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**Sustainpack**

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

Instrument: **IP**

**Deliverable 5.08**

**Report on the conditions for the synthesis of cellulose fibres/inorganic hybrids and characterization of the fibres produced thereby**

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<b>Dissemination Level</b>		
<b>PU</b>	Public	X
<b>PP</b>	Restricted to other programme participants (including the Commission Services)	
<b>RE</b>	Restricted to a group specified by the consortium (including the Commission Services)	
<b>CO</b>	Confidential, only for members of the consortium (including the Commission Services)	

## SUSTAINPACK

### WP5.1. – Fibre modification

#### **Deliverable 5.08 – Report on the conditions for the synthesis of cellulose fibres/inorganic hybrids and characterization of the fibres produced thereby**

November 2005

#### **1. Introduction**

The optimized conditions for the synthesis of cellulose/inorganic hybrids are described. All the syntheses were carried out at 1% of consistency of fibre suspension. After the synthesis, the hybrid materials were thoroughly washed and submitted to a systematic agitation method, in order to remove the particles not linked to the fibres, and submitted to characterization studies.

#### **2. TiO<sub>2</sub>/cellulose Hybrid**

For the preparation of TiO<sub>2</sub>/cellulose hybrids two distinct methods were optimised, titanyl sulphate method and titanium tetrachloride method.

##### **2.1. Synthesis**

###### **2.1.1. Titanyl sulphate method**

A solution of TiOSO<sub>4</sub> (0.25 mol.dm<sup>-3</sup>) was prepared by the dissolution of the salt in sulphuric acid solution (0.25 mol.dm<sup>-3</sup>). After total dissolution, cellulose fibres were added and the mixture was heated at 70 °C during 3 hours under vigorous stirring. After this, the composite was washed and air dried.

### 2.1.2. Titanium tetrachloride method

A  $0.2 \text{ mol.dm}^{-3}$  of  $\text{TiCl}_4$  was prepared by the addition of concentrated  $\text{TiCl}_4$  (98%) to ice-cold water, under vigorous agitation. After the solution turn out to be transparent, urea was dissolved in the molar proportion  $[\text{Ti}]/[\text{urea}]=5$ . Cellulose fibres were then added and the mixture was heated at  $70 \text{ }^\circ\text{C}$  during 6 hours under agitation. After this, the composite was washed and air dried.

## 2.2. Characterization

Using the described methodologies,  $\text{TiO}_2$ /cellulose hybrids were obtained with approximately 20 and 10% of  $\text{TiO}_2$  content (w/w), respectively from titanyl sulphate and titanium tetrachloride hydrolysis. Both methodologies produced  $\text{TiO}_2$  with the anatase structure.

Figure 1 shows SEM micrographs of the two hybrids. The main differences between hybrids is in the  $\text{TiO}_2$  particle size. Typically, for the hybrid prepared from the sulphate method, particles diameter are between 70 to 350 nm and for the second hybrid, particles diameter are around 15 to 60 nm.

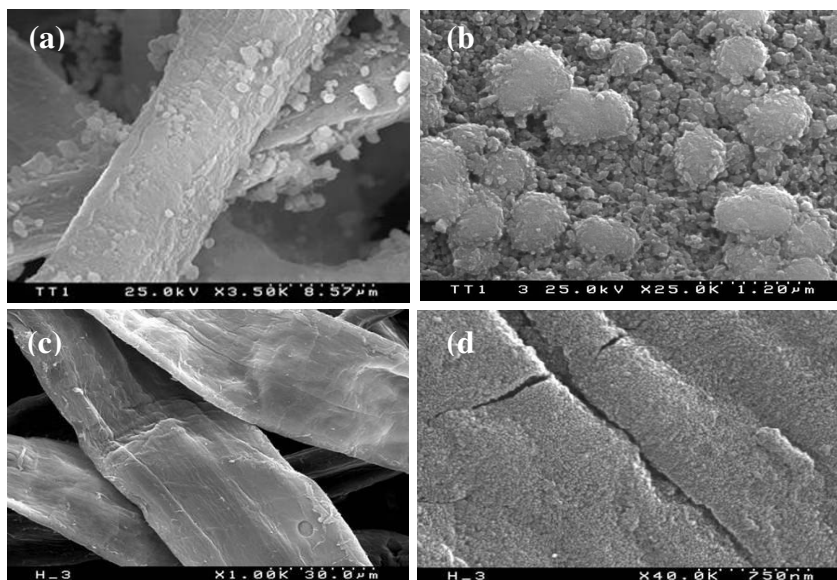


Figure 1. SEM micrographs of  $\text{TiO}_2$ /cellulose hybrids obtained from titanyl sulphate (a, b) and from titanium tetrachloride (c, d) methods.

Series of papers handsheets were prepared with these hybrids, mixing known amounts of the hybrid with blank fibres and, for comparison, equivalent series prepared with commercial  $\text{TiO}_2$  and blank fibres (blend) were prepared.

Figure 2 shows the opacity of blend and hybrid series of handsheets prepared from titanyl sulphate method as function of % $\text{TiO}_2$  included. The most interesting feature of  $\text{TiO}_2$ /cellulose hybrid is its marked impact on the opacity of handsheets, increasing from 79% in the case of blank fibres to 87% in handsheets prepared with 100% hybrid. When  $\text{TiO}_2$  was mechanically mixed with fibres ( $\text{TiO}_2$ +cellulose blend), this marked effect on the opacity of the corresponding handsheets was not observed.

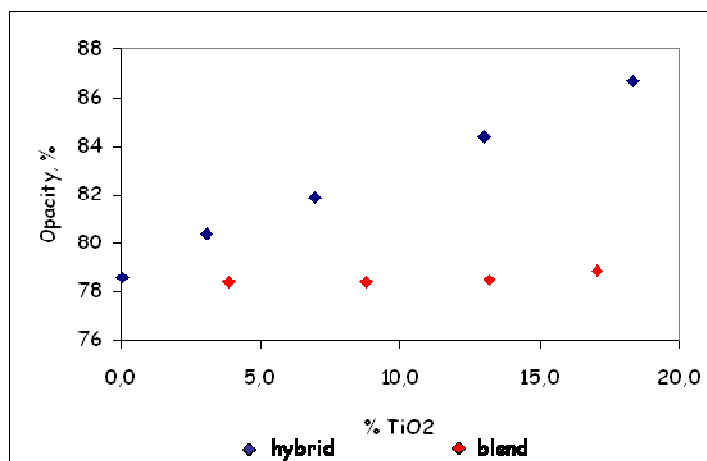


Figure 2. Percentage of opacity of blend and hybrid series of handsheets as function of % $\text{TiO}_2$  included.

The same opacity tests were performed with the second hybrid, but in this case, the  $\text{TiO}_2$  presence had no significant impact on the opacity results. It is believed that the particle size has an enormous impact on opacity of paper handsheets prepared from these hybrids.

### 3. CaCO<sub>3</sub>/cellulose hybrid

#### 3.1. Synthesis

The synthesis of CaCO<sub>3</sub>/cellulose hybrid was carried out at room temperature by preparing a solution with calcium chloride and dimethylcarbonate with concentrations respectively, 0.001 mol.dm<sup>-3</sup> and 0.005 mol.dm<sup>-3</sup>. Cellulose fibres were added to this solution under agitation. After complete wetting of the fibres, a sodium hydroxide solution was added (final concentration of NaOH in solution was 0.005 mol.dm<sup>-3</sup>). The fibres were washed up 3 minutes immediately after of the base addition.

#### 3.2 Characterization

About 6% of CaCO<sub>3</sub> in the calcite form was retained in the fibres using the described methodology. Micrographs of these hybrids (Figure 3) show spherical calcium carbonate particles with sizes ranging from 70 to 550 nm.

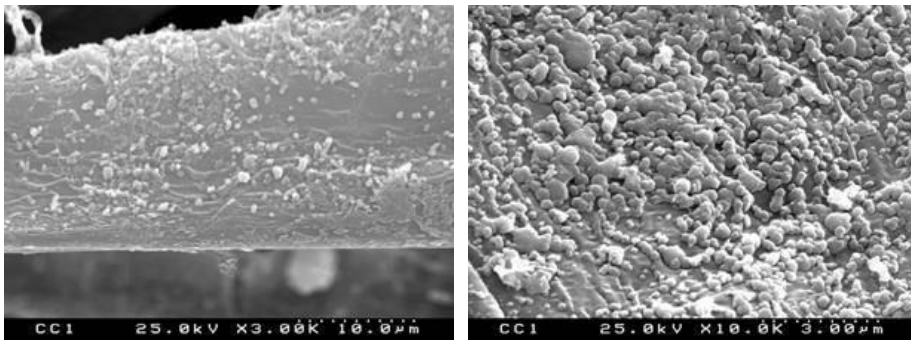


Figure 3. SEM micrographs of CaCO<sub>3</sub>/cellulose hybrids.

It was found that the CaCO<sub>3</sub> was poorly retained in fibres during the handsheets preparation. Surface modification of the fibres is being done in order to promote a better adhesion between phases.

## 4. ZnO/cellulose hybrid

### 4.1. Synthesis

Equal volumes of  $0.08 \text{ mol.dm}^{-3}$  zinc nitrate aqueous solution and  $0.4 \text{ mol.dm}^{-3}$  aqueous solution of triethanolamine were mixed at room temperature. Then, the pH of the solution was adjusted at 12.0 with NaOH. After the solution turned out to be transparent, the cellulose fibres were added and the mixture was heated at  $95^\circ\text{C}$  under reflux during 2 hours.

### 4.2. Characterization

XRD analysis of this hybrid confirms the ZnO presence. The percentage of ZnO in this hybrid determined by thermogravimetric analysis was 11%.

Figure 4 shows the hybrid surface with ZnO particles around 150 to 600 nm.

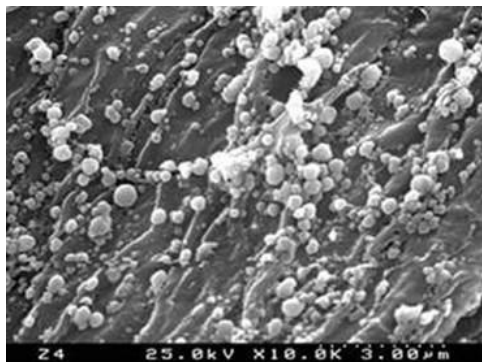


Figure 4. SEM micrographs of ZnO/cellulose hybrids.

## 5. ZnS/cellulose hybrids

### 5.1. Synthesis

Equal volumes of aqueous solutions of sodium sulphide and zinc acetate both with the concentration of  $0.02 \text{ mol.dm}^{-3}$  were mixed together with the cellulose fibres. The resulting mixture was heated at  $90^\circ\text{C}$  during 2 hours under reflux.

## 5.2. Characterization

XRD analysis of this hybrid confirms the ZnS presence. The percentage of ZnS in this hybrid determined by thermogravimetric analysis was 8%.

Figure 5 shows the hybrid surface with ZnS nanoparticles with size around 80 nm together with some agglomerates.

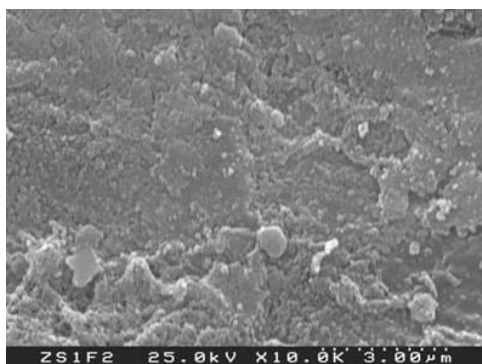


Figure 5. SEM micrographs of ZnS/cellulose hybrids.

## 6. SiO<sub>2</sub>/cellulose hybrids

### 6.1. Synthesis

Cellulose fibres were suspended in 42.5 mL of pure ethanol, then 0.75 mL of 0.2 mol.dm<sup>-3</sup> of NH<sub>4</sub>OH solution and 4.5 mL of water were added. After a good homogenization of the mixture, 2.25 mL of TEOS were added to the suspension. The final mixture was left in agitation during 24 hours at room temperature.

### 6.2. Characterization

SiO<sub>2</sub>/cellulose hybrids were obtained with about 9% of inorganic content. The surface of the fibres is covered with a silica film and nanoparticles around 70 nm (Figure 6).

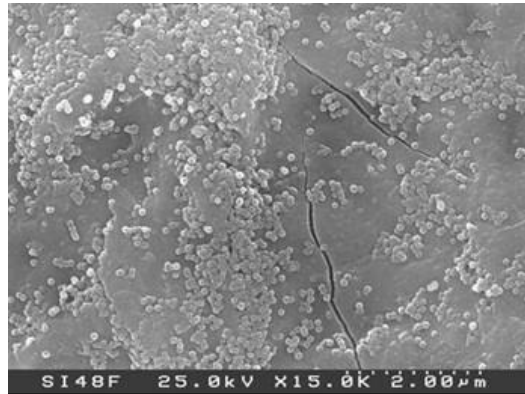


Figure 6. SEM micrographs of SiO<sub>2</sub> /cellulose hybrids.