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Sustainpack

Innovation and sustainable Development in the Fibre Based Packaging Value Chain

Instrument: **IP**

D 3.12. - Upscaling of the nanocomposite manufacturing

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Organisation name of lead contractor for this deliverable:

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Dissemination Level		
PU	Public	PU
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)	

Introduction

The following report refers to the activities and the work performed within the "Sustainpack 3 Fibre based composite films" project (SP 3) under WP 3.3 'Processability'. Its objective is to define the optimal processing conditions for the fibre and clay based composite materials.

WP 3.3 has formally started as of month 12; during the first 6 months all partners have worked (together) towards meeting two specific deliverables:

- D 3.12. - Report outlining the upscaling of the nanocomposite manufacturing
- D 3.13. - Report outlining the pros and cons of different end-product manufacturing techniques.

This report is the reflection of D 3.12 and describes the different manufacturing techniques which have been used by the different partners, individually or in co-operation. In addition, it highlights the results as obtained by using these manufacturing techniques for each partner separately.

Similar to what has been reported by KTH (D 3.04), this work can be seen as kind of a trail and error study of how well matrices and particles/fibres have worked together with the technologies used. This was presented and discussed in the most recent SP3 Progress Meeting (Bratislava). As a result more focus can be brought towards smart materials/technologies/applications combinations.

Unfortunately no significant amount of nanofibres were available for performing medium-size scale processing trials. Nano-fibres from SP2 were obtained around summer time. The amount was too limited to perform comparative nano-fibre processing trials. This is a serious concern, which needs to be tackled in order to prevent further delay in focussed SP3 nano-fibre processing developments. Supply from SP2 at kilogram scale is needed for within the next reporting period. Most work therefore refers to nano-clay biocomposite films.

Materials and technologies used by each partner; results

The activities of the CSIC on this WP have been related to develop nanocomposites of the various fillers tested (clays and cellulose fibers) in several biodegradable (PHBs and PCL) and in conventional matrices (HDPE and EVOH) for comparative purposes. Nine different commercial clays with and without modification from Nanobiomatters Ltd. were used and one very finely dispersed cellulose fiber grade from Creafill Ltd. (having an average fiber length of 60 microns and an average fiber width of 20 microns) and since more recently fibers (nanofibers) supplied by STFI. PHB was used as homopolymer and as copolymers having 8 and 12 mol% of valeriate in the copolymer composition. Solution casting routes for the biodegradable materials were carried out to evaluate the relation between filler type and composite morphology. It was found that the modified clays supplied were capable of significant exfoliation as determined by WAXS and TEM micrographs in all the materials. With these positive results PHB and PCL materials were also tested in melt blending. Blending amorphous PHB with PCL led to an improvement in mechanical properties and thermal stability without significant decrease in barrier properties. Highly exfoliated nanocomposites of the PHB/PCL and of PCL blends were successfully obtained by melt-mixing with properly modified clays. The PCL nanocomposite showed an improvement of 50% in barrier to oxygen. These PHB/PCL nanocomposites showed an improvement in the mechanical properties (decreased rigidity) with regard to the polymers and blends without clay; but the main advantage of adding nanoclays to this polymer is the increase in gas barrier properties to oxygen by a factor of two.

Regarding the melt blending route for cellulose fibers (carried out via melt mixing for 10 minutes) in HDPE, it was found that although crystallinity was slightly affected by the presence of fibers, the oxygen permeability was half that of the matrix for fiber contents of 50% (W/W). The increase in barrier properties to oxygen began to be noticeable for fiber contents above 10%. Permeability to limonene of the composite was also half that of the matrix for the material with 50% (w/w) fiber content and was also reduced in samples with fiber contents above 10%. An interesting observation is that although the water sorption increased in the composite, the oxygen permeability was not found to be dependent on relative humidity. Composites of EVOH with fibers were obtained via solution casting, although the water permeability was increased in the composites compared to the pure polymer, the retortability of

the system was enhanced by the presence of the very finely dispersed fibers holding together the structure.

Starch nanocomposites obtained by solution casting are being developed by ITENE. Several tests are performed with commercial cellulose microfibrils, however, compatibilisation with matrixes is being conducted by home made surface modification.

PLA and PHB were the matrixes selected to obtain nanocomposites by melt mixing. Tests have been carried out to optimise the extrusion parameters.

PHB nanocomposites have been obtained using a co-rotating twin screw extruder. During tests, screw configuration was modified from low to medium shear, because of problems with the material.

Temperature profile on the extruder ranged from 160 (upstream) to 170 at die. Die was a flat sheet die type, which film thickness ranged from 0.05 to 1.5 mm.

Polymer and clay were mixed previous to addition in the feeder. Plasticizers like glycerol, tributyrin, or triacetin and nucleation agents like for instance, saccharin were tested.

Two types of take off units were checked. A calender unit was tested for take off, but several problems were observed due to the sticking behaviour of the melt polymer. Take off unit selected for work was a conveyor belt, troubles related to sticking were not observed.

Parameters like pressure built up and screw speed were recorded during processing. Samples of the films obtained are being characterised by means of IR, WAXS and TEM.

During this stage, commercial clays were used for compounding. These clays were supplied by Laviosa Chimica Mineraria (Livorno).

PLA compounding tests couldn't be started by this date.

STFI-Packforsk's work within SP3.3 has focused on process development of chitosan nanocomposites and thermoformed wheat gluten nanofibre composites. MFC, paper fibre and fluff fibres have been compared as additives with regards to the moisture content, water absorption, mechanical properties and permeation properties. Materials homogeneity and fibre-matrix adhesion have been studied by microscopy, tensile tests (fibre-pull outs, etc) and gas transmission measurements.

The results show so far improved mechanical (fracture stress, strain and young's modulus) as a function of fibre content. The MFC did only slightly affect the permeability (as studied by Mocon), and the dispersion rate studied by AFM and SEM was good.

Several different production processes have been tested and evaluated. About 15 different compositions, water contents, concentration of natural dispersion agents have been studied in order to optimize the compositions and process windows.

In a joint work with STFI-Packforsk and CSIC starch films with microfibrillar cellulose (nanocellulose) have been made and characterised by KTH. A major effort was here put into obtaining the proper processability to yield good quality films. A new route of producing high quality starch/nanocellulose films have developed. It turns out that there is no need for plasticiser. This is major breakthrough and will be reported in a coming paper.

Walki Wisa has performed a pilot extrusion coating series with commercially available bio polymer. The thought is to create reference information, about the bio polymer, for the on-going bio film research work.

A&F has evaluated the following nano-composite film production methods: wet film casting and sheet extrusion with nano-clay + starch; wet film casting and sheet extrusion with nano-clay + PLA; fibre production + composite premixing, wet film casting for cellulose nano-fibre + starch. Furthermore nanofibre/starch compound, suitable for injection moulding, was produced and injection moulded. Processing of nanoclay biocomposites (starch and PLA) by using film casting and sheet extrusion turned out feasible resulting in nano-composite materials with improved mechanical and WVP properties.

Based on the partners' combined results a round-up study has been performed to evaluate manufacturing techniques based on compound composition, their intrinsic properties and film properties (exfoliation, barrier, strength)

Conclusions

Technologies which (technically and technologically) appear suitable for making nano-composite films are:

- Thermo(/compression) moulding (STFI)
- Solution casting (CSIC, A&F)
- Melt mixing (CSIC)
- Sheet extrusion (A&F)
- Extrusion coating (Walki Wisa)
- 'new route', potentially patentable (KTH, A&F)