Structure of Nanofibrillated Cellulose Monolayers at the Oil/Water Interface

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1 Ugelstad Laboratory, Norwegian University of Science and Technology; 2 Paper and Fibre Research Institute; 3 PS Interfaces

ABSTRACT

Surface modified nanofibrillated cellulose (hydrophobized by silylation) has been successfully used as stabilizer for water-in-oil emulsions. It is important to understand the nature of the hydrophobized nanofibrillated cellulose layers at the oil/water (o/w) interface in view of their excellent ability to stabilize emulsions. The hypothesis is that the nanofibrils form a strong network, leading to prevention of coalescence of the water droplets in the oil. Therefore, we have evaluated how the hydrophobized nanofibrils distribute at the o/w interface by studying layers of well characterized nanofibrillated cellulose, prepared by the Langmuir-Blodgett deposition technique. The layer structures were assessed using Atomic Force Microscopy (AFM), Field-Emission Scanning Electron Microscopy (FE-SEM) and image analysis. The results show that nanofibrillated cellulose may occur as single, dispersed fibrils as well as in networks. We conclude that it is likely that the network formation is the main mechanism by which the fibrils prevent coalescence of the emulsion droplets.

INTRODUCTION

It is well known that nanofibrillated cellulose is able to stabilize emulsions by adsorption at the oil-water interface [1]. Almost all the studies performed on the stabilization of emulsions by nanofibrillated cellulose describe oil-in-water (o/w) emulsions, due to the highly hydrophilic nature of the cellulose. Andresen and Stenius [2] and Xhanari et al [3] reported that appropriately hydrophobized nanofibrillated cellulose can be used as stabilizer for water-in-oil (w/o) emulsions. Emulsions of water in toluene, with droplet sizes up to hundreds of micrometers, which were stable towards coalescence could be prepared. It is of interest to know and understand the stabilization mechanism(s) for these emulsions.

EXPERIMENTAL

The nanofibrillated cellulose (NFC) used in this study, produced by pretreatment and mechanical disintegration of mixed softwood bleached kraft pulp [3] was surface modified by silylation [2, 3]. Drops of dispersions of NFC in dry toluene were spread on top of water in a Langmuir-Blodgett Minitrough from KSV Instruments. The toluene was evaporated and a monolayer of NFC was deposited from the water surface on glass slides by the Langmuir-Blodgett technique. Tapping Mode images at different spots of the samples were obtained using a CaliberTM Atomic Force Microscope (AFM) from Veeco Instruments with anisotropic silicon probes (rectangular cantilever). Digital images were acquired with a Hitachi S3000 VP-SEM and a Zeiss Ultra field-emission SEM for assessment of the nanofibril networks formed at the oil/water interfaces.

RESULTS AND DISCUSSION

NFC samples of intermediate and relatively low degree of surface substitution were investigated [3]. Table 1 presents a summary of the samples prepared. The stability of the emulsions was characterized by the change with time of the relative volume of emulsified layer with respect to the total emulsion volume.

Table 1: Samples overview

<table>
<thead>
<tr>
<th>Sample</th>
<th>Degree of surface substitution (DSS)</th>
<th>Concentration (% w/v)</th>
<th>Ability to stabilize emulsions</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cel 1</td>
<td>0.5</td>
<td>0.15</td>
<td>+</td>
</tr>
<tr>
<td>Cel 2</td>
<td>0.5</td>
<td>0.05</td>
<td>+</td>
</tr>
<tr>
<td>Cel 3</td>
<td>0.4</td>
<td>0.15</td>
<td>+</td>
</tr>
<tr>
<td>Cel 4</td>
<td>0.3</td>
<td>0.15</td>
<td>-</td>
</tr>
</tbody>
</table>
Figure 1 shows that at the o/w interface the NFC can occur as single dispersed fibrils as well as form networks. This behavior was observed in the Cel 1-3 samples. The network formation seems to prevent the coalescence of the emulsions droplets, thus providing the emulsion stability. As shown in figure 2, no or in some cases a minor degree of network formation was observed in the Cel 4 sample. Apparently this was not sufficient to stabilize the emulsions. In this case the fibrils formed mainly dense agglomerates, probably because they were not sufficiently hydrophobic to become well dispersed in the toluene.

**CONCLUSIONS**

The stability of the emulsions stabilized by NFC is apparently due to the development of nanofibril networks at the o/w interface. Thus, appropriately hydrophobized NFC is a useful material for the stabilization of w/o emulsions against coalescence.

**ACKNOWLEDGEMENTS**

This work was supported by the Research Council of Norway, Södra Cell AB, Akzo Nobel and Jotun A/S.

**References:**

3. Xhanari K., Syverud K., Stenius P., “Emulsions stabilized by microfibrillated cellulose: the effect of hydrophobization, concentration and o/w ratio”, *Journal of Dispersion Science and Technology* accepted for publication (2010/243)
STRUCTURE OF NANOFIBRILLATED CELLULOSE MONOLAYERS AT THE OIL/WATER INTERFACE

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Per Stenius, Ugelstad Laboratory, NTNU
Outline

- Introduction
- Motivation and objectives of the study
- Cellulose nanofibrils: preparation and surface modification
- Sample preparation – Langmuir-Blodgett (LB) technique
- Image analysis – Quadtree decomposition method
- SEM and AFM analysis
- Network formation and emulsion stability
- Conclusions
Introduction

An emulsion is a dispersion of one immiscible liquid in another.

- Important industrial applications:
  - food
  - cosmetics
  - pharmaceutics
  - petroleum

- Thermodynamically unstable
  - stabilized by surfactants and/or colloidal particles
  - cellulose (oil-in-water emulsions)

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Motivation

- Surface modified (hydrophobized) nanofibrils by silylation
- Toluene as oil phase
- Water-in-toluene emulsions
- Stable against coalescence
- Droplets size higher than 200 µm

Optical micrograph of emulsion\(^2\)


\(^3\) Xhanari K., Syverud K., Stenius P., accepted for publication in *Journal of Dispersion Science and Technology* (2010)
Objectives of the study

To understand:

✓ nature of the cellulose nanofibril layer at the water/oil (w/o) interface
✓ stabilization mechanism of water-in-toluene emulsions

Methods used in the study:

✓ LB deposition technique
✓ Image analysis (Quadtree decomposition) of scanned images
✓ AFM & SEM analysis
Emulsions stability - Breaking processes

Emulsion

Creaming

Coalescence

Phase separation (breaking)

Sedimentation
Proposed emulsion stabilization mechanism

Cellulose nanofibrils: preparation and surface modification

<table>
<thead>
<tr>
<th>Starting pulp</th>
<th>Softwood bleached kraft pulp</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pretreatment⁵</td>
<td>Claflin mill</td>
</tr>
<tr>
<td>Fibrillation</td>
<td>Homogenizer</td>
</tr>
<tr>
<td>Surface modification⁶</td>
<td>Silylation</td>
</tr>
</tbody>
</table>

\[
\text{Cell-OH} + \text{Cl-Si-i-C}_3\text{H}_7 \rightarrow \text{Cell-O-Si-i-C}_3\text{H}_7 + \text{HCl}
\]

<table>
<thead>
<tr>
<th>Sample</th>
<th>DSS</th>
<th>Concentration (% w/v)</th>
<th>Ability to stabilize emulsions</th>
</tr>
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<tbody>
<tr>
<td>Cel 1</td>
<td>0.5</td>
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Langmuir-Blodgett deposition
Scanner images

- Flatbed scanner
- 2400 DPI
- Lateral resolution: ~ 10 µm/pixel
- 10 x 10 mm² area for image analysis
Image analysis - Quadtree decomposition method

- Requirement: STDEV of grey-levels in the images

Fibril images

QT, Requirement 1

Image analysis - Quadtree decomposition method

- STDEV 1 >> STDEV 2
- lower STDEV → higher decomposition steps

Fibril images

QT, Requirement 2
Image analysis - Quadtree decomposition method

<table>
<thead>
<tr>
<th>Sample</th>
<th>nQT/mm²</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cel 1</td>
<td>547</td>
</tr>
<tr>
<td>Cel 2</td>
<td>200</td>
</tr>
<tr>
<td>Cel 4</td>
<td>8</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Code</th>
<th>Sample</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>A + D</td>
<td>Cel 1</td>
<td>DSS=0.5; 0.15% w/v</td>
</tr>
<tr>
<td>B + E</td>
<td>Cel 2</td>
<td>DSS=0.5; 0.05% w/v</td>
</tr>
<tr>
<td>C + F</td>
<td>Cel 4</td>
<td>DSS=0.3; 0.15% w/v</td>
</tr>
</tbody>
</table>
SEM analysis

<table>
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<tr>
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<th>Sample</th>
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<tbody>
<tr>
<td>A + C</td>
<td>Cel 1</td>
<td>DSS=0.5; 0.15% w/v</td>
</tr>
<tr>
<td>B + D</td>
<td>Cel 3</td>
<td>DSS=0.4; 0.15% w/v</td>
</tr>
</tbody>
</table>
SEM analysis

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<td>Cel 1</td>
<td>DSS=0.5; 0.15% w/v</td>
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<td>B + D</td>
<td>Cel 3</td>
<td>DSS=0.4; 0.15% w/v</td>
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</table>
SEM analysis

Cel 4 sample

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</tr>
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<tbody>
<tr>
<td>Cel 4</td>
<td>DSS=0.3; 0.15% w/v</td>
</tr>
</tbody>
</table>
AFM analysis

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<tr>
<th>Code</th>
<th>Sample</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>Cel 1</td>
<td>DSS=0.5; 0.15% w/v</td>
</tr>
<tr>
<td>B</td>
<td>Cel 3</td>
<td>DSS=0.4; 0.15% w/v</td>
</tr>
<tr>
<td>C</td>
<td>Cel 4</td>
<td>DSS=0.3; 0.15% w/v</td>
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</table>
Network formation and emulsion stability

<table>
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</table>
Conclusions

- At the oil/water interface the cellulose nanofibrils can occur as single dispersed fibrils as well as form networks.

- The stability against coalescence of the water-in-toluene emulsions stabilized by surface modified nanocellulose is apparently due to the development of nanofibril networks at the toluene/water interface as shown by the SEM and AFM images (Cel 1-3 samples).

- The ability of the cellulose nanofibrils to form networks depends on the degree of surface substitution. The nanofibrils with DSS<0.4, which gave no stable emulsions, form dense and small agglomerates at the toluene/water interface (Cel 4 sample).

- Thus, sufficiently surface modified nanofibrillated cellulose is a useful stabilizer for water-in-toluene emulsions.
Acknowledgments

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