Starch Based Thickening agents for Personal Care Surfactant Systems

Fraunhofer Institut Angewandte Polymerforschung

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3. Summary
Profile of qualification of a modern thickening agent for surfactant systems

1. Requirements and objectives

- high viscosity by low application concentration
- long-term stability over a pH-range ~4 – 9
- electrolyte und surfactant compatibility
- high transparency of the gel
- simple workability (quick swelling and pH-adjustment)
- biological degradation
- cheap
- toxicological harmlessness
- satisfy appliance properties (e.g. no gluey feeling on the skin)
1. Requirements and objectives

Used surfactant systems

14% Surfactant  2% Chemical modified starch

1.) Nonionic surfactant $\rightarrow$ Alkyl polyglucoside (APG)
   ➢ high kindness to the skin
   ➢ not easy to thicken
   ➢ synergistic effect with anionic surfactants

2.) Anionic Surfactant $\rightarrow$ Sodiumlaurethsulfate (SLES)
   ➢ less kindness to the skin as APG
   ➢ easier to thicken
1. Requirements and objectives

Objectives for this project

- Synthesis of a starch based thickener for personal surfactant systems
- high transparency
- formulations should obtain a customary viscosity (~ 6000 mPas)
2.1 Carboxymethylation of starch

1\textsuperscript{st} Approach of resolution

Use of Carboxymethyl starch as thickening agent

\[
\begin{align*}
\text{NaOH; } i\text{-PrOH; } 40^\circ\text{C, 4.5h} \\
\text{CO}_2\text{-Na}^+ \\
\text{Cl-CH}_2\text{-COOH}
\end{align*}
\]
2.1 Carboxymethylation of starch

Shear viscosity of 2% CMS-solutions

- CMS obtain a thickening effect for APG
- CMS with a DS~1 shows maximum shear viscosity
2.1 Carboxymethylation of starch

Transparency of 2% CMS-solutions

- Only solutions of CMS without APG are bright.
- Solutions of CMS with APG are milky white with low transparency.

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2.2 Hydrophobic modification of Carboxymethyl starch

2nd Approach of resolution

Use of hydrophobic carboxymethyl starch as thickening agent
2.2 Hydrophobic modification of carboxymethyl starch

**Hydrophobic substitution of carboxymethyl starch**

- **Etherification**
  - e.g. Reaction with 1,2-Epoxyalkanes
  - Alkyl halogenides

- **Esterification**
  - e.g. Reaction with Acid halogenides
2.2 Hydrophobic modification of carboxymethyl starch

Possibilities for synthesis

Starch

1. Hydrophobation
   Alkylation (hom.)
   Carboxymethylation (het.)

2. Hydrophilation
   Carboxymethylation (het.)
   Hydrophobation: Reaction with 1,2-Epoxyalkanes
   Hydrophilation: Reaction with Monochloroacetic acid

1. Hydrophililation
   Carboxymethylstarch (het.)
   Alkylation (het.)
2.2 Hydrophobic modification of carboxymethyl starch

Homogeneous Hydrophobation

2 Reaction channels

Bien et al. NaOH (0.5 eq); Na$_2$SO$_4$ (0.5 eq); Epoxyalkanes (1.2 eq)

Funke et al. KOH (0.8 eq); Epoxyoctane (1.0 eq)
2.2 Hydrophobic modification of carboxymethyl starch

**Homogeneous Hydrophobation**

![Chemical structure and reaction conditions]

- $C_6 \rightarrow \text{2-Hydroxyhexyl starch }$ DS = 0.8
- $C_8 \rightarrow \text{2-Hydroxyoctyl starch }$ DS = 0.7
- $C_{10} \rightarrow \text{2-Hydroxydecyl starch }$ DS = 0.9
- $C_{12} \rightarrow \text{2-Hydroxydodecyl starch }$ DS = 0.9
2.2 Hydrophobic modification of carboxymethyl starch

Molar mass distribution of waxy maize starch

- starch isn’t complete decomposed
- remaining starch chains can react with 1,2-epoxyalkanes

![Graph](image)

- wms after reaction
- waxy maize starch
Heterogeneous Hydrophilation

1. Carboxymethylation of 2-Hydroxyoctylstarch with 1-3 eq MCE
2. Studies of these starch derivatives in surfactant system
3. Using the best results to synthesise C₆, C₁₀ and C₁₂ hydrophobic starches
2.2 Hydrophobic modification of carboxymethyl starch

Shear viscosity of 0.5% 2-Hydroxyalkylcarboxymethyl starch solutions

Shear viscosity [mPas] at shear rate = 2.55 s⁻¹

![Graph showing shear viscosity for different starch derivatives](image)

<table>
<thead>
<tr>
<th>Starch Derivative</th>
<th>DS₂-Hydroxyalkyl</th>
<th>DS₃-Carboxymethyl</th>
</tr>
</thead>
<tbody>
<tr>
<td>C₆-CMS</td>
<td>0.8</td>
<td>0.83</td>
</tr>
<tr>
<td>C₈-CMS</td>
<td>0.7</td>
<td>0.92</td>
</tr>
<tr>
<td>C₁₀-CMS</td>
<td>0.9</td>
<td>0.84</td>
</tr>
<tr>
<td>C₁₂-CMS</td>
<td>0.9</td>
<td>0.65</td>
</tr>
</tbody>
</table>

(C₆ = 2-Hydroxyhexyl; C₈ = 2-Hydroxyoctyl; C₁₀ = 2-Hydroxydecyl; C₁₂ = 2-Hydroxydodecyl)
2.2 Hydrophobic modification of carboxymethyl starch

Transparency of 0.5% 2-Hydroxyalkylcarboxymethyl starch solutions

<table>
<thead>
<tr>
<th>Starch Derivative</th>
<th>0% Surfactant</th>
<th>14% APG</th>
</tr>
</thead>
<tbody>
<tr>
<td>C6-CMS</td>
<td>95</td>
<td>21</td>
</tr>
<tr>
<td>C8-CMS</td>
<td>95</td>
<td>60</td>
</tr>
<tr>
<td>C10-CMS</td>
<td>92</td>
<td>68</td>
</tr>
<tr>
<td>C12-CMS</td>
<td>74</td>
<td>54</td>
</tr>
</tbody>
</table>

(DS = Degree of Substitution; C6 = 2-Hydroxyhexyl-; C8 = 2-Hydroxyoctyl-; C10 = 2-Hydroxydecyl-; C12 = 2-Hydroxydodecyl)

<table>
<thead>
<tr>
<th>Starch Derivative</th>
<th>DS&lt;sub&gt;2-Hydroxyalkyl&lt;/sub&gt;</th>
<th>DS&lt;sub&gt;Carboxymethyl&lt;/sub&gt;</th>
</tr>
</thead>
<tbody>
<tr>
<td>C&lt;sub&gt;6&lt;/sub&gt;-CMS</td>
<td>0.8</td>
<td>0.83</td>
</tr>
<tr>
<td>C&lt;sub&gt;8&lt;/sub&gt;-CMS</td>
<td>0.7</td>
<td>0.92</td>
</tr>
<tr>
<td>C&lt;sub&gt;10&lt;/sub&gt;-CMS</td>
<td>0.9</td>
<td>0.84</td>
</tr>
<tr>
<td>C&lt;sub&gt;12&lt;/sub&gt;-CMS</td>
<td>0.9</td>
<td>0.65</td>
</tr>
</tbody>
</table>

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2.2 Hydrophobic modification of carboxymethyl starch

Analysis by static light scattering (SLS)

\[ \ln(K^*c/R(\theta)) = q^2 \]

- 2-Hydroxyoctyl carboxymethyl starch
- Carboxymethyl starch
- Alkylpoly glucoside

\[ DS_{CM} = 0.9 \]
\[ DS_{2,HO} = 0.7 \]

Carboxymethyl starch
2-Hydroxyoctyl-CMS

DS_{CM} = 1.1
2.2 Hydrophobic modification of carboxymethyl starch

APG solutions with different hydrophobic modified CMS

CMS  C₈/CMS  C₁₀/CMS  C₁₂/CMS
2.3 Variation of the surfactant system

3rd Approach of resolution

Use of surfactant mixture APG/SLES
2.3 Variation of the surfactant system

Shear viscosity and transparency of different surfactant mixtures

- by adding SLES viscosity and transparency of the formulations increase
- max. of viscosity and transparency by adding 3% SLES
- addition of >3% SLES viscosity and transparency decrease

Shear viscosity and transparency of different surfactant mixtures

Shear viscosity [mPas] at shear rate = 2.55 s⁻¹

Transparency [%]

2-HDOCMS 14% APG 0% SLES
2-HDOCMS 14% APG 1% SLES
2-HDOCMS 14% APG 2% SLES
2-HDOCMS 14% APG 3% SLES
2-HDOCMS 14% APG 5% SLES

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2.3 Variation of the surfactant system

Comparison of formulations with and without SLES

1% 2-HDOCMS  
14% Alkylpoly glucoside

1% 2-HDOCMS  
14% Alkylpoly glucoside

$\eta(\gamma=2.55 \text{ s}^{-1}) = 5165 \text{ mPas}$  
$T = 70 \%$

$\eta(\gamma=2.55 \text{ s}^{-1}) = 8160 \text{ mPas}$  
$T = 91 \%$
3. Summary

- Selective aqueous surfactant systems can be stable thicken by modified CMS (~0.5% concentration).
- Viscosity and transparency can be controlled by varying the DS hydrophobic-hydrophilic and addition of SLES.
- In principle application as emulsifying agent for O/W-emulsion possible.
Thanks to

➢ Dr. Waltraud Vorwerg for the GPC and SLS data
➢ Dr. Jürgen Kunze for recording the $^{13}$C-NMR data
➢ Inst. Dr. Schrader for the cooperation
➢ Agency for renewable resources for the financial support