ABSTRACT SUMMARY

In this study, biodegradable films consisting of polylactic acid (PLA) and nano-crystalline cellulose (NCC) have been produced in order to study their use as future implant materials. The two materials have been shown to have poor adhesion. To increase the compatibility, the surface of NCC was modified with PLA-chains. The thermal and mechanical properties as well as the water permeability were investigated and compared for different ratios of filler material.

INTRODUCTION

Polylactic acid (PLA) is a biodegradable polymer with low toxicity and high mechanical strength (1). These properties make the polymer suitable for products ranging from packaging materials to biomedical devices such as sutures, implants and drug delivery systems. The use of biodegradable implants has also been considered to be an alternative to metal implants. The advantage is mainly that the implant does not need to be removed, resulting in less trauma and pain for the patient.

Even though PLA has mechanical strength, it may sometimes not be enough for example if a bone is highly loaded. The mechanical strength can then be improved by the addition of nano-particles. In this study we have reinforced the material by the use of nano-crystalline cellulose (NCC). NCC is also a degradable polymer, which results in a totally degradable implant.

However, the adhesion between PLA and cellulose has been shown to be poor, resulting in an inflexible and brittle material. Therefore, we attached PLA chains onto the surface of the NCC particles via a ring opening polymerization (Figure 1). Composite films with varying amount of NCC were thereafter produced via solvent casting.

An important factor to consider for biodegradable implants is the degradation. PLA is degraded via hydrolysis of the ester bond and therefore the water transport within the material is of interest. Also, mechanical and thermal properties as well as the morphology of the materials were studied.

EXPERIMENTAL METHODS

NCC was produced as earlier described in literature (2). The modification was performed by a ring opening polymerization of L-lactide in presence of NCC (Figure 1). Briefly, the water in the NCC suspension was exchanged into DMSO, and L-lactide, tin(II)ethylhexanoate and benzyl alcohol was added and the reaction was performed at 130°C for 17 hours while stirred. The final product was washed with water and acetone in several steps.

Modification was confirmed by Infrared spectroscopy (IR), ss-NMR and the behavior of the particles in different solvents.

Composite films with 1, 5 and 10 wt% of NCC were produced via solvent casting. The solvent was exchanged into dichloromethane (DCM) prior casting and PLA was added and left to dissolve. The solution was poured into a petridish and the solvent was allowed to evaporate overnight. Pure PLA films were produced in the same manner. The films were kept in a desiccator until use.

The mechanical and thermal properties were studied using an Intron 5565A device, and a Perkin Elmer Pyris 1 Differential Scanning Calorimetry respectively. The morphology was studied in a Scanning Electron Microscope (Leo Ultra FEG-SEM). Water permeability was measured in diffusion cells were the film was placed between a donor and an acceptor chamber. Tritium labeled water was added to the donor chamber and the accumulation of the water was sampled over time. The radioactivity was measured in a Perkin Elmer Liquid Scintillation Analyzer. The permeability of the material was calculated from the linear region of a plot of the accumulated water against time.
RESULTS AND DISCUSSION
The surface modification of NCC was determined from the appearance of a carbonyl peak in the IR-spectra and the ss-NMR spectra (not shown here). The dispersibility (Figure 2) of the modified (right) and unmodified (left) NCC is shown in different solvents. NCC is known to have a good dispersibility in water due to the surface charges (Figure 2a). The modified NCC showed a tendency to flocculate and sediment over time, probably due to hydrophobic interactions. However, when NCC was placed in organic solvents the modified NCC was well dispersed while unmodified NCC formed aggregates (Figure 2b-c).

![Figure 2: Photographs showing the dispersibility of 0.7% (w/w) of modified NCC (left) and NCC (right) in different solvents. (a) Water (b) Isopropyl alcohol (c) Dichloromethane.](image)

The mechanical properties showed an increase in Young’s modulus for the unmodified NCC films up to 55% compared to the pure PLA film. At the same time, the elongation of the composite films decreased with 50%. However, for the unmodified NCC the value of moduli and elongation was quite constant. The crystallinity for the pure PLA and composite film with unmodified NCC was less than 2%. The crystallinity increased to 4% and 7% when 5 respectively 10 wt% of modified NCC was added, showing that the modified NCC may function as a nucleating agent in the films. The morphology of the cross-sections of the films was studied with SEM and the pure PLA film (Figure 3a) showed a smooth surface. The composite films had a rougher surface, however the modified NCC seems to be better incorporated to the matrix material (Figure 3b) than the unmodified NCC (Figure 3c).

![Figure 3: SEM images showing the cross-section of (a) pure PLA, (b) PLA with 5 wt% modified NCC, (c) PLA with 5 wt% unmodified NCC.](image)

The water permeability is presented in Figure 4 and the addition of the unmodified NCC did not show a significant different for the permeability. However, the addition of modified NCC resulted in increased water permeability. This was not an expected result though the crystallinity is higher in the unmodified NCC films; the permeability was believed to decrease. A possible explanation is that the water permeability increases due to that there are some voids or channels formed along the interface between the particles and the matrix material, which may function as a path for water to be transported through the material.

![Figure 4: Water permeability of composites of PLA and unmodified NCC (◊) and modified NCC (●). The error bars represent the standard deviation of each value.](image)

CONCLUSION
The addition of NCC to a PLA film resulted in an increased or constant Young’s modulus, which may be desired in an implant. The crystallinity was not affected by the addition of unmodified NCC while the modified NCC increased the crystallinity six times. However, the water transport through the composite films was increased when the modified NCC was added. This may be an important factor to consider if the composite material is to be used in an implant, since PLA is degraded by hydrolysis and an increased water transport may result in a faster degradation.

REFERENCES

ACKNOWLEDGMENTS
The project is part of the VINN Excellence SuMo Biomaterials (Supermolecular Biomaterials – Structure dynamics and properties). The financial support from the Centre is gratefully acknowledged.