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**Sustainpack**

**Innovation and sustainable Development in the Fibre Based Packaging Value Chain**

Instrument: **IP**

D5.26. New modified fibres (using the co-continuous concept) start to be delivered for composite processing (WP5.2), and for characterisation (WP5.3)

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<b>Dissemination Level</b>		
<b>PU</b>	Public	xx
<b>PP</b>	Restricted to other programme participants (including the Commission Services)	
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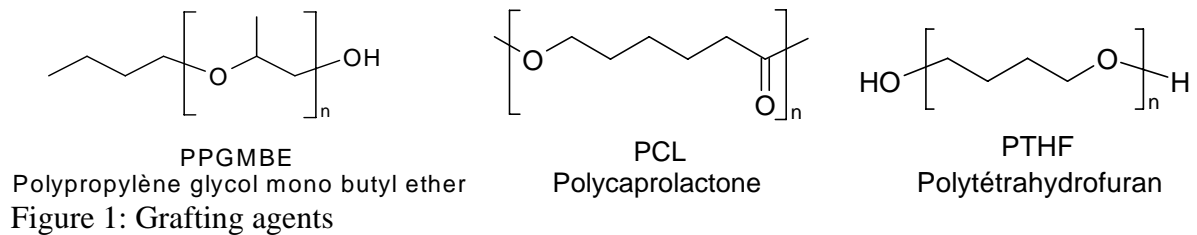
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INPG-EFPG

### ***Introduction - Novel co-continuous composite materials***

The valorisation of renewable materials derived from biomass in composite materials gains more and more prominence. Market forces demonstrate a drive towards products benign to our natural environment, an important reason for the increased importance of renewable materials. Cellulose fibre modification constitutes an essential step in the valorisation of cellulosic fibres in composite materials. Not only do these modifications improve the compatibility between the matrix material and the reinforcing fibre, they also serve as a protective surface layer. Improved fibre-matrix compatibility at their interface improves adhesion between the two phases, resulting in a more effective stress transfer from the weaker matrix phase to the reinforcing fibres.

Our current research is focussed on improving the fibre-matrix interface and on a simple process to thermoform composite materials with high fibre content. Both these constraints can be accommodated by modifying the surface of the cellulosic fibres with long polymeric chains that are able to interdiffuse upon heating. The long polymeric surface modification, covalently linked to the fibre, will thus guarantee a perfect stress transfer between matrix and interface. In addition, sufficient surface modification will also remove the need for a separate polymer matrix materials by acting as the continuous phase after heat-induced interdiffusion of the surface modification. An added advantage of this approach is the inherent increase in fibrous material that can be included in the final composite material.

The abundance of reactive surface hydroxyl groups makes them prime targets for surface modification of the cellulose fibres. Between 0,1 and 2% of hydroxyl groups in crystalline, paper or regenerated cellulose are found at the surface. A non-swelling solvent is used in this work to ensure modification of the cellulosic fibre is constrained to the surface and no significant reaction takes place within the fibre. In addition, the relatively high molecular weight of the grafting agents will also inhibit diffusion of the grafting agents into the fibres. The polymer materials used in this work are: Polypropylene glycol mono butyl ether (PPGBE, 4000g/mol), polytetrahydrofuran (PTHF, 2900g/mol) and polycaprolactone (PCL, 65000g/mol). Their chemical structures are shown in figure 1.



Three supports have been used in this study:

- Whatman paper (filter paper) with a cellulose content of 99.9%
- Microcrystalline cellulose (Avicell), obtained as a powder of aggregates and which is used extensively in composite materials
- OULU fibres (dry refined wood fibres obtained from the University of Oulu, Finland) with an appearance of cotton wadding

Whatman paper has been used to prove the overall concept, by modification of the filter paper surface with the earlier described grafting agents. The modified surfaces of the filter paper are then placed on top of each other and heated under pressure. After release of the pressure and cooling down of the sample, it was found that both filter papers were glued to each other, validating the concept and the ability to form co-continuous composites. By varying the length of the grafted polymer chain, it was established that the chain needed a minimum of 150 atoms in order to allow chain interdiffusion and thus material cohesion. Avicell and OULU fibres are being used to form actual composite samples with polymer grafts of longer chain length. OULU fibres are obviously the more attractive ones, due to their much higher aspect ratio when compared to Avicell.

### ***Modification process***

Several characterisation techniques have been employed to verify and measure the extent of modification, such as contact angle measurements, infrared spectroscopy, scanning electron microscopy, etc.

The grafting process is performed in several sequential steps. After drying the grafting agents, one of the two reactive chain ends (PCL or PTHF in Fig.1) is blocked using a monoisocyanate (phenylisocyanate). The other reactive chain end is subsequently reacted with a diisocyanate (2,4-tolylene diisocyanate) of which only one moiety reacts (the para-isocyanate has been found to be seven times more reactive than the isocyanate in the meta position relative to the methyl group). Both isocyanates are shown in Figure 2. Dibutyl tin dilaurate is used as catalyst for the isocyanate-alcohol reaction. The other remains unreacted and is used in the

last step to react with the hydroxyl groups at the cellulose surface. The reaction is followed by infrared spectroscopy. Fig. 3 shows a representative spectrum of the grafting agent right before addition to a cellulose substrate. One can clearly see the existence of urethane bonds due to the different grafting reactions, while the remaining isocyanate signal indicates the existence of unreacted isocyanates to be used for grafting to the cellulose surface hydroxyl groups. After reaction between the grafting agents and the cellulose fibres at 80°C for 7 days while stirring vigorously, the fibres are soxhlet extracted for 24 hrs using dichloromethane to remove free catalyst and unreacted grafting agents.

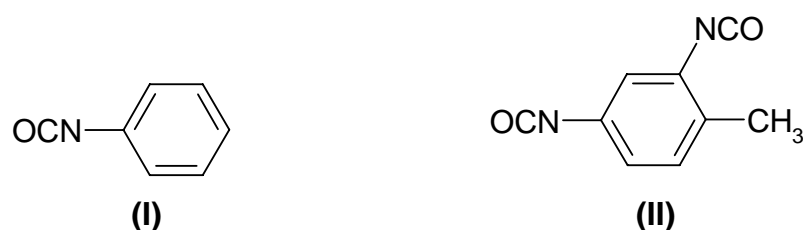


Fig. 2: Chemical structures of (I) phenyl isocyanate and (II) 2,4-tolylene diisocyanate

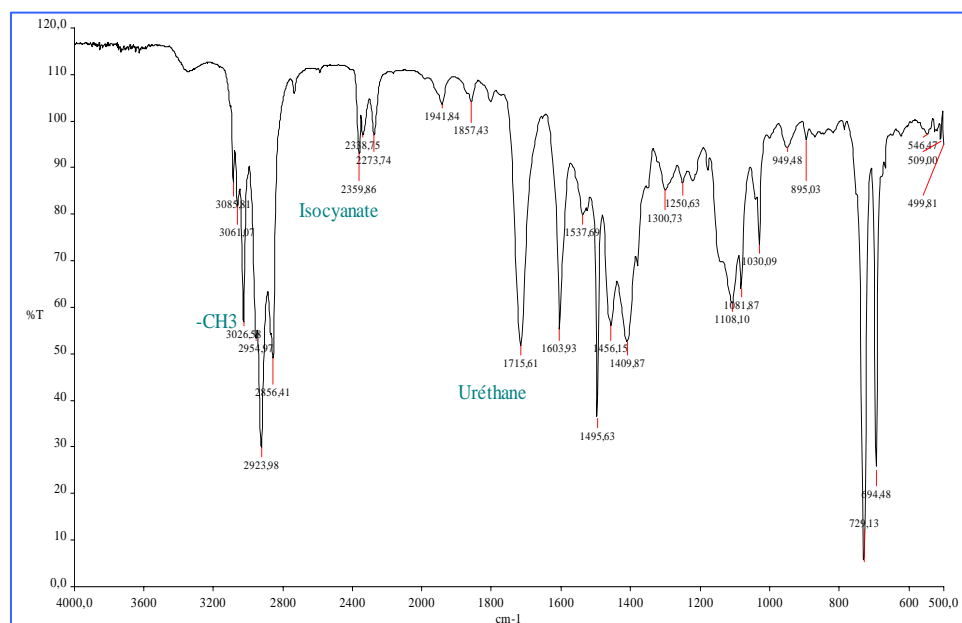


Fig.3 : FTIR spectrum of the grafting solution

### ***Modification characterisation***

Characterisation of the extent of reaction has been performed by contact angle measurements, FTIR spectroscopy and elemental analysis, as described in earlier reports. Both techniques clearly substantiated the success of the surface modifications. The effect of the surface modifications on the fibrous surface was also visualised using Scanning Electron Microscopy, as reported in Deliverable 5.6.

### ***Composite manufacturing and property characterisation***

After successful modification of Avicell and Oulu fibres with the earlier introduced three grafting agents, significant amounts of these modified fibres have been produced to allow for composite manufacturing. Two different approaches are being investigated, in order to determine the effect of the manufacturing step on the properties of the materials: a solvent casting technique and a thermoforming technique.

Solvent casting involves the use of a good solvent for the polymer graft. This solvent dissolves the polymer graft and helps their interdiffusion. Slow evaporation of the solvent at room temperature results solidification of the composite material while also ensuring interdiffusion and thus cohesion of the polymer grafts. Acetone is currently being tested to see whether smooth films can be formed.

Composite samples are also being formed at 100°C under vacuum in a mould. Modified fibres are placed in a preheated mould, which is closed and subsequently placed in a heated oven under vacuum for 15min. The mould is left to cool after which the composite is demoulded. The formed composite samples are currently being tested in linear deformation mode using Dynamical Mechanical Analysis, non-linear deformation mode and DSC. Their water uptake is also being investigated and ongoing. These results will be reported when the experiments are concluded.