

# Cellulosic Nanofibre Composites

M.J.A. van den Oever, G. Perez Sanchez <sup>\*</sup>, G. Yilmaz  
Wageningen UR – A&F bv, PO Box 17, 6700 AA Wageningen, The Netherlands  
E-mail: [martien.vandenoever@wur.nl](mailto:martien.vandenoever@wur.nl)  
Tel.: +31 317 480105

## Abstract

Cellulosic nanofibres were made from sulphite bleached softwood using mechanical action. Fibre dimensions were evaluated with FE-SEM. The average diameter was found to be below 100 nm. Composites containing up to 50% of these cellulosic nano fibres and starch were prepared using a wet film casting method. Three routes for preparation were evaluated for their effect on mechanical performance of the resulting films. All resulting films were translucent and showed an increase in strength of a factor of 1.5 larger than for conventional flax-PP composites. The failure strain remained at the same level. Nanofibre inclusion did not result in a significant effect on the oxygen barrier properties of starch films up to at least 30 wt.% fibre in starch. Furthermore, the sensitivity of starch to water was reduced. Barrier properties against O<sub>2</sub> and H<sub>2</sub>O were improved by addition of 4 wt.% of nanoclay. Nanoclay addition up to 4 wt.% had no significant effect on the films strength, stiffness and strain at failure.

## Introduction

Recently, agrofibre and wood fibre reinforced composites are gaining ever increasing interest all over the world, becoming competitive with glass fibre reinforced plastics on a performance/cost basis. Annually, ca. 200 kton natural fibre reinforced composites find application in Europe [Nova, 2008]. Wood polymer composites (WPC's) find an outlet in decking and siding applications. Agrofibres mat reinforced thermoplastic (NMT) and thermoset composites are mainly used in automotive industry thus far. Agrofibre extrusion compounds for injection moulding applications are currently used in niche markets and are ready for larger scale market introduction [Carus, 2007].

Natural fibres are in fact composites themselves (also see Figure 1) [Bos, 2002; Fahlén, 2002]. The technical fibres are a composite of strong elementary plant cells (fibres), which on their turn are composed of nanofibres. These fibrils consist of crystalline cellulosic regions with estimated stiffness of around 130 GPa [Berglund, 2005] and high strength. The nanofibrils have a diameter down to below 50 nanometer scale range [Purz, 1998; Dufresne, 2000; Zimmermann, 2004] which makes them invisible when well dispersed in a transparent polymer [Iwamoto, 2005].

Obviously, cellulose nanofibres have the potential to form the basis of the next generation of natural fibre composites. However, they are well incorporated in plant and wood structures, witness the wide application of wood and plant fibres and witness the extensive procedures on gram scale used to produce cellulose nanofibres [Nakagaito, 2005; Chakraborty, 2005]. Therefore, the challenge is to efficiently extract these strong and stiff nanoscaled cellulosic fibres from plant tissues without damaging the fibre too much, while at the same time producing significant amounts with economical feasibility.

This presentation addresses the preparation and properties of cellulosic nanofibre composites based on softwood fibres in a thermoplastic starch matrix. Because cellulosic (nano)fibres tend to agglomerate after being formed, different routes of mixing the nanofibres and the

---

<sup>\*</sup> Current address: Endesa Energia S.A., Ribera del Loira nº 60, 28042 Madrid (Spain).

polymer are discussed. Addition of nanoclay is discussed for its effect on barrier properties. Future prospects are included in the finalizing conclusions.

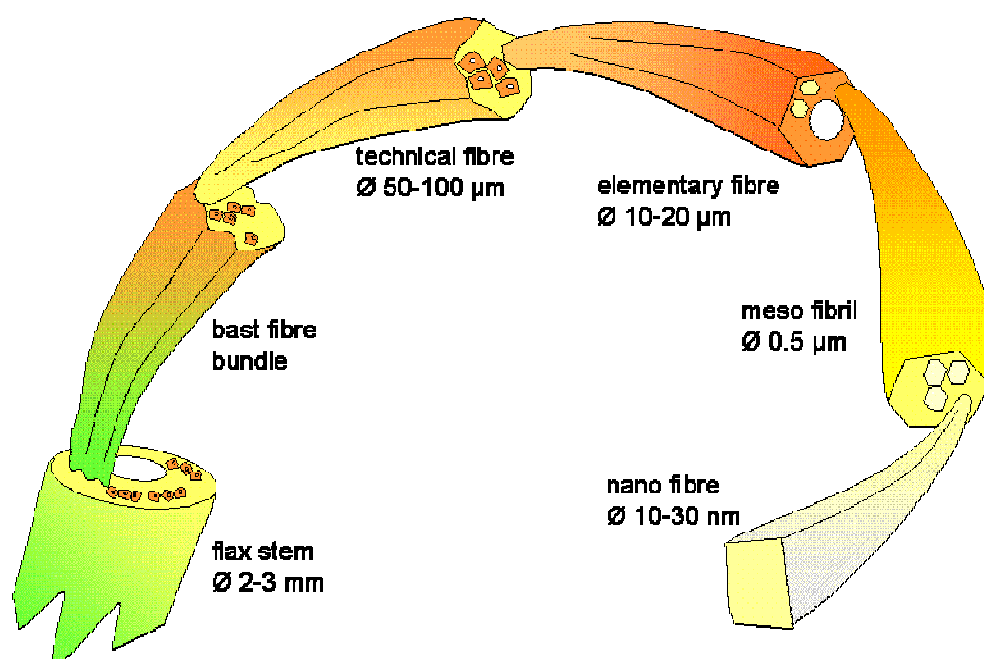


Figure 1. Schematic representation of flax bast fibres (after Bos et al., 2002).

## Experimental

### Material

Sulphite bleached softwood fibre (Ecocell) was supplied by Sappi Nijmegen, the Netherlands, in sheet form. Native potato starch (Avebé, The Netherlands) was gelatinised and plasticized with 20 wt.% glycerol (Chemproha Chemiepartner b.v., The Netherlands). Sodium Cloisite was supplied by Districhem bv, The Netherlands.

### Nanofibre production

Fibres were soaked in water at 1% dry matter content (DM) for 16 hours prior to disintegration in a Messmer Disintegrator MK.III C at 3,000 RPM for 10,000 rounds. This dispersion, containing 200 gram DM fibres, was refined in a Valley beater for 5 hours. The fibres were refined further in batches of 3 litre and 1.5% DM using an APV Gaulin homogenizer at 500 bar pressure for 5 passages on average.

### Mixing routes

Three routes for mixing the fibres and (gelatinized) polymer were applied: mixing before Valley beating of the fibres (route A); mixing after Valley beating, but before homogenization of the fibres (route B); after homogenization of the fibres (route C). For route A, mixing was performed in the Valley beater; for routes B and C an Ultra Turrax was used for 10 minutes at 20,500 RPM.

### **Composite production**

The obtained dispersions were vacuum extracted in order to remove air inclusions. The dispersions, 1.5% DM, were cast into polystyrene containers of 11\*11\*1 cm<sup>3</sup> and dried at 23°C and 50% relative humidity.

The compositions that were prepared to study the effect of mixing route had a nanofibre content of 30 wt.%. Composites containing 10, 30 and 50 wt.% nanofibre in thermoplastic starch were made by route B.

Plasticized starch with 20 wt.% glycerol was processed by applying the same refining procedure and cast to films as a reference.

Additionally, films based on 30 wt.% nanofibre and 4 wt.% nanoclay in starch have been prepared by route B.

### **Test methods**

Scanning electron microscopy was used to evaluate the morphology of the prepared films. The analysis was performed at room temperature using a Jeol JSM-6300F (FE-SEM) scanning microscope. Samples evaluated with FE-SEM include fibres after Valley beating and after homogenization as well as a tensile fracture surface of a composite film produced by applying mixing route A.

The density of the films was calculated by dividing film weight by sample area and the average film thickness. The film thickness was determined using a TMI MI-21 with an accuracy of 1 µm.

For evaluation of the mechanical properties, the composite films were cut into dogbone shaped samples with dimensions of the parallel part 35\*15 mm<sup>2</sup>. Samples were conditioned at 23°C and 50% RH for at least 1 week before the mechanical properties were determined. Uniaxial tensile tests were performed in 5-fold using a Zwick universal tester, type Z010 at a grip to grip separation of 75 mm and an extensometer gauge length of 20 mm. The crosshead speed was 1 mm/min for the modulus and 10 mm/min for the strength.

Transparency was determined using a Datascolor Elrepho 2000 with diffuse illumination via a photometer sphere (DIN 5033) and according to DIN 53147. Films of ca. 100 µm were used, 5 films were used to simulate an infinite stack of films. The difference between measured transparency values when using 4 or 5 films was insignificant.

Water vapour permeability (WVP) was determined at 30, 50, 60 and 70 % relative humidity (RH). The WVP determination was made using a method based on the weight change of boxes containing dried silica gel that were covered with the composite films when stored at the indicated RH conditions.

Oxygen transmission rate (OTR) was determined at 23°C using a MOCON OX-TRAN type 2/20 MH at RH values in the range 35–90%.

## Results and discussion

### Film morphology

The observations show that fibre diameter has been reduced significantly during Valley beating from ca. 10–20  $\mu\text{m}$  for the starting softwood material to ca. 0.02–1  $\mu\text{m}$  after beating (Figure 2). During homogenization, in particular the thick fibres have been refined further and average fibre diameter drops well below 100 nm (Figure 3). The theoretical yield of nanofibres is 100%, only small losses have been observed due to splashing.

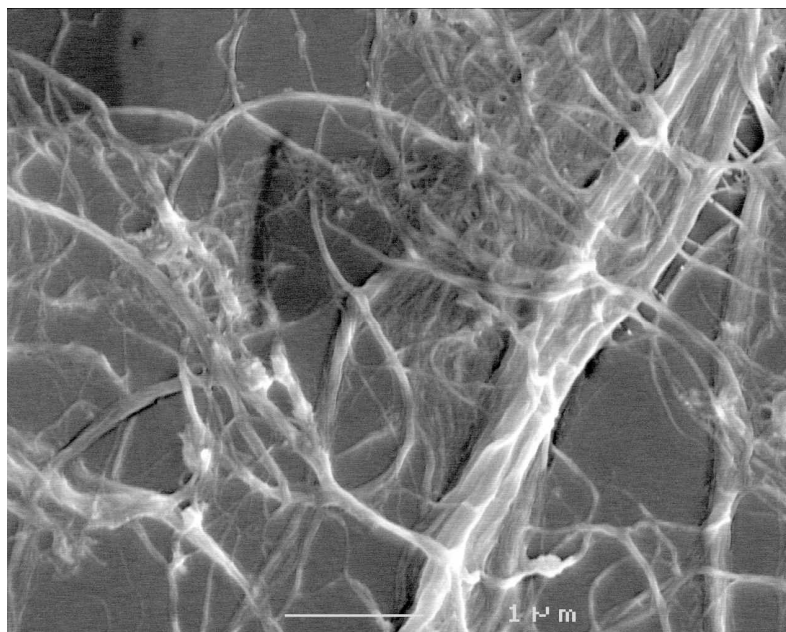


Figure 2. FE-SEM graph of softwood fibres, after Valley beating.

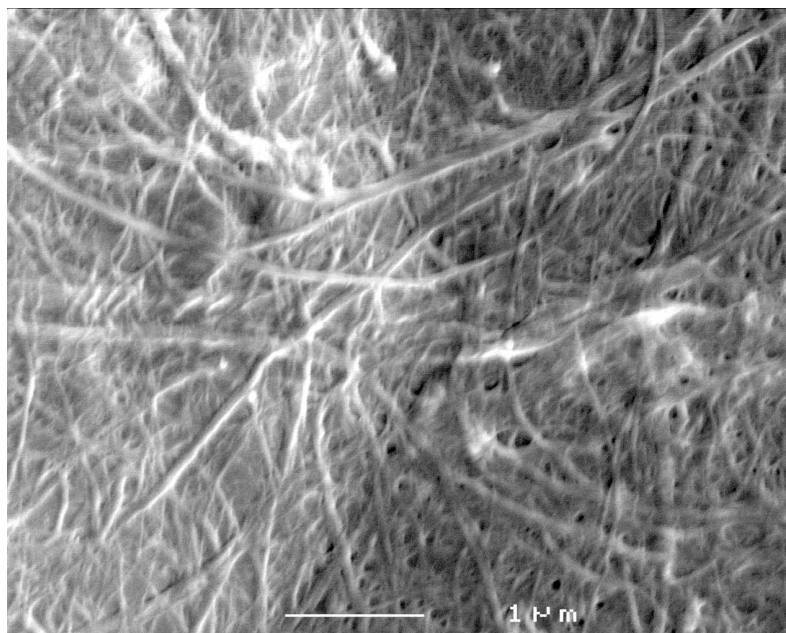


Figure 3. FE-SEM graph of softwood fibres, after Valley beating and homogenization.

The fracture surface of a cellulosic nanofibre-thermoplastic starch composite film indicates good fibre matrix adhesion (Figure 4). The structure looks very condensed, although some voids are visible which seem to be air inclusions. One other reason for the voids could be fibre pull out. The condensed structure is confirmed by the density of 1.27–1.41 g/cm<sup>3</sup> for the nanofibre-starch films when compared to 1.28–1.38 g/cm<sup>3</sup> for the starch films.

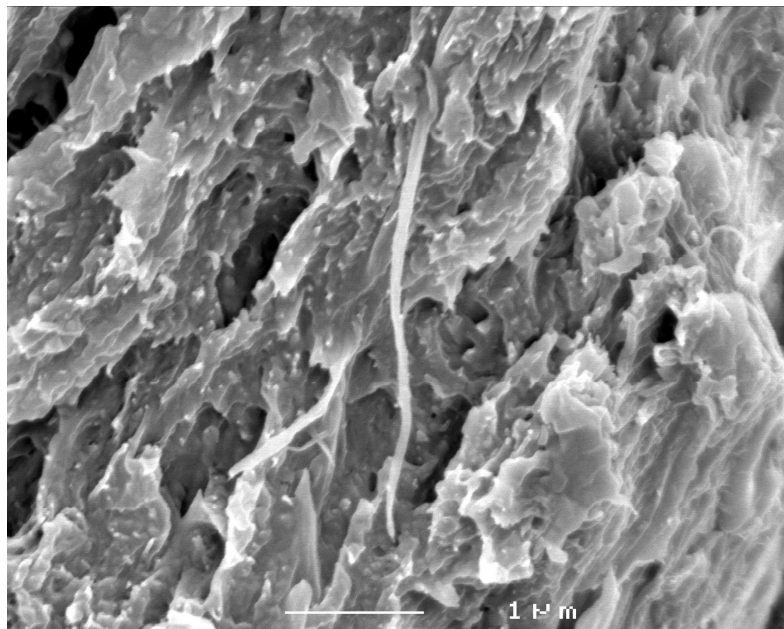


Figure 4. FE-SEM graph of fracture surface of a 30wt.% nanofibre/thermoplastic starch composite, produced by mixing route A.

#### Mechanical properties

During the initial stages of the research, composites based on cellulosic nanofibres prepared from hemp bast fibre by route C exhibited very poor mechanical performance. This was thought to be due to fibre agglomeration, which hinders adequate impregnation with the polymer. The hypothesis was that if the polymer is able to impregnate the nanofibre as soon as it is formed (route A), less fibre agglomerates will occur in the composite than when ready nanofibres are mixed with a polymer (route C). And less agglomerates would mean less weak spots. However, the effect of mixing route on the strength performance of the composite films was small (Figure 5), in contradiction with this hypothesis. These data suggest that either ready made cellulosic nanofibres do not agglomerate or that fibre agglomerates have no significant negative effect on composites strength at the conditions applied.

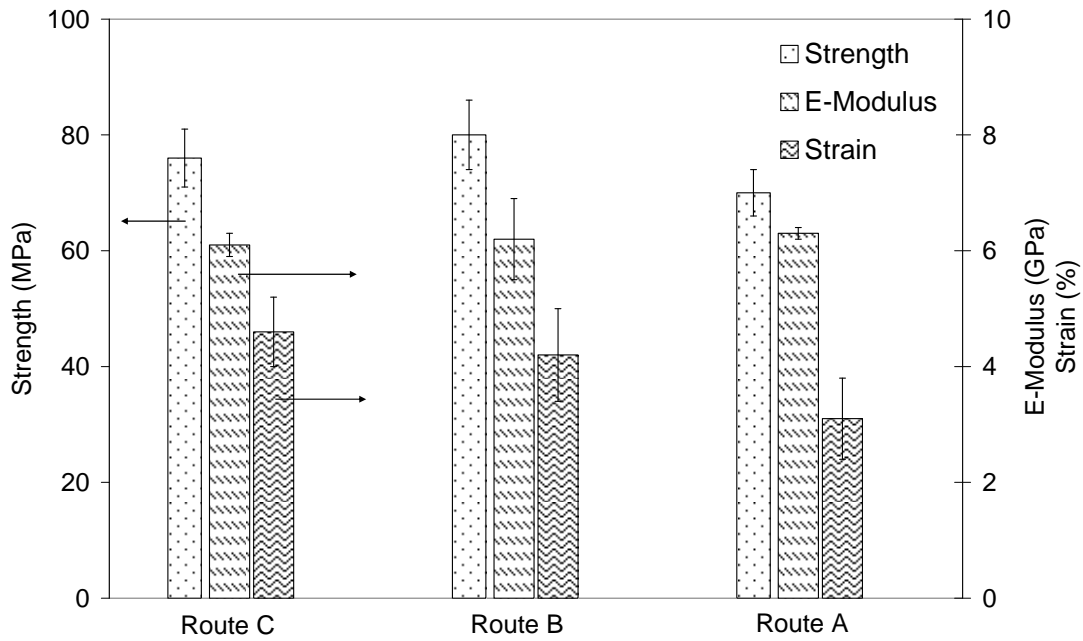


Figure 5. Effect of mixing route on tensile properties of 30 wt.% nanofibre-starch composites.

Results of the tensile measurements are given in figure 6. Strength and stiffness of starch films increase by a factor of 2.7 and 3.5 respectively upon incorporation of 50% fibres. In particular the strength increase is higher compared to that of conventional flax-PP composites which show a tensile strength of 67 MPa only at 50 wt.% fibre content, although flax is supposed to be one of the strongest natural fibres available [Van den Oever, 2000; Carus, 2007]. It has been observed that the failure strain remained at the same level, whereas fibre reinforcement usually causes a decrease of the failure strain.

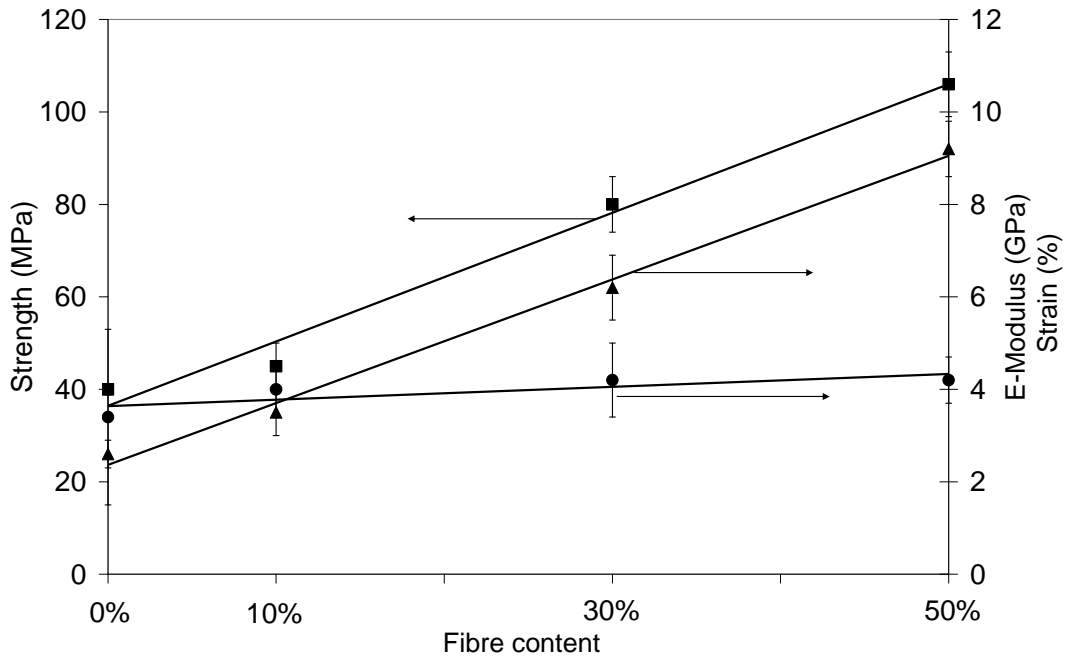


Figure 6. Tensile properties of nanofibre/starch composites produced by route B: strength (■), E-modulus (▲), Strain at failure (●).

Initial soaking tests in water revealed that the nanofibres enhanced the structural integrity of starch films to a large extent.

#### Transparency

Although the films are based on substantial amounts of wood fibre, transparency is very high (Figure 7). Up to 30% nanofibre, 100  $\mu\text{m}$  thick films can be looked through remarkably well.

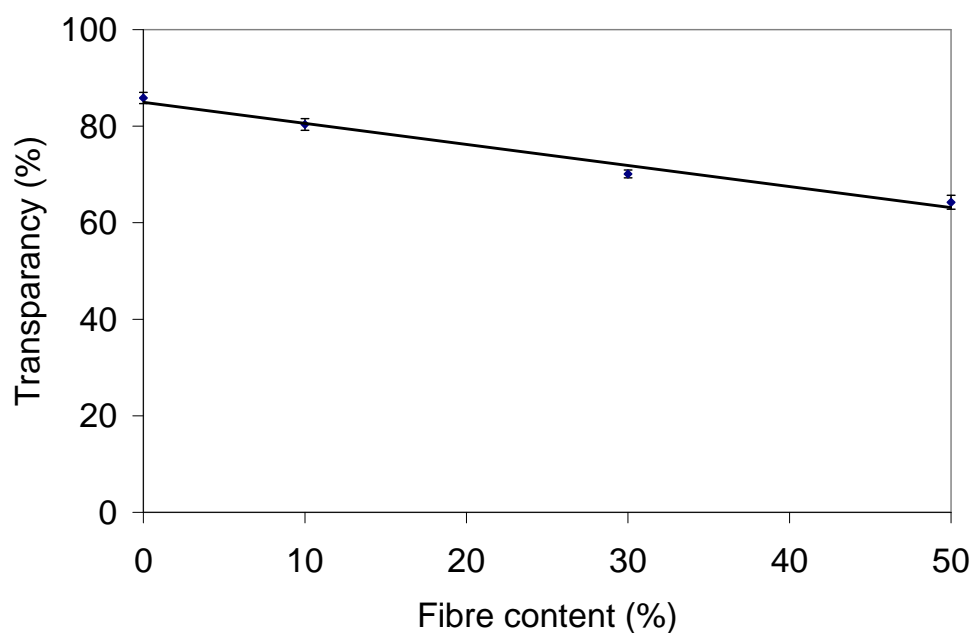


Figure 7. Transparency of nanofibre/starch composites produced by route B.

#### Permeability

Starch based films are known for their high oxygen barrier properties. This however is only the case in a limited RH range and minimal amount of plasticizers. The results show that the incorporation of cellulosic nanofibres has no significant influence the oxygen transmission rate (OTR) of starch (Figure 8). Regarding water vapour barrier properties, an improvement at 60% RH has been obtained by incorporation of cellulosic nanofibres (Figure 9).

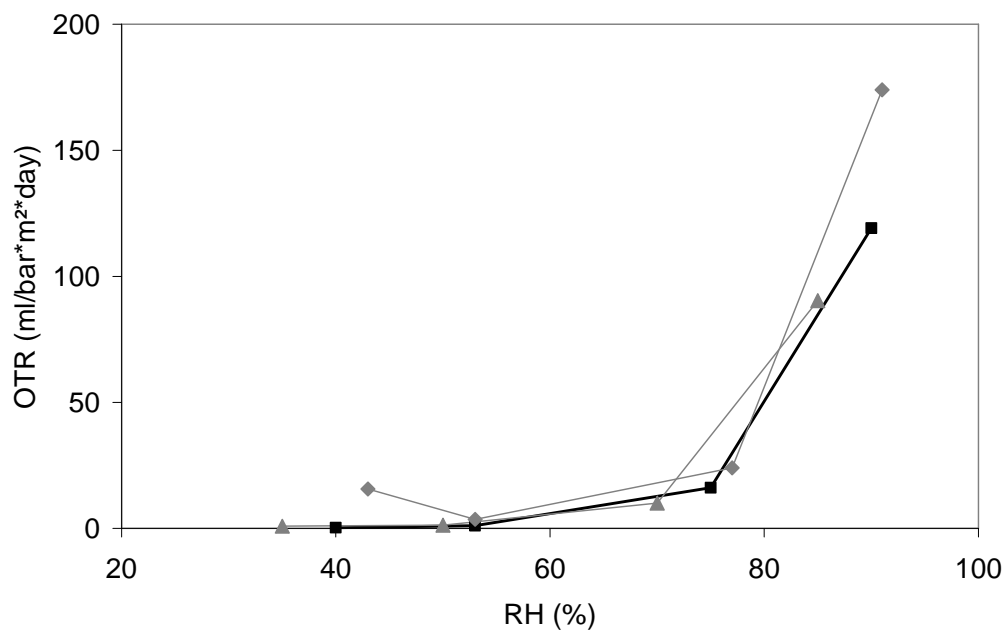


Figure 8. Oxygen transmission rate vs. relative humidity, normalized to values for 100  $\mu\text{m}$  thick films: starch (■), 30% nanofibre-starch produced by route A (◆) and route B (▲).

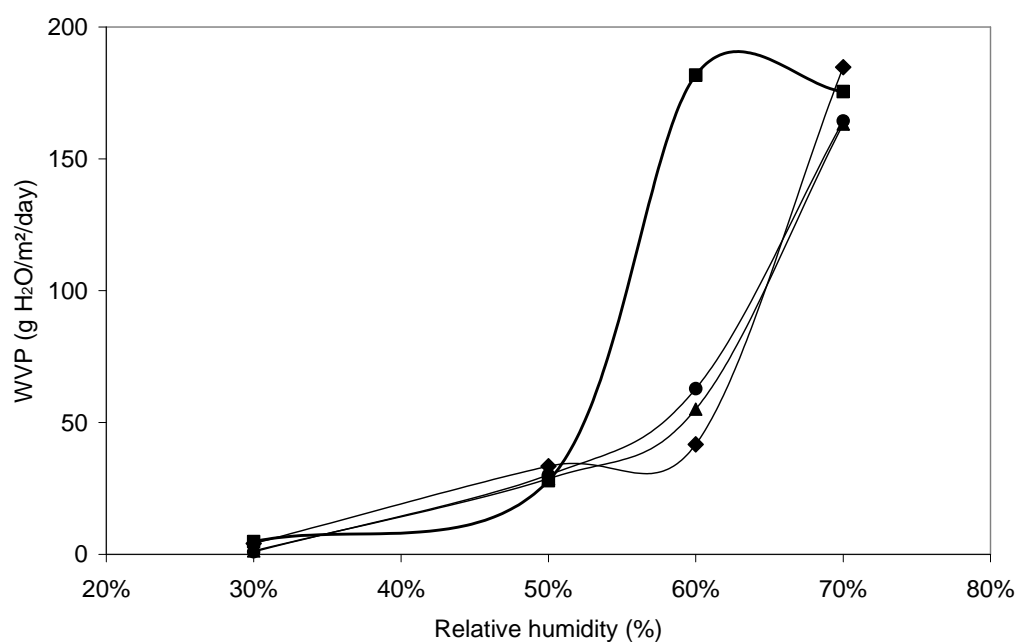


Figure 9. Water vapour permeability vs. relative humidity, normalized to values for 100  $\mu\text{m}$  thick films: starch (■), 30% nanofibre-starch produced by route A (◆), route B (▲), route C (●).

#### Nanofibre/nanoclay composites

It appeared that addition of 4 wt.% of nanoclay further improved the barrier against  $\text{O}_2$  and  $\text{H}_2\text{O}$ . However, addition of nanoclay had no effect on the films strength, stiffness and strain at failure.



## Conclusions and future prospects

The production of strong and stiff softwood based cellulosic nanofibre-starch films appears technically feasible. The strength improves a factor of 1.5 more than for conventional flax-PP composites. At the same time, the nanofibre-starch composites exhibit transparency up to 50% fibre content.

Up to at least 30 wt.% in starch, nanofibres do not deteriorate the excellent oxygen barrier properties of starch. Furthermore, the sensitivity of starch to water is reduced.

The results indicate that the problems such as water sensitivity and poor water vapour barrier properties which are associated with starch based materials can be addressed using a composites approach. This means that applicability of starch based materials not only limits to film applications, but also may be useful in coatings, paints, water resistant glues as well as 3D structures such as plates, packaging materials or even hybrid fibres.

## Acknowledgement

Financial support from the EU, within the framework of the integrated project Sustainpack, is acknowledged.

## References

- Berglund L., 2005. 'Cellulose-Based Nanocomposites' in Natural Fibers, Biopolymers and Biocomposites, Mohanty, Misra & Drzal, Eds, CRC Press, Boca Raton.
- Bos H.L., Van den Oever M.J.A., Peters O.C.J.J., 2002. 'Tensile and compressive properties of flax fibres for natural fibre reinforced composites', J. Mat. Sci., 37, 1683-1692.
- Carus M., Gahle C., Pendarovski C., Vogt D., Ortmann S., Grotenhermen F., Breuer T., Schmidt C., 2007. 'Studie zur Markt- und Konkurrenz-situation bei Naturfasern und Naturfaser-Werkstoffen (Deutschland und EU)', Gölzower Fachgespräche, Band 26, Fachagentur Nachwachsende Rohstoffe e.V.
- Chakraborty A., Sain M., Kortschot M., 2005. 'Cellulose microfibrils: A novel method of preparation using high shear refining and cryocrushing', Holzforschung, 59, 102-107.
- Dufresne A., Dupeyre D., Vignon M.R., 2000. 'Cellulose Microfibrils from Potato Tuber Cells: Processing and Characterization of Starch-Cellulose Microfibril Composites', Journal of Applied Polymer Science, 76, 2080-2092.
- Fahlén J., Salmén L., 2002. 'On lamellar Structure of the Tracheid Cell Wall', Plant Biology, 4, 339-345.
- Iwamoto S., Nakagaito A.N., Yano H., Nogi M., 2005. 'Optically transparent composites reinforced with plant fiber-based nanofibers', Applied Physics A, 81, 1109-1112.
- Nakagaito A.N., Yano H., 2005. 'Novel high-strength biocomposites based on microfibrillated cellulose having nano-order-unit web-like network structure', Applied Physics A, 80, 155-159.
- Nova Institut, 2008. 'Injection moulding with natural fibres', Reinforced Plastics, 52 (4), 18-25.
- Purz H.J., Fink H.P., Graf H., 1998. 'Zur Struktur cellulosischer Naturfasern', Das Papier, 6, 315-324.
- Van den Oever M.J.A., Bos H.L., Van Kemenade M.J.J.M., 2000. 'Influence of the Physical Structure of Flax Fibres on the Mechanical Properties of Flax Fibre Reinforced Polypropylene Composites', Applied Composite Materials, 7, 387-402.
- Zimmermann T., Pohler E., Geiger T., 2004. 'Cellulose Fibrils for Polymer Reinforcement', Advanced Engineering Materials, 6, 754-761.