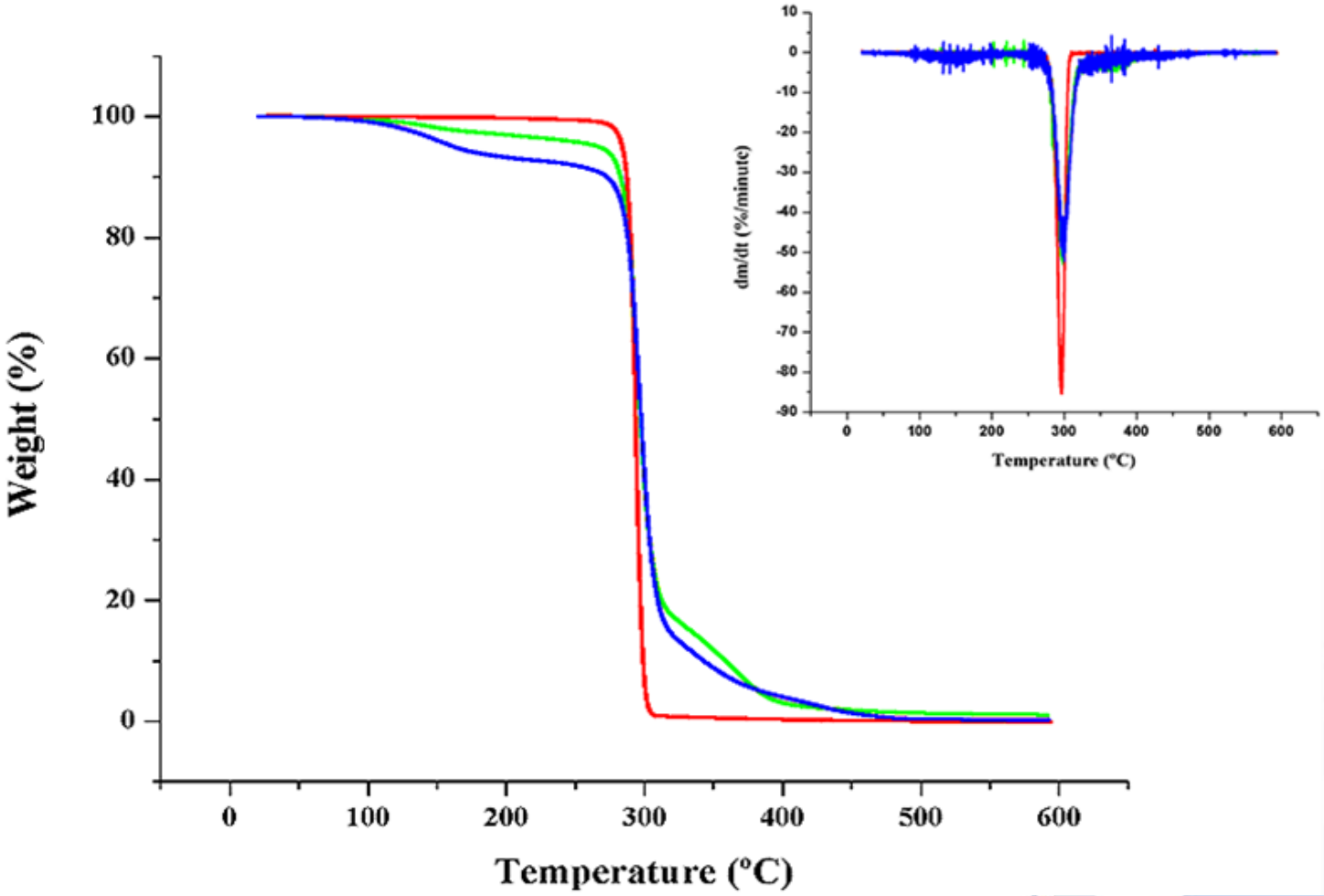




PHB microfibers produced by strain LB400 from mannitol

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POLYHYDROXYALKANOATES



TGA thermograms and DTG (derivative curves of TGA) of PHB microfibers using xylose (green line), mannitol (blue line), and commercial PHB (red line).

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International Journal of Biological Macromolecules 106 (2018) 692–697

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International Journal of Biological Macrom

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Bacterial polyhydroxybutyrate for elect…on

Francisca Acevedo[a,b,*], Pamela Villegas[c], Vi… …mosilla[a], Rodrigo Navia[a,d], Michael Seeger[c]

[a] Scientific and Technological Bioresource Nucleus, BIOR… …aco, Chile
[b] Department of Basic Sciences, Faculty of Medicine, … …, Chile
[c] Laboratorio de Microbiología Molecular y Bio… …& Centro de Biotecnología (CBDAL), Universidad Técnica Federico Santa María, Valparaíso, Chile
[d] Department of Chemical Engineerin… …or Biotechnology and Bioengineering (CeBiB), Universidad de La Frontera, Casilla 54-D, Temuco, …

ARTIC…

Arti… …7

…anoate
…ning
…spun fiber

ABSTRACT

Nano- and microfibers obtained by electrospinning have attracted great attention due to its versatility and potential for applications in diverse technological fields. Polyhydroxyalkanoates (PHAs) are biopolymers synthesized by microorganisms such as the bacterium *Burkholderia xenovorans* LB400. In particular, LB400 cells are capable to synthesize poly(3-hydroxybutyrate) (PHB) from glucose.

The aim of this study was to produce and characterize electrospun fibers obtained from bacterial PHBs. Bacterial strain LB400 was grown in M9 minimal medium using xylose and mannitol (10 g L^{-1}) as the sole carbon sources and NH_4Cl (1 g L^{-1}) as the sole nitrogen source. Biopolymer-based films obtained were used to produce fibers by electrospinning. Diameter and morphology of the microfibers were analyzed by scanning electron microscopy (SEM) and their thermogravimetric properties were investigated. Bead-free fibers using both PHBs were obtained with diameters of less than 3 μm. The surface morphology of the microfibers based on PHBs obtained from both carbon sources was different, even though their thermogravimetric properties are similar. The results indicate that the carbon source may determine the fiber structure and properties. Further studies should be performed to analyze the physicochemical and mechanical properties of these PHB-based microfibers, which may open up novel applications.

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Carbon source for LB400 growth may influence PHB electrospun-based microfibers morphology

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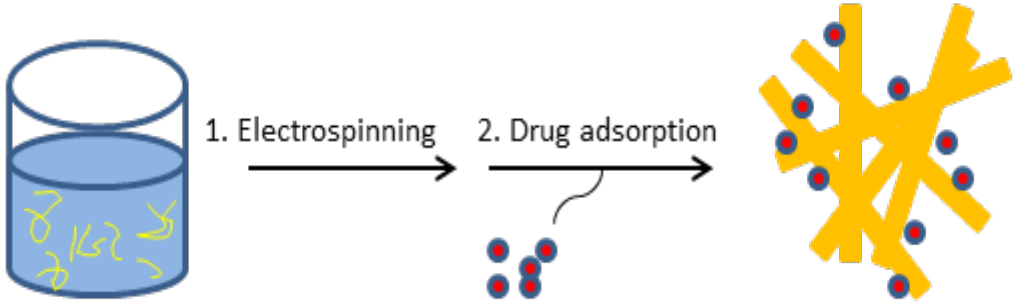
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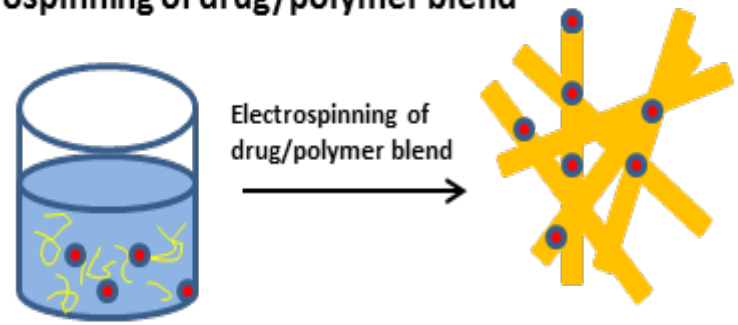
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DRUG CONTROLLED RELEASE

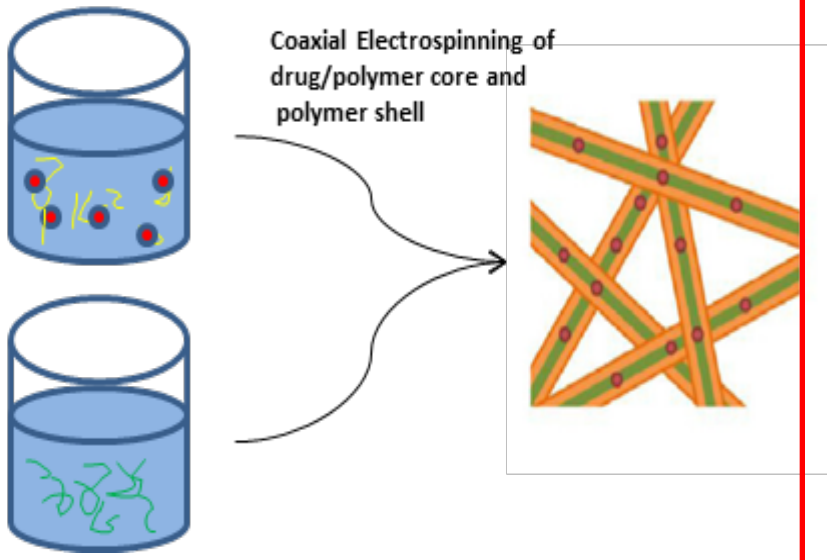
Post-spinning modification



Electrospinning of drug/polymer blend



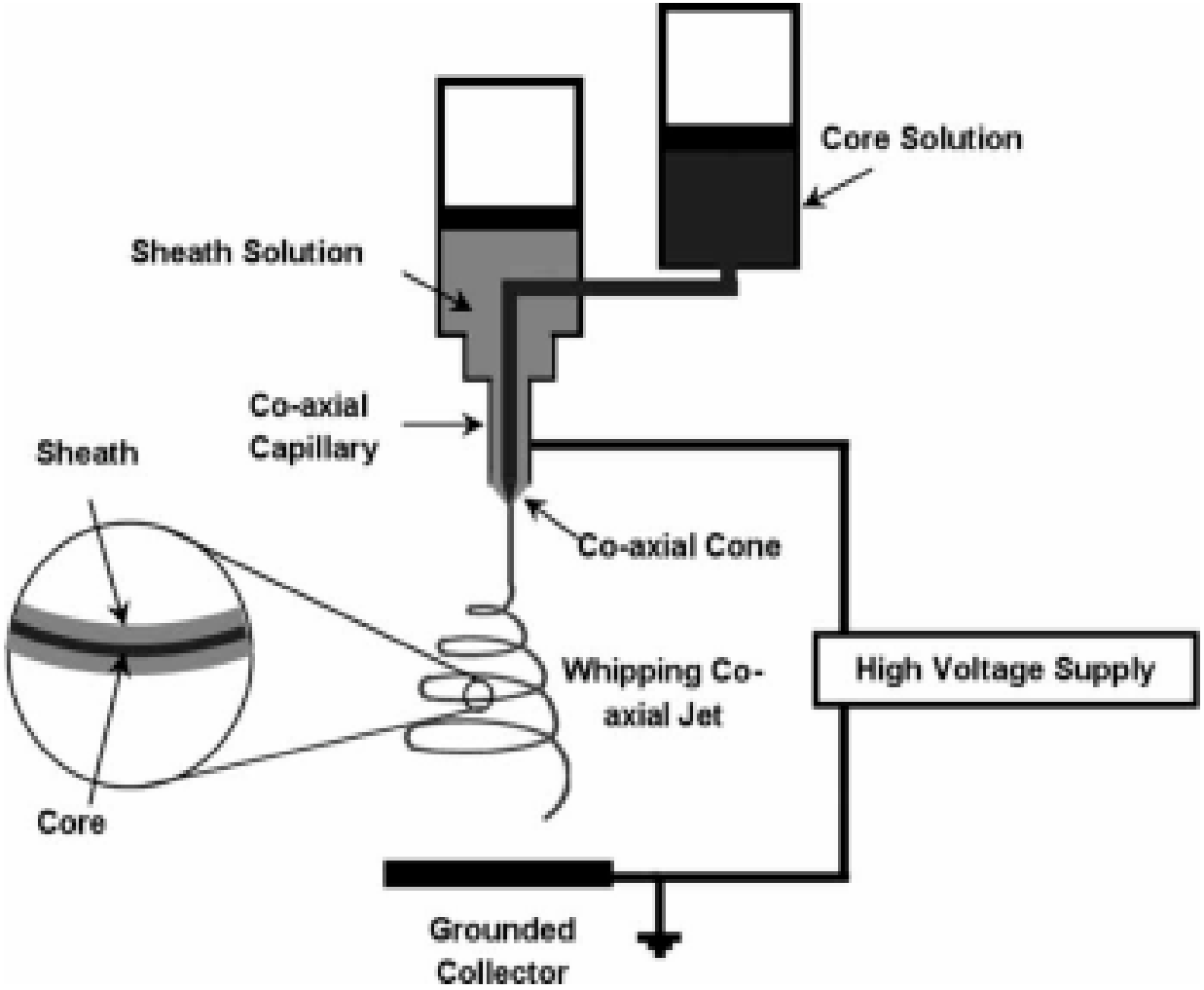
Core-shell electrospinning



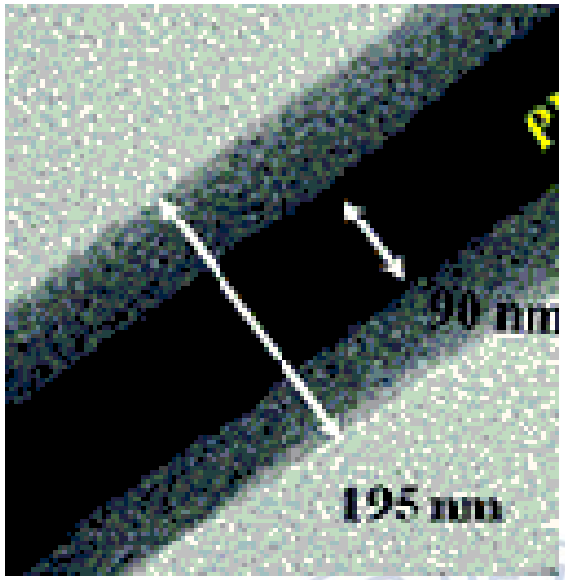
Techniques of loading drug within and onto electrospun nanofibers (polymers: yellow or green; drug: red) (taken from Meinel et al., 2012)

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CO-AXIAL ELECTROSPINNING

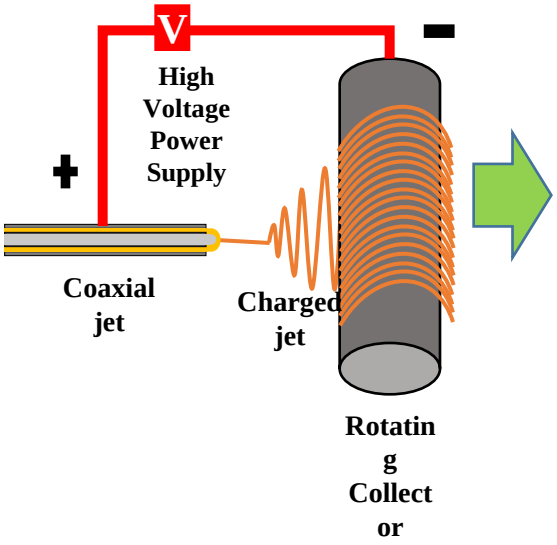


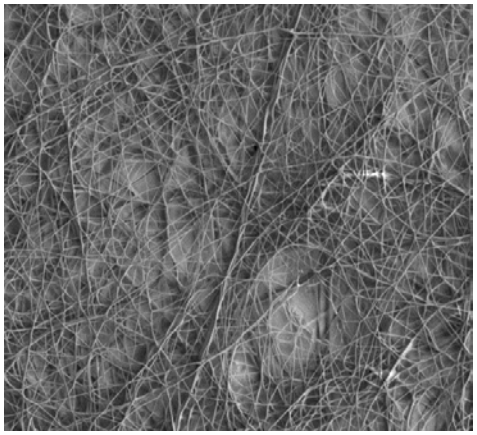
Elahi et al., 2013

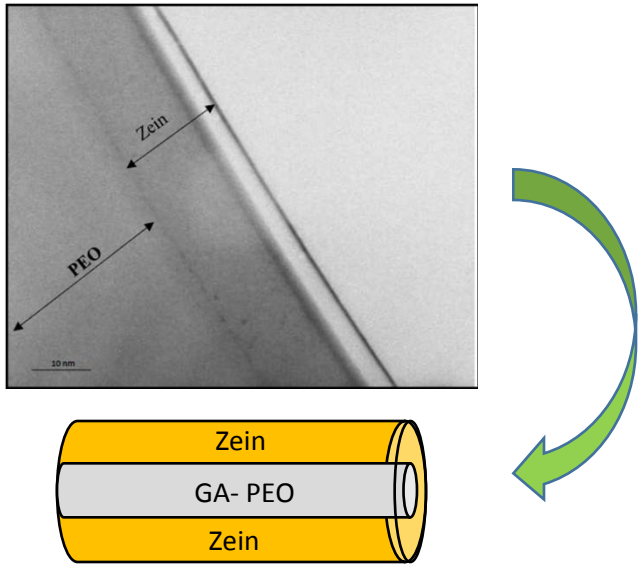


Pakravan et al., 2012

1. Gallic acid (GA) loaded PEO-core/zein-shell nanofibers



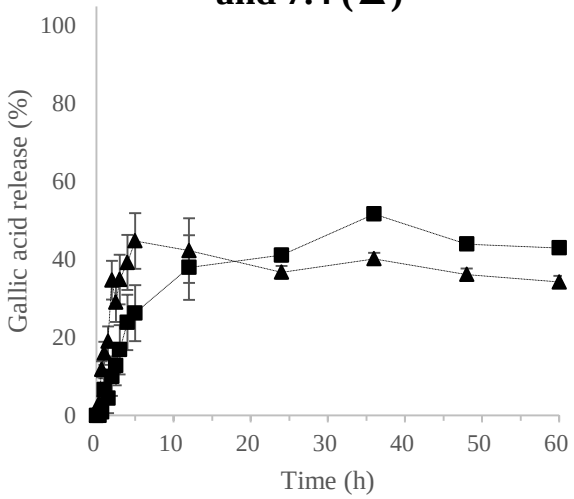




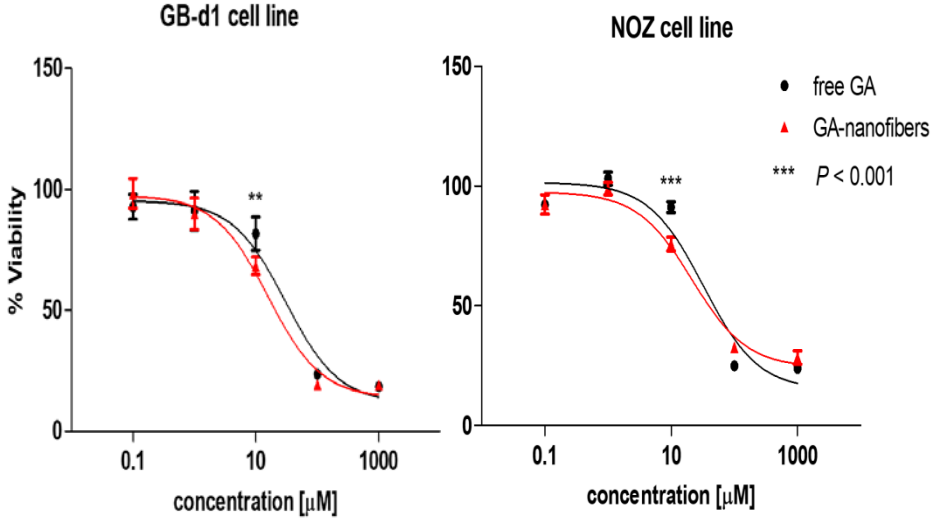
2. GA-nanofiber characterization

- *FESEM*
- *FTIR*
- *TGA/DSC*
- *Specific surface area*
- *Pore size distribution*

3. GA release profiles from PEO/zein nanofibers at pH 1.5 (■) and 7.4 (▲)



4. Viability of GB-d1 and NOZ cell (gallbladder cancer cells) line exposed to free GA or GA-nanofibers



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DRUG CONTROLLED RELEASE

(BIO)POLYMERS USE FOR BIOMEDICAL APPLICATIONS

- Biocompatible
- Biodegradable
- Non toxic

Zein

- **Stable at acid pH (gastric fluid)**
- **Resistent to proteolitic enzimes**
- **Hydrofobic**

PEO

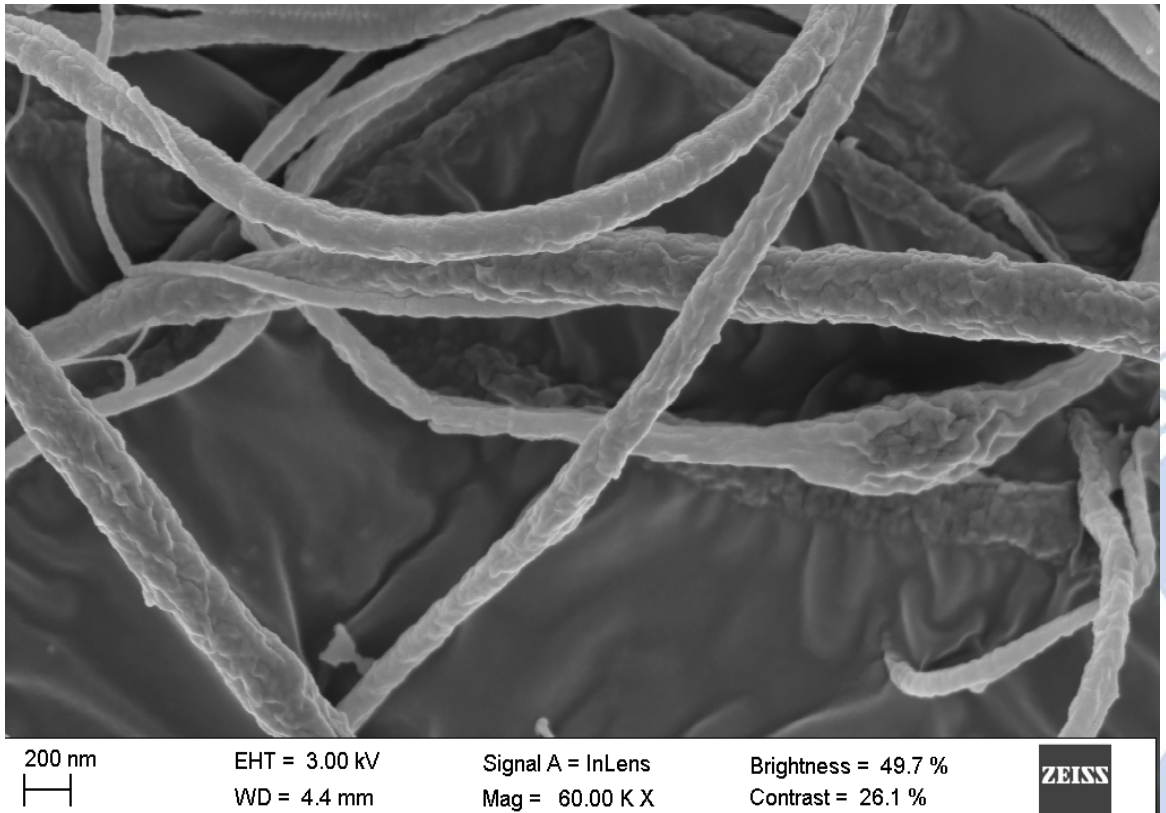
- **Simple for electrospinning and fiber generation**

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DRUG CONTROLLED RELEASE

Produced Nanofibers

Zein 20 % p/v/PEO 10% p/v, 25 kV
Ym=0.913
Diameter 269.5 ± 59.1 nm



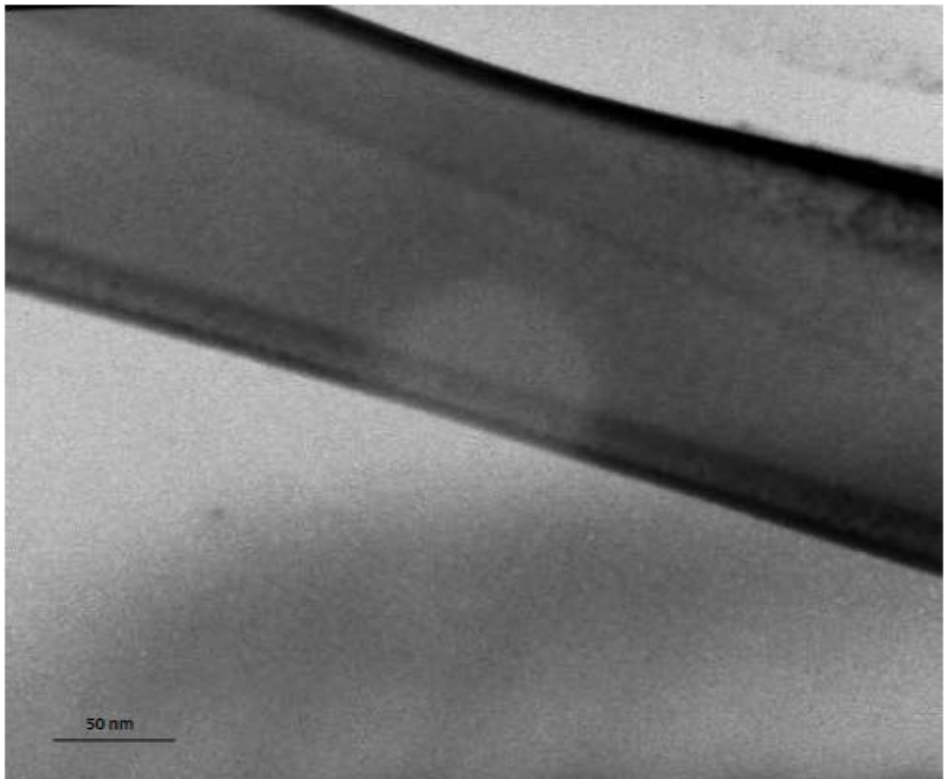
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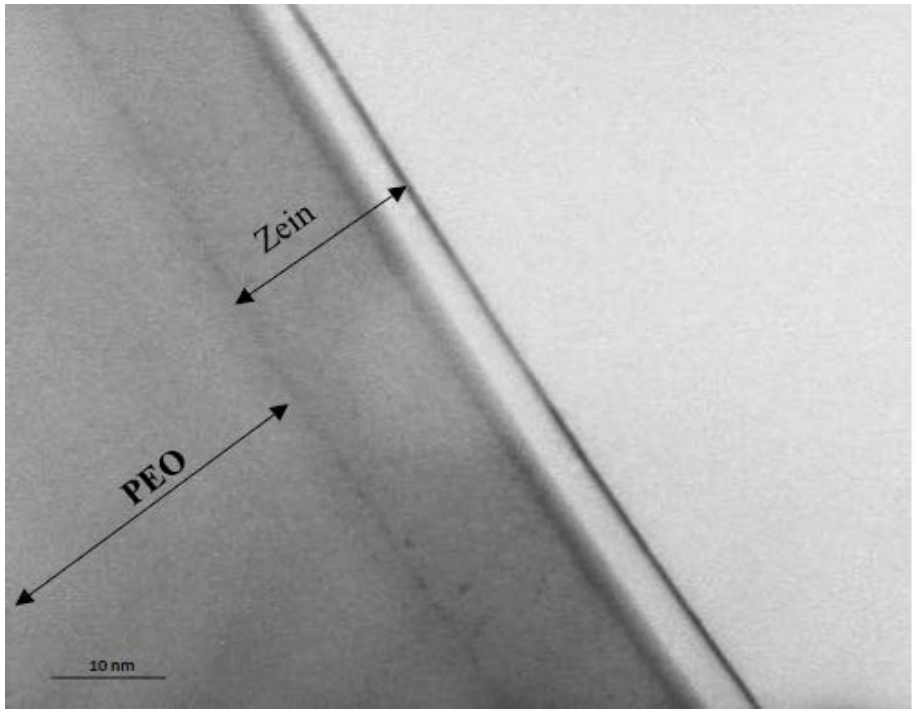
Produced Nanofibers

TEM analysis a) ×20.000 magnification b) ×30.000 magnification.

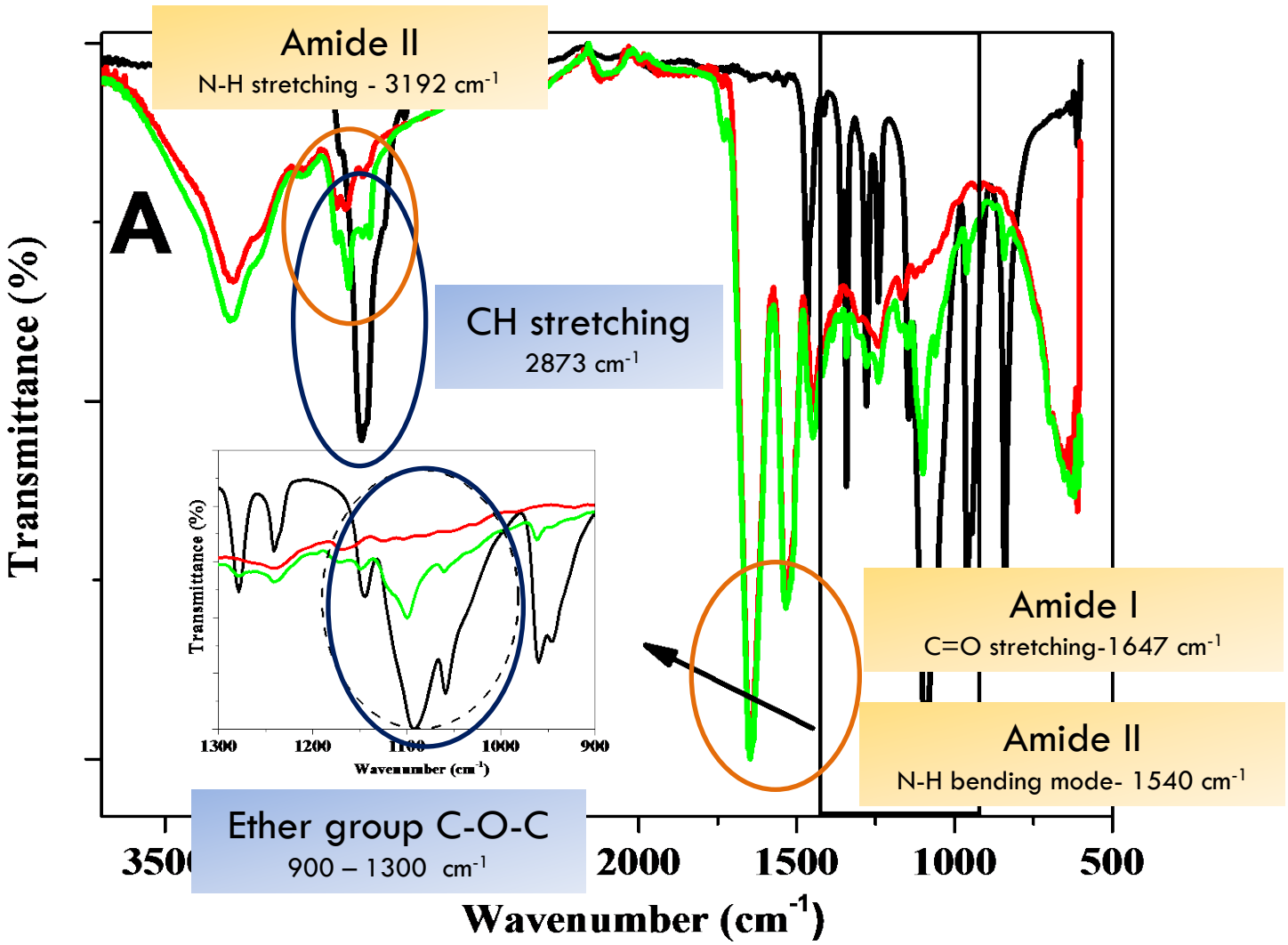
a)



b)

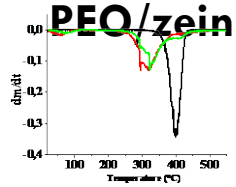


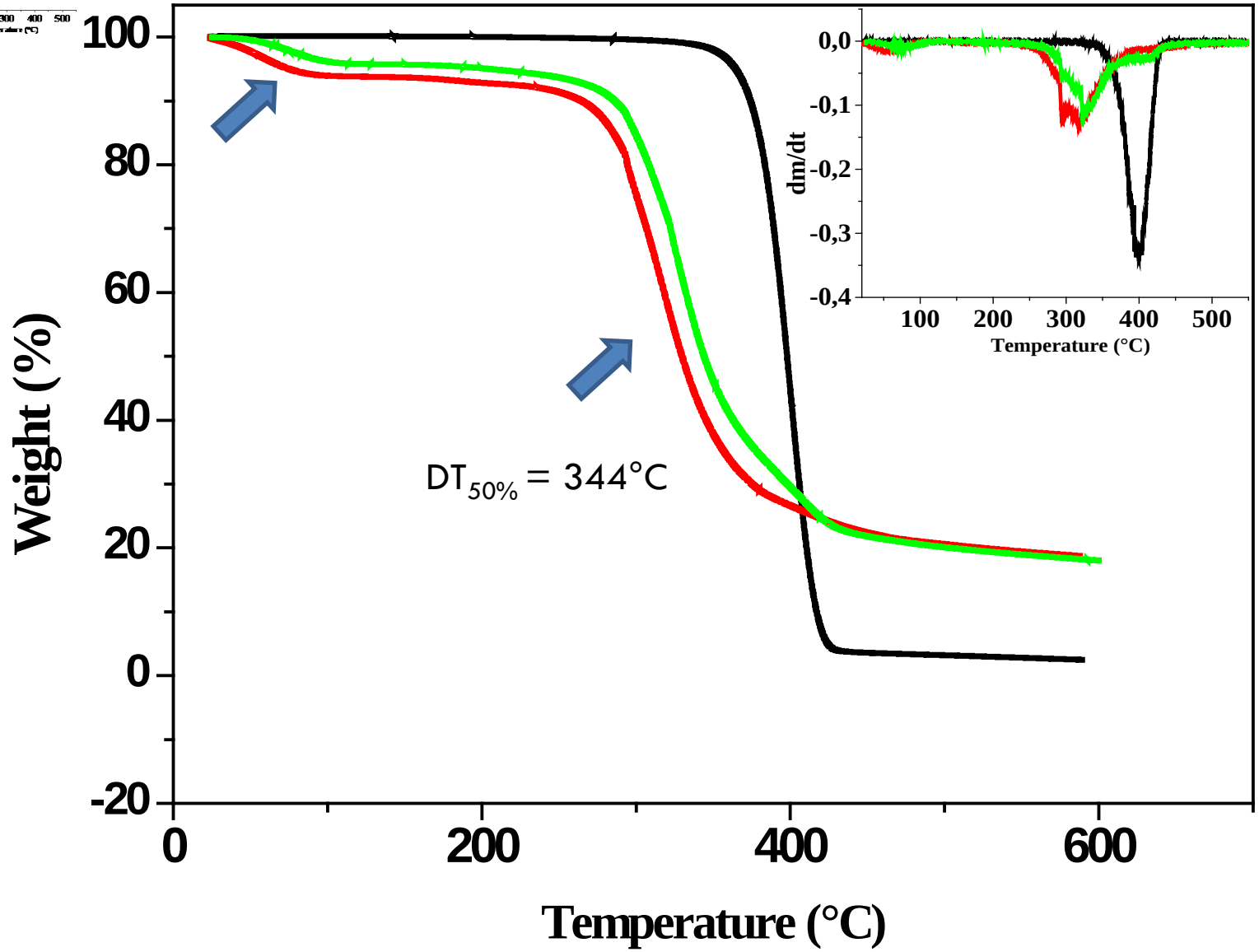
FTIR spectra for PEO (-------), zein (-------), and PEO/zein nanofibers (-------).



No new vibrations were detected in the produced nanofibers

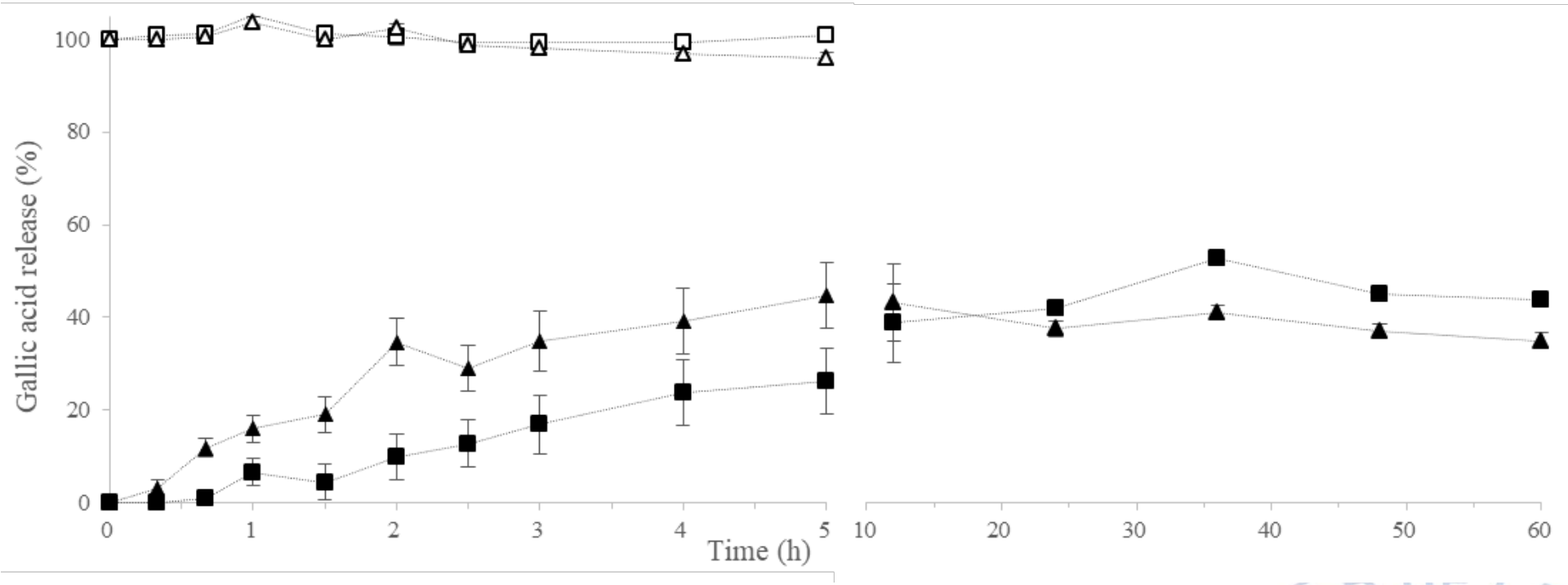
TGA thermograms and first-derivative curves (DTG) of PEO (-----), zein (------), and PEO/zein nanofibers (------).



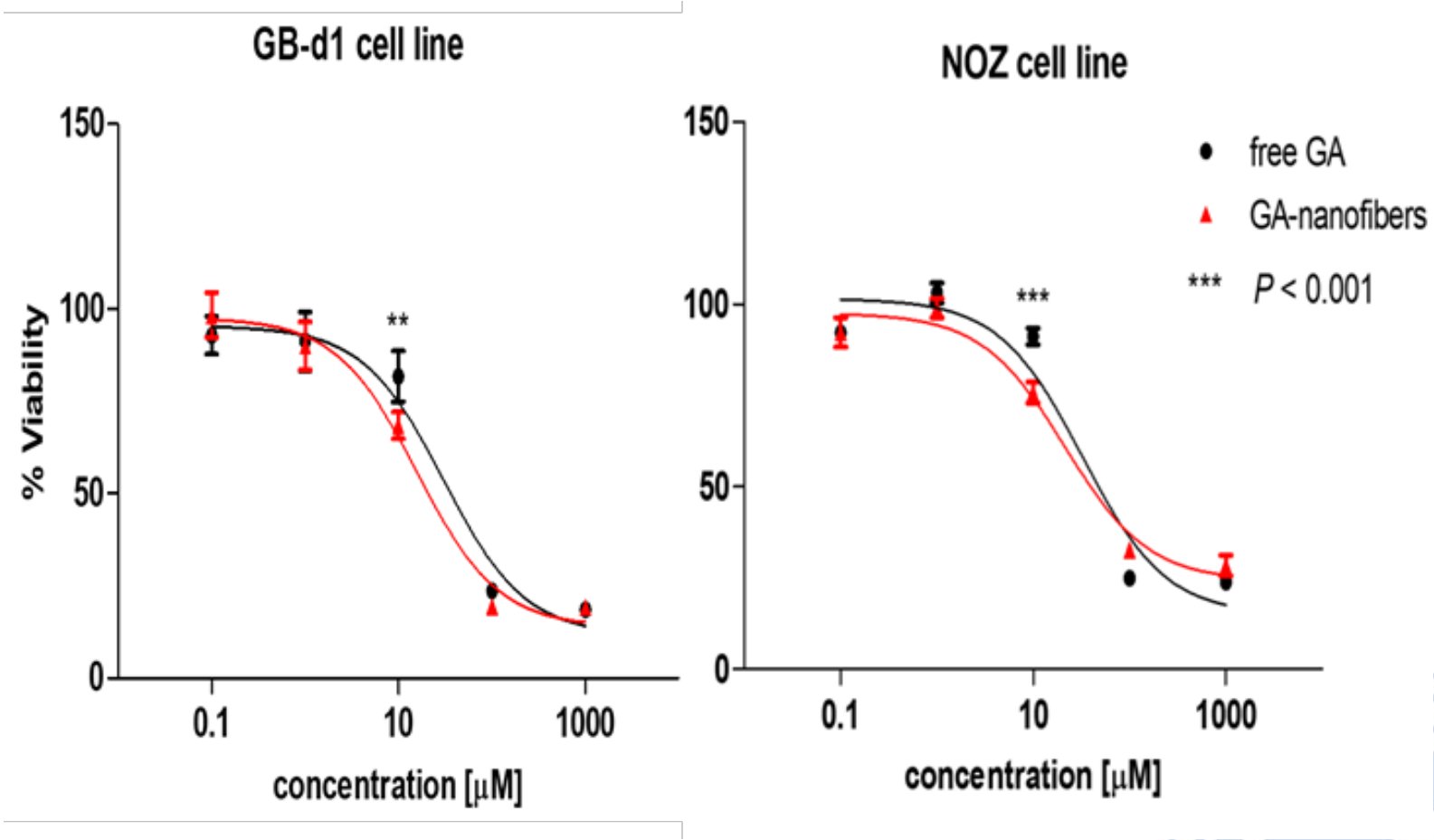


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DRUG CONTROLLED RELEASE



Gallic acid release profiles from PEO/zein nanofibers at pH1.5 (■) and 7.4 (▲) at 37°C compared with free GA at pH1.5 (□) and 7.4 (Δ)



Viability of GB-d1 cell line and NOZ cell line exposed to free GA or GA-nanofibers. Blank nanofibers did not cause toxicity events on the cells (100% viability).

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Gallic acid loaded PEO-core/zein-shell nanofibers present chemopreventive action on gallbladder cancer cells

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- APPLICATION II: POLYHYDROXYALKANOATES
- APPLICATION III: DRUG CONTROLLED RELEASE
- **CONCLUSIONS**

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CONCLUSIONS

- Polarity of solvents has great impact on morphology and diameter in microalgal composite nanofibers

- Carbon source for LB400 growth may influence PHB electrospun-based microfibers morphology

- Gallic acid loaded PEO-core/zein-shell nanofibers present chemopreventive action on gallbladder cancer cells

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Electrospun-based biopolymers: Trends and applications

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