



## Permeability of water and oleic acid in composite films of phase separated polypropylene and cellulose stearate blends



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### ABSTRACT

Cellulose esters with long carbon side chains (e.g. stearate) were produced via a homogenous reaction in ionic liquids. The degree of substitution was calculated to approximately 2. The melt rheology was studied for the pure cellulose esters but also combinations of the esters and polypropylene to study the processability of a blended composite material. It was shown that the compatibility between the two components was weak, which resulted in a phase-separated composite material. The morphology and permeability of water and oleic acid of the composite films were studied and it was shown that the water permeability decreased upon addition of the cellulose ester to the polymer. The permeability of oleic acid was however unchanged, which is most probable a result of high solubility in the cellulose ester rich domains of the composites. Also, the following hypothesis is stated: cellulose stearate influence the polypropylene crystallization process by decreasing the size of spherulites.

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## 1. Introduction

Cellulose can be combined with commercial polymers and is therefore a promising candidate for reduced usage of fossil-based polymers. At the same time, the introduction of different types of cellulose can improve mechanical properties of the received composites (Goffin et al., 2011; Zugenmaier, 2006). The major problem using cellulose as filler is the poor compatibility to common matrix polymers due to differences in chemical structure, which limits its applicability (Bax & Müssig, 2008; Gardebjer et al., 2016; Junior de Menezes, Siqueira, Curvelo, & Dufresne, 2009; Raj, Balnois, Helias, Baley, & Grohens, 2012). Modifying cellulose with saturated and/or unsaturated organic acids results in cellulose esters. The use of cellulose esters could result in increased compatibility between cellulose and different polymers (Besson & Budtova, 2012; Jandura, Kokta, & Riedl, 2001). If the esters attached to cellulose are long enough (e.g.  $n \geq 12$  carbon atoms), the cellulose esters will show thermoplastic properties, which increases the chances of good mixing during for example extrusion with a more hydrophobic polymer. The cellulose esters can be commercially produced by heterogeneous phase reaction chemistry, where acid anhydrides

and sulfuric acid catalysts are used (Shimizu & Hayashi, 1989). However, this process is limited to short-chain esters (e.g. up to four carbons). To produce cellulose esters with longer chains, acid chlorides and pyridine has to be used in heterogeneous conditions (Malm, Mench, Kendall, & Hiatt, 1951). A drawback using heterogeneous reaction conditions is that the final degree of substitution often is low (Kwatra, Caruthers, & Tao, 1992). This can and has been solved by performing a homogeneous reaction in liquids, where the hydroxyl groups of cellulose are more accessible. The major problem is then to dissolve the highly crystalline cellulose. In recent years, it has become popular to use ionic liquids, in which cellulose can be totally dissolved (Liebert & Heinze, 2008), to increase the degree of substitution.

Cellulose esters have previously been added to different plastics to produce composites (Besson & Budtova, 2012; Jandura et al., 2001). One of the most widespread methods for production of composites is preparation of cellulosic long fibers (from hemp, flax, cotton and other) and further blending with a commercial available polymer (Cheremisinoff, 1997), such as polypropylene (PP). Extrusion and batch mixing are commonly used techniques for dispersing cellulose in a polymer melt; and such dispersions could further be processed by injection molding and/or thermoforming. However, using extrusion, injection molding and/or thermoforming requires high temperature for mixing to occur. Cellulose fibers are not possible to melt, which limits the degree

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of mixing. Another disadvantage is that cellulose loses physically and chemically bonded water at high temperatures, which impairs mechanical properties of the fibers and also affects the compatibility to the matrix (explained by the formation of gas bubbles in the interface between the polymeric matrix and cellulose as water evaporates). Chemical dehydration also causes cellulose to change color significantly (Panaitescu et al., 2007). All these disadvantages limit processing temperature to less than 200 °C (Monteiro, Calado, Rodriguez, & Margem, 2012), and processing time to less than 2 min (Kalia et al., 2011) for cellulose containing materials. Using cellulose esters, which are thermoplastic, could be a solution to some of the mentioned problems connected to the production.

To optimize the compatibility and improve adhesion between cellulose and more hydrophobic polymers, a pretreatment of cellulose is usually needed. However, even if the compatibility should be improved in theory, demixing (or phase separation) can appear which in those cases result in enrichment of the polymers in separate phases (Piculell, Bergfeldt, & Nilsson, 1995). For a composite material with a lower amount of added cellulose esters small particles are expected, while an addition of a higher amount of cellulose esters is expected to result phase-separated material. Phase-separation depends for example on temperature, time and physicochemical properties of the polymers (Piculell et al., 1995). In this study, we investigated the melt rheology for blends of PP and cellulose stearate to investigate the processability. Cellulose esters were produced using ionic liquid as solvent and reaction media, different amounts of the cellulose ester was added to melts of PP and composites were produced via melt extrusion followed by pressing. The morphology of the composites was studied. Finally, the permeability of water and oleic acid was measured to study the effect of different morphological structures.

## 2. Hypothesis

Immiscible blends of CS and PP could be prepared by hot melt extrusion compounding. Due to significant difference in melting temperatures of components CS particles form flake-shaped structures. Introduction of cellulose stearate into polypropylene changes crystallization processes by decreasing spherulite size of PP. This in its turn effects permeability of PP to water and oleic acid.

## 3. Materials and methods

### 3.1. Materials

The ionic liquid 1-butyl-3-methylimidazolium chloride ([BMIM]Cl) was synthesized by reaction of chlorobutane and 1-methylimidazole described by Huddleston and co-workers (Huddleston et al., 2001). Components of ionic liquid and stearoyl chloride were purchased from Sigma-Aldrich Company (USA). Cellulose stearate (CS) was prepared in accordance to method described in literature (Barthel & Heinze, 2006; Huang et al., 2011). Acid-free  $\alpha$ -cellulose (highly pure filter paper DF 604) supplied by Hahnemuhle FINEART (Germany) was used for production of cellulose stearate. Molecular weight of cellulose was calculated to 100,000 g/mol according to Mark-Kuhn-Houwink equation and molecular weight of cellulose stearate was determined to 120,000 g/mol by gel permeation chromatography (both studies were reported earlier (Šumichin, Tarasova, Kudrjašova, & Krumme, 2013)). Polypropylene HD120MO supplied by Borealis Polymers Co, Austria were used for production of composites.

### 3.2. Production of cellulose esters

#### 3.2.1. Solvent preparation

The [BMIM]Cl was prepared by mixing 1.5 mol of chlorobutane with 1 mol of 1-methylimidazole in a refluxed flask. Mixture was stirred for 72 h at 80 °C until two phases appeared. The top phase consisted of unreacted material and was removed by washing with ethyl acetate. The final product of [BMIM]Cl was a yellow viscous liquid which was dried under vacuum at 90 °C to eliminate residual ethyl acetate.

#### 3.2.2. Synthesis of cellulose esters

In short, filter paper was grinded in a Retsch SM100 mill with 1 mm grid, followed by drying of the powder under vacuum at 105 °C overnight. 1 g of cellulose was dissolved in 100 g of [BMIM]Cl by stirring at 100 °C for 12 h under vacuum. Thereafter, the temperature was decreased to 80 °C and vacuum replaced with nitrogen atmosphere. 5 g of stearoyl chloride was added dropwise to the solution and the reaction time was set to 1.5 h. A white product was precipitated from the solution and the product was washed three times in methanol, followed by filtration and drying under vacuum at 45 °C.

#### 3.2.3. Characterization of cellulose esters

Successful surface modification was confirmed using infrared spectroscopy (FT-IR) and <sup>1</sup>H NMR. Spectra were acquired on a Bruker AV-300 spectrometer, USA. Cellulose esters in deuterated chloroform were measured at 25 °C and tetramethylsilane was used as an internal standard. The degree of substitution was determined by a titration method based on Eberstadt method, where a saponification reaction is followed by adding NaOH to a polymer in ethanol mixture and following back titration with HCl. Details of CS synthesis and characterization are described in (Šumichin et al., 2013).

### 3.3. Rheological measurements

For rheological studies, the materials were hot-melt pressed (CS at 100 °C and 80 bar and blends of PP and PP+CS at 150 °C and 80 bar). Pellets of the extruded material were pressed in a stainless steel round-shape mold (26 mm diameter and 1.06 mm thickness) in the same conditions as was use for film preparation. During preparation the temperatures of the mold and the temperature of the pressing plate were controlled by contact thermocouple thermometer (Summit STD-62, Korea).

To study rheological properties of blends an Anton Paar Physica MCR501 rheometer, Germany, with cone-plate measuring geometry was used. To prevent oxidation the experiments were carried out in nitrogen atmosphere and did not last longer than 10 min at a temperature of 190 °C. Flow curves obtained at shear rate  $\dot{\gamma}$  range from 0.001 to 100 s<sup>-1</sup>. Complex viscosity was determined in the range of angular frequencies  $\omega = 0.01$  to 600 rad/s. A constant strain of  $\gamma = 5\%$  was determined from the linear viscoelasticity region (LVR). Amplitude sweep test to determine the LVR was done at a frequency of 1 Hz.

### 3.4. Preparation and characterization of composite films

Composites of PP and CS were prepared by hot-melt blending in conical twin-screw HAAKE MiniCTW micro-compounder (USA). CS in powder form were first melted and mixed at 100 °C and 100 rpm for 5 min (in cycled flow regime). Blends of PP and pretreated CS with different CS to PP ratios (8, 20, 40 and 50 wt% of CS) were prepared by mixing at 150 °C and 100 rpm for 10 min (in cycled flow regime). To prevent, or at least minimize thermal degradation of cellulose backbone, 0.1 wt% of powdered BHT antioxidant was

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