In-situ polymerization of poly(ε-caprolactone) onto lignocellulosic fibres from date palm tree leaflets

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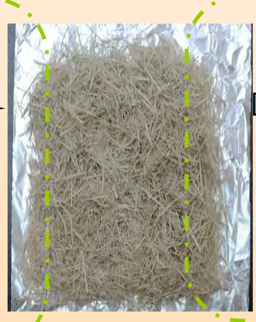
Objective

Valorisation of lignocellulosic fibres (LCF) of date palm tree (*Phoenix L. dactylifera*) via preparation of composites based on these fibres and the synthetic biodegradable polymer poly(ε-caprolactone) (PCL).

Date palm tree

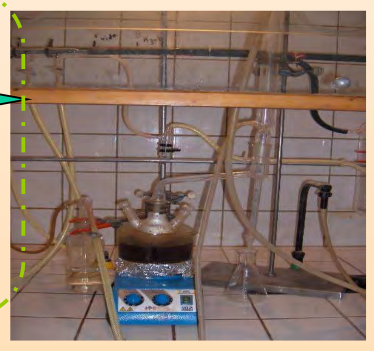
1-Production

❖Cleaned, ground and Sohxlet extracted date palm tree leaflets



Cut and depigmented fibres

2-Drying



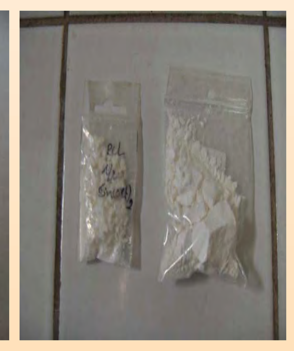
Azeotropic distillation

Desiccator drying

3– Polymerization

❖LCF
❖ε-CL
❖*Sn(Oct)2*

Grafted fibres



Ungrafted PCL

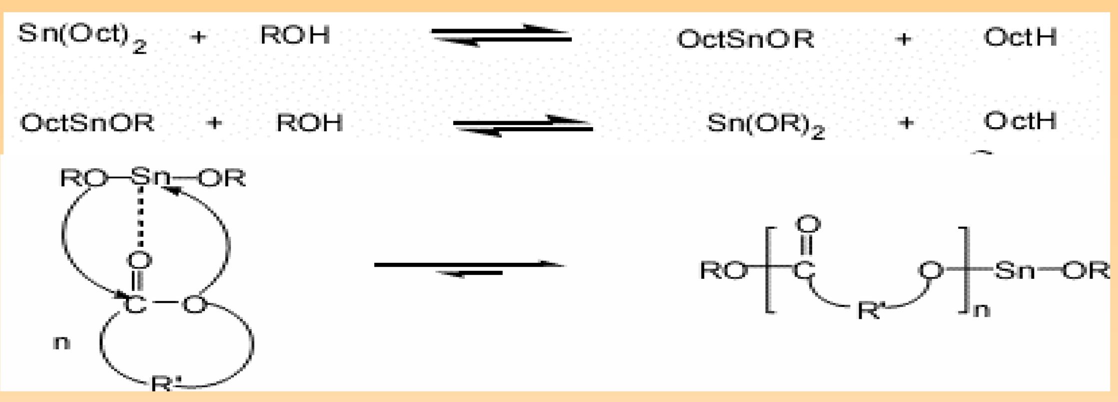
Current work

Introduction

The objective of this work is the grafting of polycaprolactone onto lignocellulosic fibres from date palm tree leaflets to improve their surface. Several factors affect the grafting, specifically, the fibres drying method, the polymerization temperature, the polymerization time and the monomer/catalyst (ε-caprolactone / tin octoate) ratio were studied.

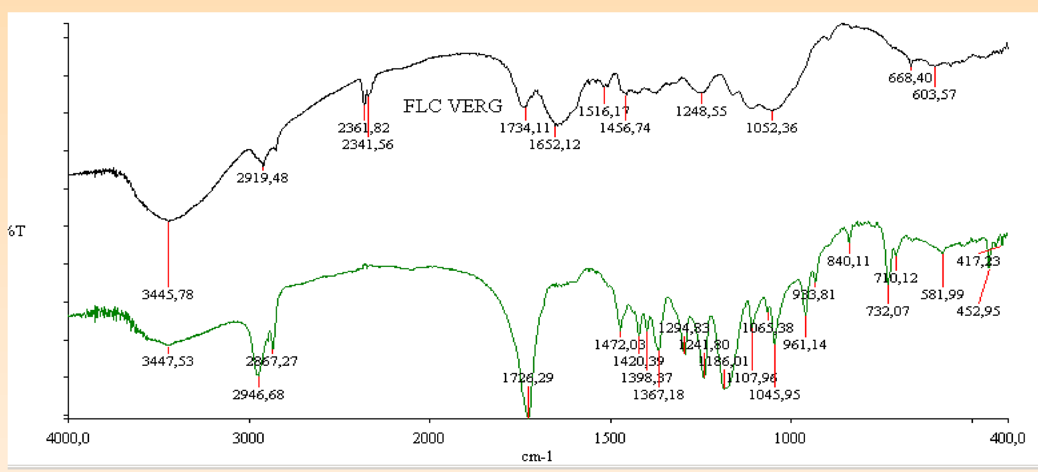
Experimental part

The ROP polymerization of ε-caprolactone in presence of $Sn(oct)_2$ needs a co-initiator (usually an alcohol), which in our case are the hydroxyl groups of the lignocellulosic fibres. The mechanism of polymerization is the following :



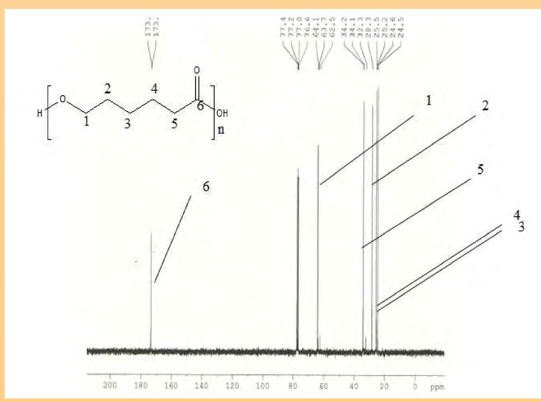
Characterization

FT-IR spectroscopy

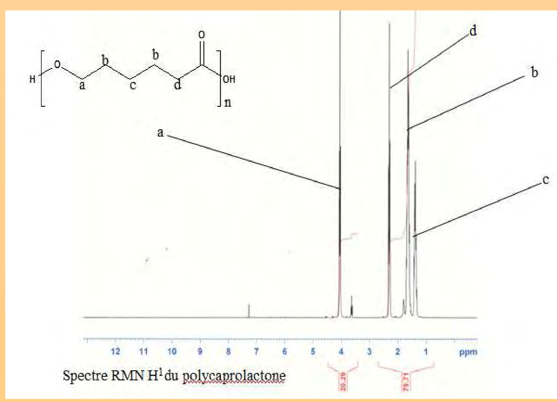


IR spectra of pristine LC fibres (---) and PCL grafted LC fibres (---)

NMR analysis

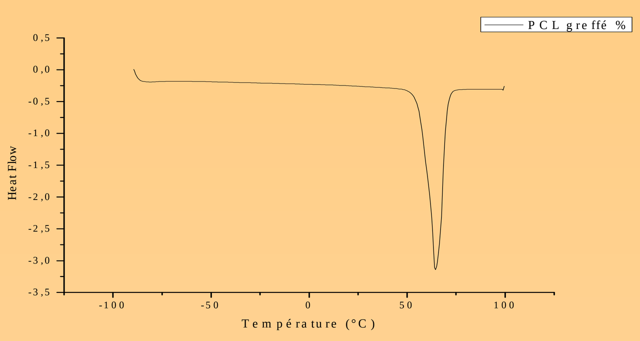


^{13}C NMR spectrum of PCL



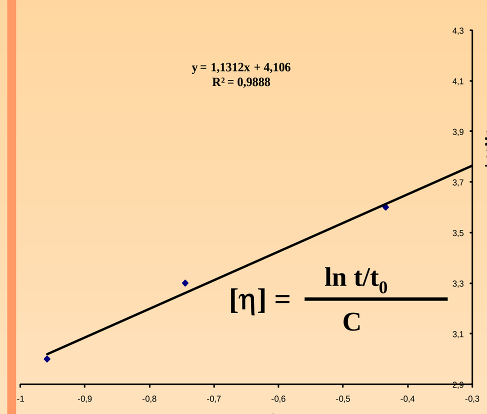
^{1}H NMR spectrum of PCL

DSC analysis



DSC thermogram of polycaprolactone

Calculation of the molar weight by viscosimetry



$$[\eta] = \frac{\ln t/t_0}{C}$$

Calibration curve:

Log Mn (Logη)

Sample	Viscosity (dl/g)	Log η	Mn	Log Mn
PCL 4000	0.368	-0.434	4000	3.6
PCL 2000	0.18	-0.744	2000	3.3
PCL 1000	0.118	-0.928	1000	3

Calculation of the molar weight from the calibration curve

Study of the polymerization parameters

Effect of the drying method

Sample	Viscosity (dl/g)	Mn	Polymerization	M/ Sn	Temperature (°C)	Time (h)
Desiccator dried LCF	0.325	3374	Bulk	100	110	24
Azeotropic LCF	0.624	15034	Bulk	100	110	24

Polymerization of ε-caprolactone in the presence of LCF dried by azeotropic distillation and desiccator dried LCF at T=110ºC, t=24h and monomer/catalyst=100

Effect of the polymerization temperature

Sample	Viscosity (dl/g)	Mn g/mol	Polymerization	M/ Sn	Temperature (°C)	Time (h)
Azeotropic LCF	0.467	5394	Bulk	100	120	24
Azeotropic LCF	0.624	7487	Bulk	100	110	24

Influence of the temperature in the polymerization of ε-caprolactone in the presence of LCF dried by azeotropic distillation for t=24h, monomer/catalyst=100

Effect of the polymerization time

Sample	Viscosity (dl/g)	Mn g/mol	Polymerization	M/ Sn	Temperature (°C)	Time (h)
Azeotropic LCF	0.624	7487	Bulk	100	110	24
Azeotropic LCF	0.656	7922	Bulk	100	110	48
Azeotropic LCF	0.486	5643	Bulk	500	110	24
Azeotropic LCF	0.636	7650	Bulk	500	110	48

Influence of the polymerization time in the molar weight of ε-caprolactone in the presence of LCF dried by azeotropic distillation at T=110ºC and monomer/catalyst=100 and 500

Conclusion & Perspectives

We verified that ε-polycaprolactone was well grafted onto the lignocellulosic fibres, thus the molar weights of the prepared polymers intimately depended on the experimental parameters. Our work will continue with the implementation of biocomposites based on biodegradable matrices reinforced with pristine and modified lignocellulosic fibres from date palm tree by in-situ polymerization of poly(ε-caprolactone).

Keywords

Poly(ε-caprolactone), lignocellulosic fibres, date palm tree, ROP, biodegradable.

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