



NMP3 - CT - 2004 - 500311

Sustainpack

Innovation and sustainable Development in the Fibre Based Packaging Value Chain

Instrument: **IP**

D5.43. Report on the new way to modify the fibers for their incorporation into matrices

Due date of deliverable: 071015 (month 40)
Actual submission date: 071030 (month 40)

Start date of project: **2004-06-01** Duration: **4 years**

Organisation name of lead contractor for this deliverable: EFPG

Revision

Project co-funded by the European Commission within the Sixth Framework Programme (2002-2006)		
Dissemination Level		
PU	Public	X
PP	Restricted to other programme participants (including the Commission	
RE	Restricted to a group specified by the consortium (including the Commission	
CO	Confidential, only for members of the consortium (including the Commission Services)	

WP 5.1.1 Chemical modifications

D5.43. Report on the new way to modify the fibers for their incorporation into matrices

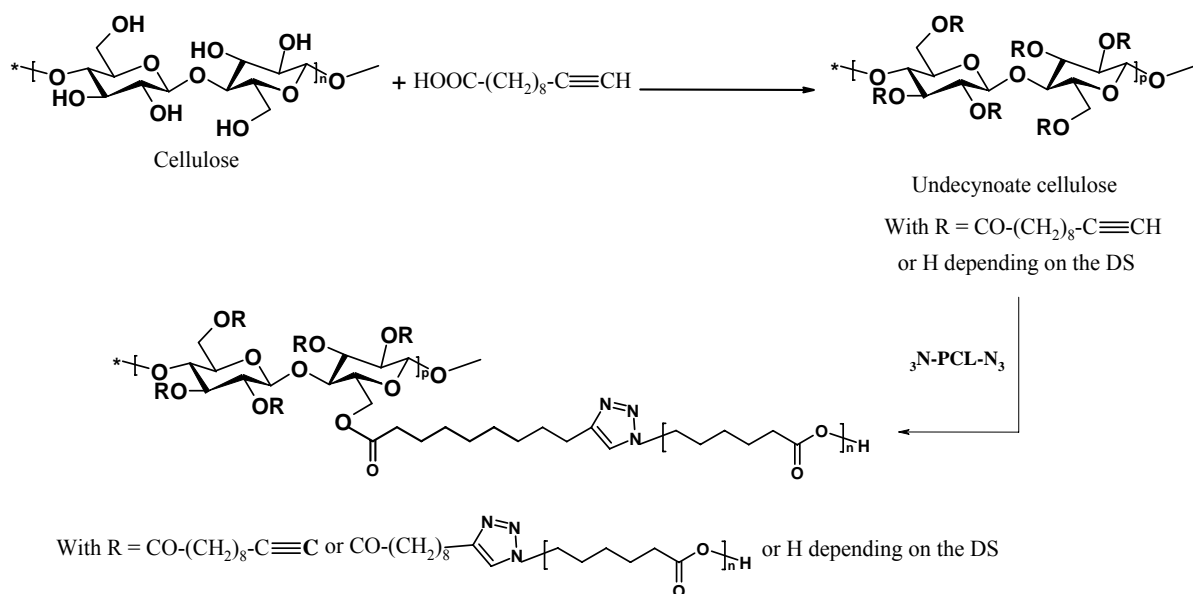
Objectives :

During last decades, plastic-made materials have daily invaded our consumption society. Their use is still growing and they took an important role in our economy. A large amount of this family of material is employed in packaging, car industry, agriculture and furniture. As a consequence, there is an accumulation of petroleum-based packaging waste in environment. As petroleum is a fossil resources and its production is announced to reach a peak within the few next decades, alternative solutions must be found. Thus, it is necessary to prepare new materials from sustainable resources and with improved mechanical properties. That's why biobased or biodegradable composites materials could be a promising solution mixing environmental and mechanical aspect. The use of cellulosic fibres as reinforcement is one of studied solution. This natural fibre is renewable and its mechanicals properties are interesting compared with glass fibres. However, mechanical properties are dependant on the quality of the fibre-matrix interface. In fact, since cellulose fibre surface is polar (hydrophilic) because of the presence of numerous hydroxyl groups, it is necessary to modify it chemically to ensure a better surface compatibility and adhesion with the non-polar (hydrophobic) matrices. Polycaprolactone (PCL) and Oulu cellulose fibres were respectively chosen as matrix and reinforcement. PCL was preferred because of its biodegradability. Oulu cellulose fibres have been chosen because of the ornification of their surface obtained thanks to dry refining treatment, which limits polarity difference between fibre and the non polar matrix. Nevertheless, such an operation does not yield good hydrophobisation of the fibres and a

chemical treatment of their surface is needed, in order to compatibilize them with the matrix. Several solutions exist as already described in previous deliverables. In this report, we will focus on new way to graft the polymer on the fibre. The chains lengths are expected to be long enough to allow the formation of a continuous film by hot-pressing or to favour mixing with polymeric chains. It is what we call the co-continuous approach.

In previous study, we have tried to graft PCL and cellulose using a diisocyanate as a mediator molecule, but the first results showed that grafting was not sufficient. That's why we have developed a new way of grafting based on click chemistry strategy.

Because of its large molecular weight, PCL should not diffuse into the fibre and only surface grafting should occur. This advantage constitutes also a drawback, because the large molecular weight of PCL induces an important steric hindrance, which affects negatively the grafting density. In order to overcome this limitation, we decided to move away PCL from the fibres surface by using a spacer chain. An 11-Carbon atoms spacer is first grafted onto the cellulose surface followed by the PCL grafting onto this spacer. This strategy is illustrated in scheme 1. Recently, the 1,3-dipolar cycloaddition of azides and terminated alkynes by copper(I) catalyst (known as "click chemistry" reaction) has been widely used in the synthesis of end- or pendent functionalized polymers, new monomers and macromonomers, block copolymers^[1-2]. As this method is very efficient and is known to be environmental friendly we decided to use it for the final step of our work.

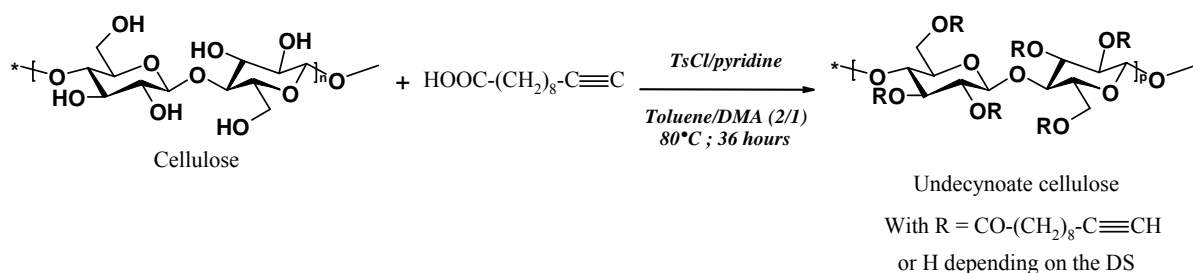


Scheme 1: Strategy used for the modification of cellulose fibres.

This methodology was first studied on avicel cellulose powder as model prior to Oulu cellulose fibres. For each step of scheme 1, experimental conditions and product characterization are detailed below.

I- Esterification of cellulose powder

The esterification of cellulose powder was realised in toluene/DMA (2/1) solvent which allowed the modification of only *superficial* surface hydroxyl groups. Among the many methods employed to obtain esters from carboxylic acids, we chose that calling upon the use of TsCl/Pyridine as activating system, as describe by Sealey and Heinze^[3]. According to this method, 10-undecyanoic acid (0,4 eq./AGU) was grafted onto cellulose powder by reaction with equimolecular concentration of TsCl and pyridine under stirring at 80°C for 36 hours (scheme 2). After cooling down to room temperature, this mixture is filtered and the powder washed off with water and ethanol to get ride of acid, TsCl and pyridine. Finally, after Soxhlet extraction with methylene chloride to remove possible secondary product, the undecynoate cellulose powder was dried at 50°C for 48 hours.



Scheme 2: Esterification of cellulose powder with 10-undecynoic acid.

FTIR spectroscopy was used to compare cellulose powder before and after grafting. The IR spectra of dry modified cellulose is presented in Figure 1 and displays, as expected, the apparition of the characteristic band at 1726 cm^{-1} ($\text{C}=\text{O}_{\text{ester}}$), but the intensity of signal associated to hydroxyl groups at 3445 cm^{-1} did not decreased. The low intensity of the ester band noticed can be attributed to the modest amount of surface hydroxyl groups esterified, to compare with the total internal and inaccessible hydroxyl groups. It was not possible to observe the $\text{C}\equiv\text{C}$ bands at $2100\text{--}2260\text{ cm}^{-1}$ for the same reason. The $\text{C}\equiv\text{C}\text{--H}$ signal (3300 cm^{-1}) is overlapped by the peak corresponding to hydroxyl group signal at 3345 cm^{-1} . In addition, no tosylation occurred since no corresponding bands of tosylate groups at 1364 and 1177 cm^{-1} (SO_2 function) have been observed during the esterification. This was confirmed by the absence of sulphur atoms in elemental analyses (table 1).

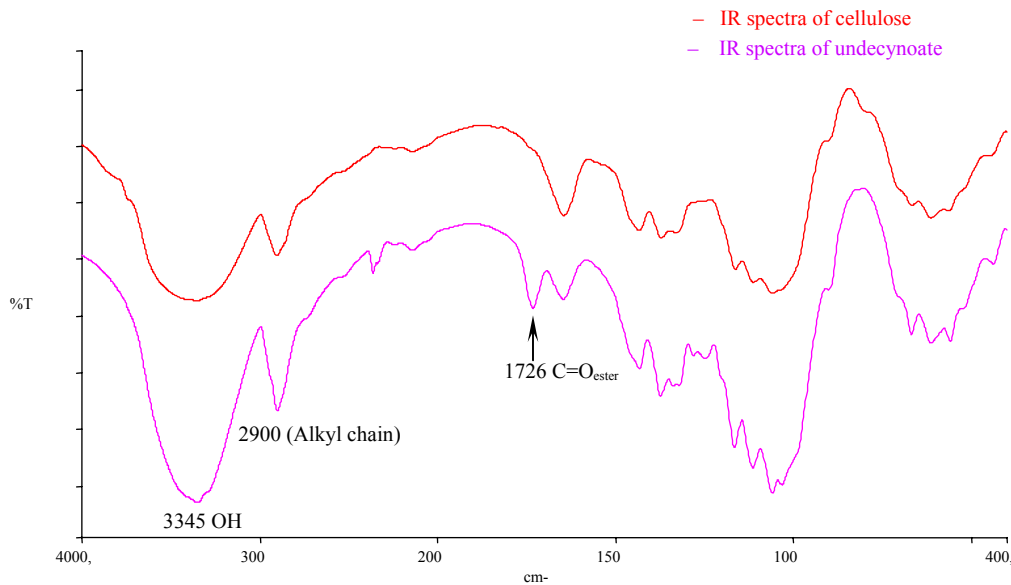


Figure 1: Comparative IR spectra of undecynoate cellulose ester and cellulose.

The degree of substitution of 10-undecynoic acid per anhydroglucose units (DS) was determined by elemental analysis according to the following formula.

$$DS = \frac{72,066 - \%C \times 162,14}{\%C \times 164,2452 - 132,121}$$

The calculated DS was found to be 0.1, which shows that esterification also take place in the fibres because of the low molecular weight of the reagent used.

Table 1: Elemental analyses results of esterified fibres.

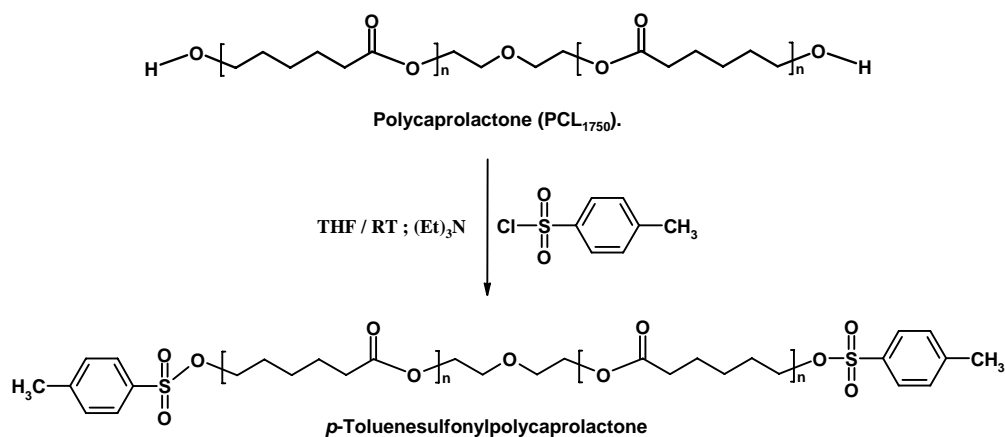
	C	H	O	S
Sample 1	47.97%	6.59%	43.09%	110 ppm
Sample2	48.36%	6.74%	---	105 ppm

II- Conversion of polycaprolactone into azido-polycaprolactone

The second step of this work is to convert commercial polycaprolactone-diol (PCL-diol) into azido-polycaprolactone (N_3 -PCL- N_3). This was achieved in two steps. First, PCL-diol is tosylated by *para*-Toluenesulfonylchloride which is a very good leaving group and then tosylated PCL is converted in azido-polycaprolactone by nucleophilic displacement using sodium azide.

Step1: *para*-Toluenesulfonylation of polycaprolactone-diol

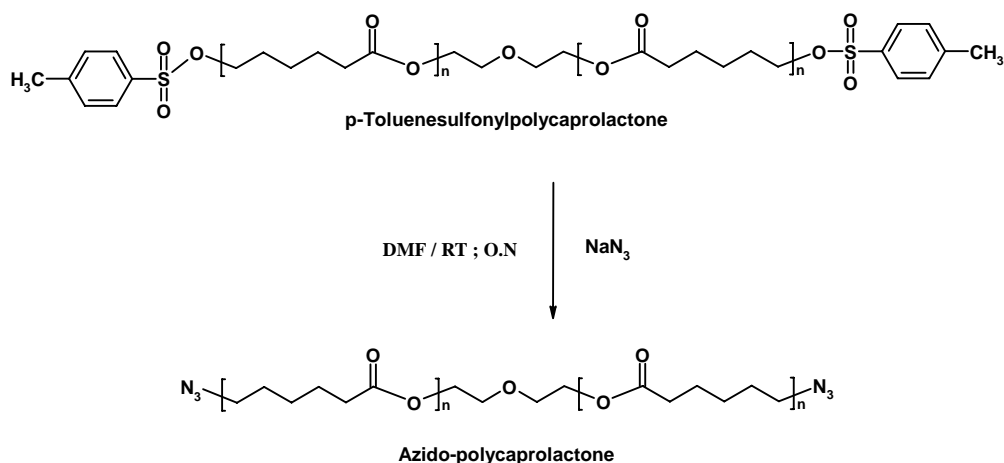
Commercial polycaprolactone-diol from Sigma Aldrich (M_n 1250 ; [36890-68-3]) was tosylated using a mixture of TsCl/ Et_3N (Scheme 3). TsCl (57,15 mmol ; 10,9 g ; 5 eq./PCL) in THF (40 ml) was dropwisely added to a stirred solution of PCL-diol (11,43 mmol ; 20 g), Et_3N (57,15 mmol ; 8 mL ; 5eq./PCL) in THF (40 ml) at room temperature, and the mixture was stirred for 1 day (Scheme 3). Insoluble products were filtered out and the clear reaction mixture was poured into a bath of ethyl ether at 0 °C, in excess. The precipitated product, *p*-Toluenesulfonylpolycaprolactone (TsO-PCL-OTs) was vacuum-dried and 85% of yield was obtained.



Scheme 3: *para*-Toluenesulfonylation of polycaprolactone-diol.

Step2: Azidation of *para*-Toluenesulfonylpolycaprolactone

p-Toluenesulfonylpolycaprolactone was converted into azido-polycaprolactone by nucleophilic displacement (Scheme 4). *p*-Toluenesulfonylpolycaprolactone is reacted with 2 eq./TsCl of sodium azide in DMF at room temperature overnight. Insoluble products were filtered out and the clear reaction mixture was poured into a bath of an excess of hexane at 0°C. After filtration, the precipitated product, azido-polycaprolactone (N₃-PCL-N₃) was dried in vacuum in 92% yield.



Scheme 4: Conversion of *para*-Toluenesulfonylpolycaprolactone into azido-polycaprolactone.

FTIR spectra of the dried azido-polycaprolactone corroborate the conversion, since the characteristic band at 2096 cm⁻¹ (N₃) appeared, as shown in Figure 2.

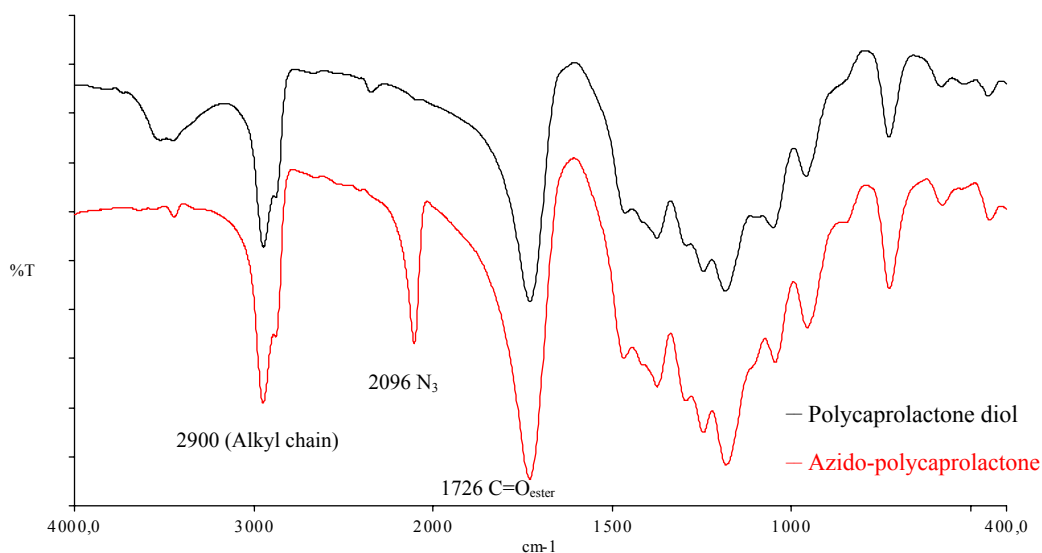
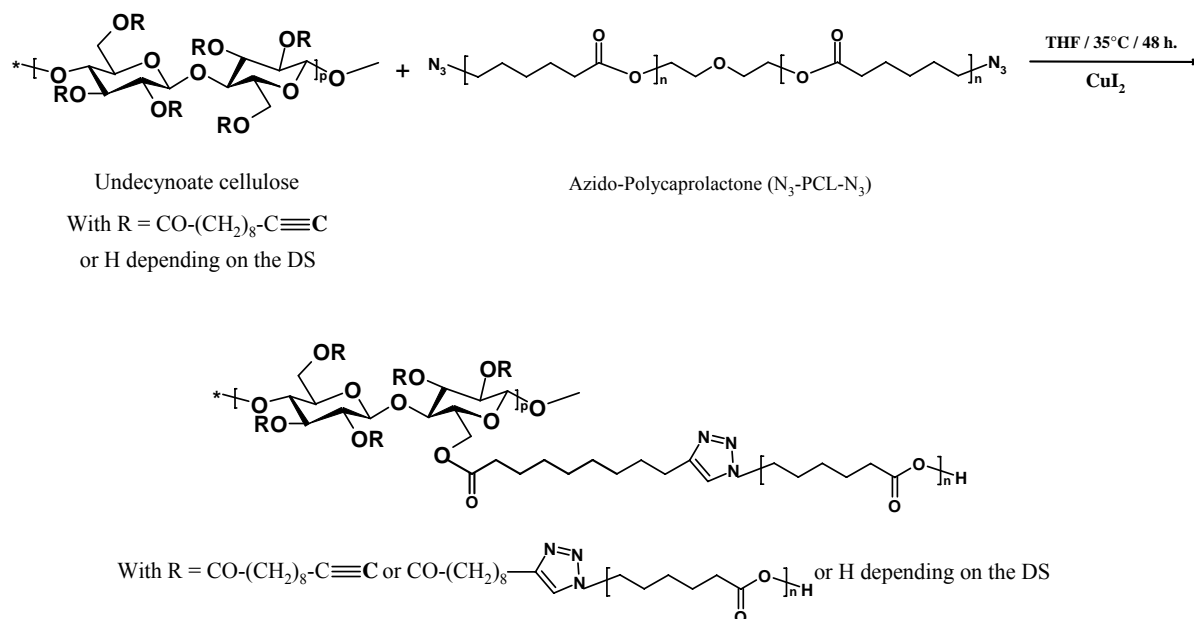


Figure 2: Comparative IR spectra of azido-polycaprolactone and polycaprolactone-diol.

III- Click reaction between undecynoate cellulose and azido-polycaprolactone

Azido-polycaprolactone was grafted onto undecynoate cellulose by “click chemistry”.^[4] Equimolecular concentration of undecynoate cellulose and azido-polycaprolactone were allowed to react in THF, at 35°C under stirring (Scheme 5). The reaction was copper catalysed (0,5 eq.). After 48 hours reaction time, the mixture was filtered and washed with methylene chloride. After Soxhlet extraction with water and methylene chloride to remove copper and ungrafted azido-polycaprolactone, the cellulose derivatives were vacuum-dried before being characterized.



Scheme 5: Grafting of azido-polycaprolactone onto undecynoate cellulose.

The IR spectra of grafted cellulose present the expected signals. The characteristic band at 1730 cm^{-1} ($C=O_{\text{ester}}$) is more intense because of the presence of the polyester grafted (Figure 3). We can also notice that the signal at 2900 cm^{-1} is more intense too, because of numerous alkyls groups present in polycaprolactone. The band at 2096 cm^{-1} clearly disappeared.

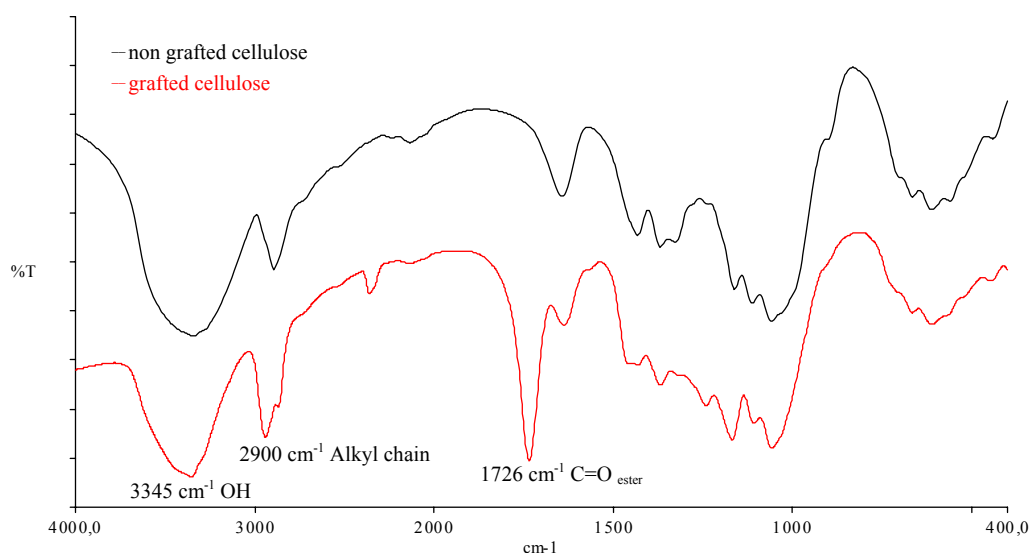


Figure 3: Comparative IR spectra of cellulose powder before and after grafting.

Conclusion

Successful surface grafting of polycaprolactone-diol onto avicel powder have been achieved in 4 steps. This new methodology should lead to more substituted cellulose since click chemistry is very effective and the spacer moves away the high molecular matrix. Characterisation of the grafted polymer is still under progress. This methodology will be applied to graft Oulu cellulose fibre with polycaprolactone of different molecular weight. We hope by this way to obtain a composite material by hot-pressing the grafted cellulose fibres.

References:

- [1]- Optseen, J.A., Van Hest, J.C.M. *Chem. Commun.* **2005**, 57-59.
- [2]- Vogt, A.P., Summerlin, B.S. *Macromolecules* **2006**, 39, 5286-5292.
- [3]- Heinze T., Liebert T.F., Pfeiffer K.S., Hussain M.A., *Cellulose*, **2003**, 10, 283-296.
- [4]- Hafrén J., Zou W., Corbova A. *Macromol. Rapid. Commun.* **2006**, 27, 1326-1366.