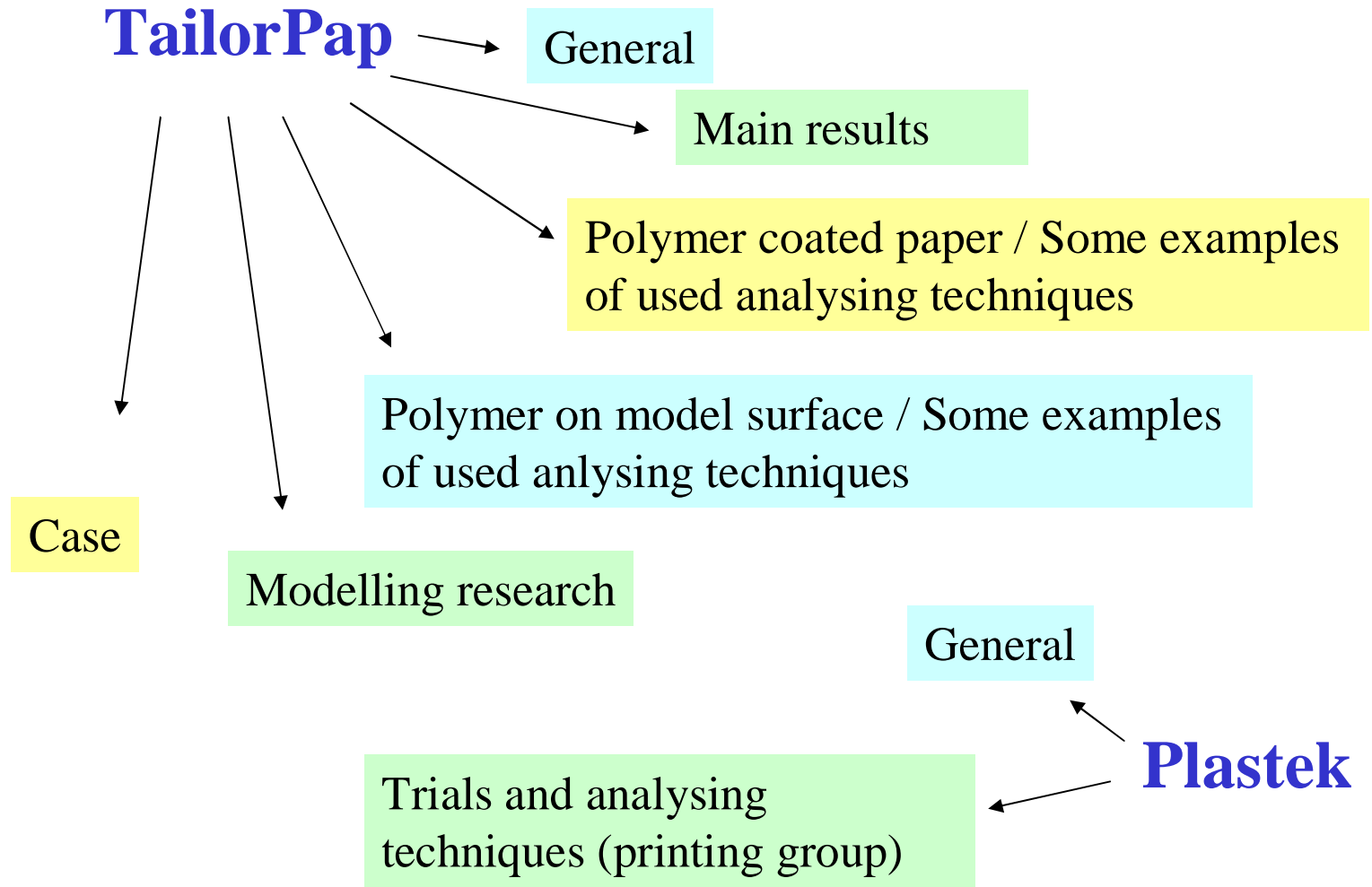


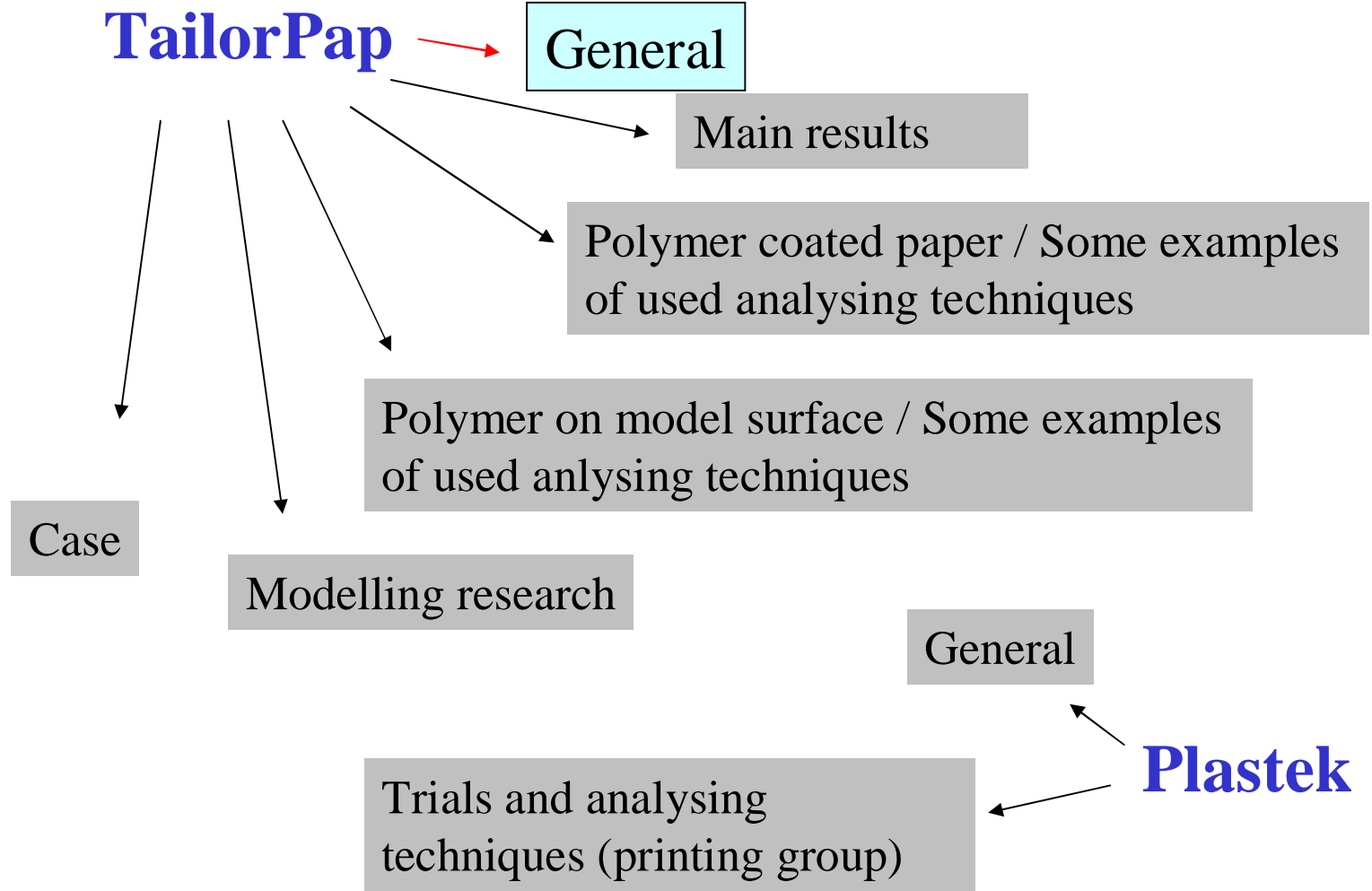
**Tailoring paper printability  
with small amount of polymers  
or  
with plasma treatment**

Kirsi Kataja  
Senior research scientist  
VTT (Technical Research Centre of Finland)  
Print surfaces team

21.9.2006, COST E32, Ljubljana

# Contents of the presentation:





TailorPap

# Tailored and interactive paper – TailorPap

1.10.2003 – 31.12.2006

Project coordinator: Kirsi Kataja, VTT

**NETCOAT**

 **TEKES**

# TailorPap

## Research partners:

**VTT** (Polymers, Converting, Print surfaces, Functional printing)

**HUT** (Laboratory of Forest Products Chemistry, Laboratory of Polymer Technology)

**University of Jyväskylä** (Departments of Applied and Inorganic Chemistry)

Top Analytica (purchased research services)

## Financial support is provided by:

**Finnish National Technology Agency (TEKES)**

**VTT (Technical Research Centre of Finland)**

**Metso Paper Oy**

**UPM-Kymmene Oy**

**M-Real Oyj**

**Stora Enso Oy**

**Ciba Specialty Chemicals Oy**

**Kemira Oy**

**Myllykoski Paper Oy**

# TailorPap

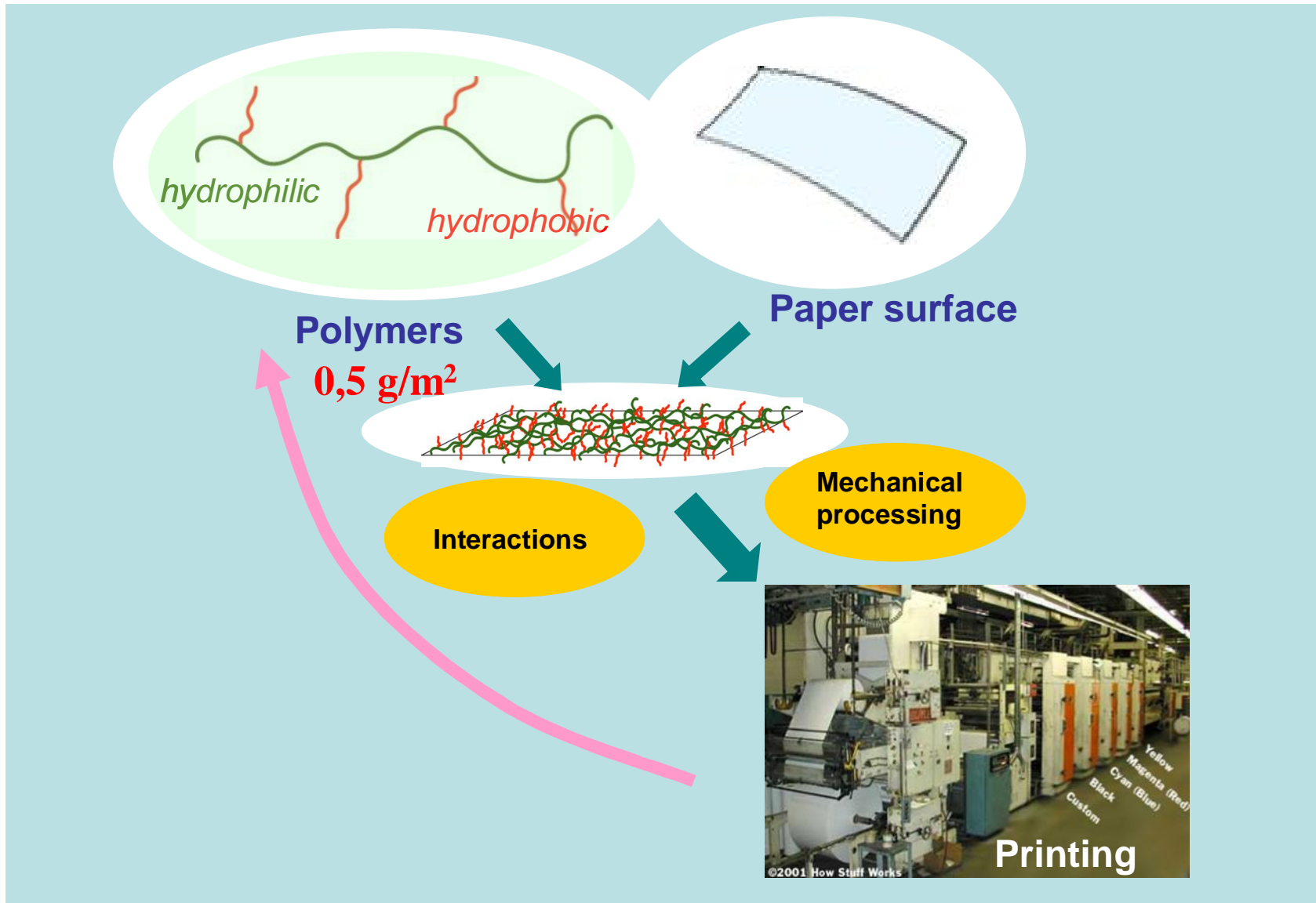
## MAIN OBJECTIVES

Chemical characteristics, in addition to physical properties of paper, are significant in the printing process, but their effects are not known well enough.

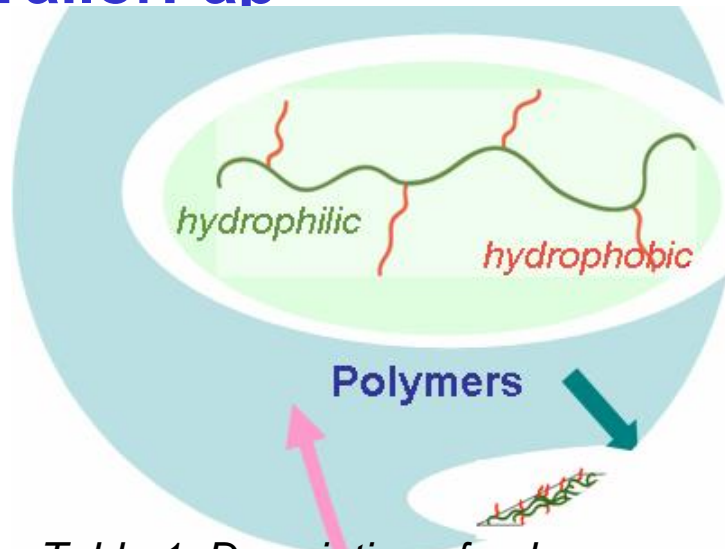
The main objectives of the project are

1. Simplified base paper
  - surface properties would be adjusted by chemical treatment
2. Control the absorption characteristics of paper for even and low absorption of printing ink
  - tailor the paper surface by small amounts ( $<0,5 \text{ g/m}^2$ ) of chemicals
3. Control curl of paper to improve the quality in digital printing

# TailorPap



# TailorPap



## Polymers

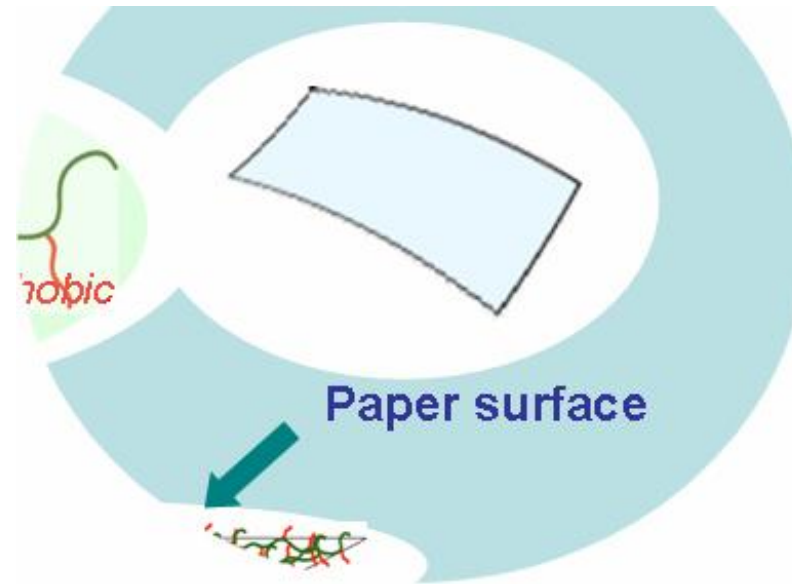
- modified starches
- synthetic amphiphilic polymers
- commercial polymers

Table 1: Description of polymers mentioned in this presentation

Code	Polymer type	Additional information
N2	Nonionic starch	
N3	Nonionic starch	Increased hydrophobicity (compared to N2)
N1	Nonionic starch	Increased hydrophobicity (compared to N3), dispersion
A1	Anionic starch	
A2	Anionic starch	
C1 /C2	Cationic starch	Increased hydrophobicity, dispersion
P1	Amphiphilic block copolymer	PEO based hydrophilic block.
P2	Amphiphilic block copolymer	Increased hydrophobicity in h-phobic block compared to P1.
P3	Amphiphilic block copolymer	PEO block longer than in P1.
PVA101-1	Polyvinyl alcohol	Commercial

# TailorPap

## Paper



Base paper grades used in the studies of controlling the absorption characteristics of paper were

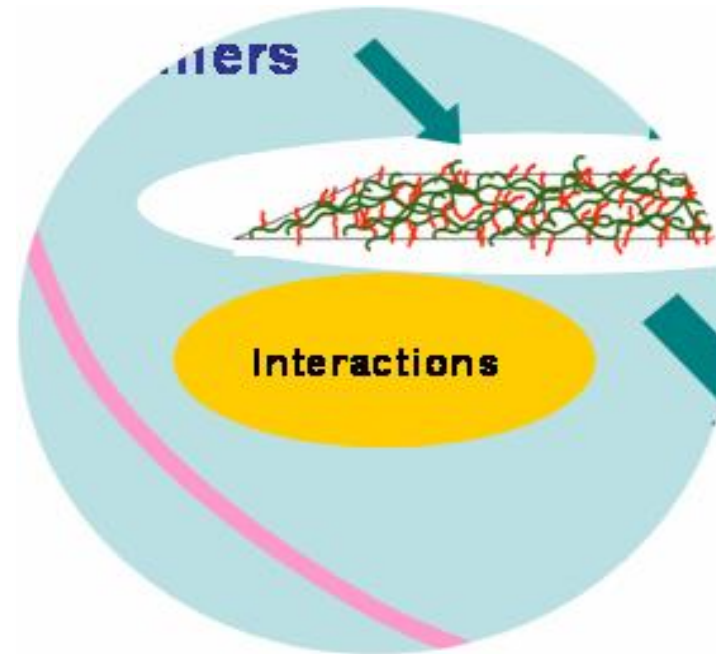
- wood free FP base paper (Stora Enso Oulu Mill, PM 7, 58 g/m<sup>2</sup>)
- wood containing LWC base paper (UPM Kymmene Kaukas paper mill, 45 g/m<sup>2</sup>)

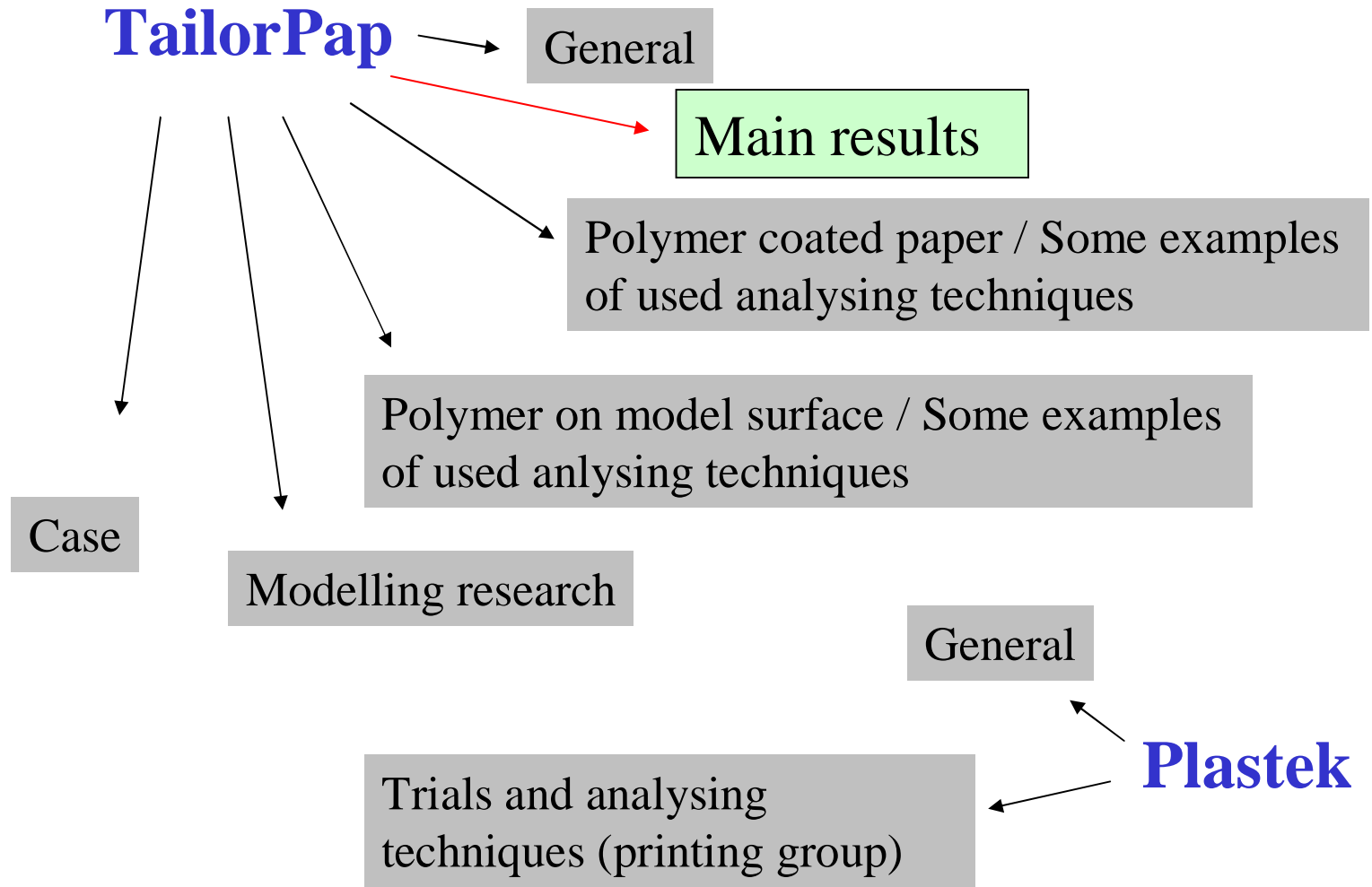
The commercial mineral pigment coated end products (*FP end* and *LWC end*) has been used as references in the project.

# TailorPap

## Model surfaces

- *hydrophilic silica  $\text{SiO}_2$*
- *hydrophobic silica  $\text{SiO}_2$*
- *polystyrene surface*
- *cellulose surface*





### Objectives 1. and 2.

- **<0,5 g/m<sup>2</sup>**, even distribution of coating
- Water absorption can be dramatically influenced.
- The absorption of **solvent or oil based printing inks** can be delayed.

Note: This low amount of polymer does not block the surface:

Absorption is affected by chemistry!

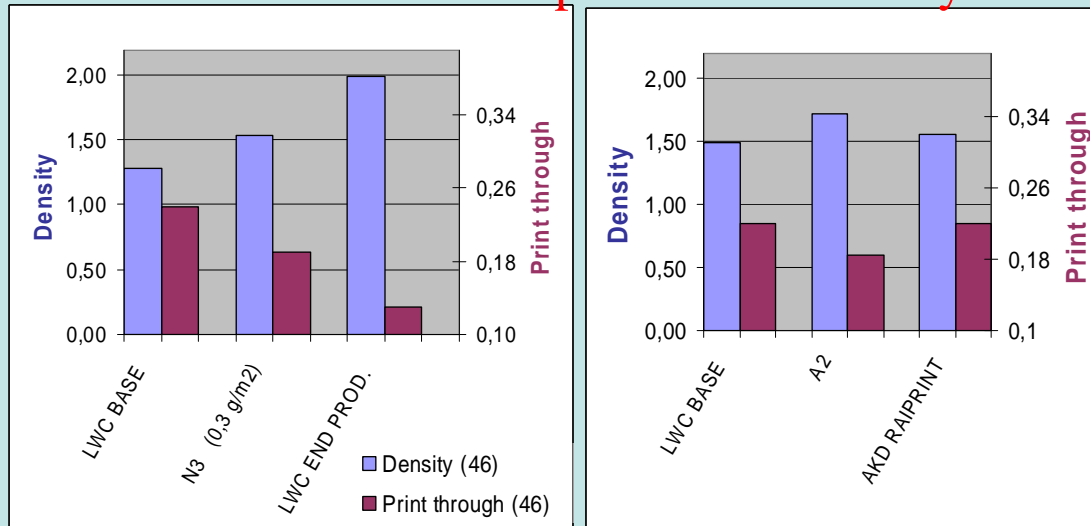
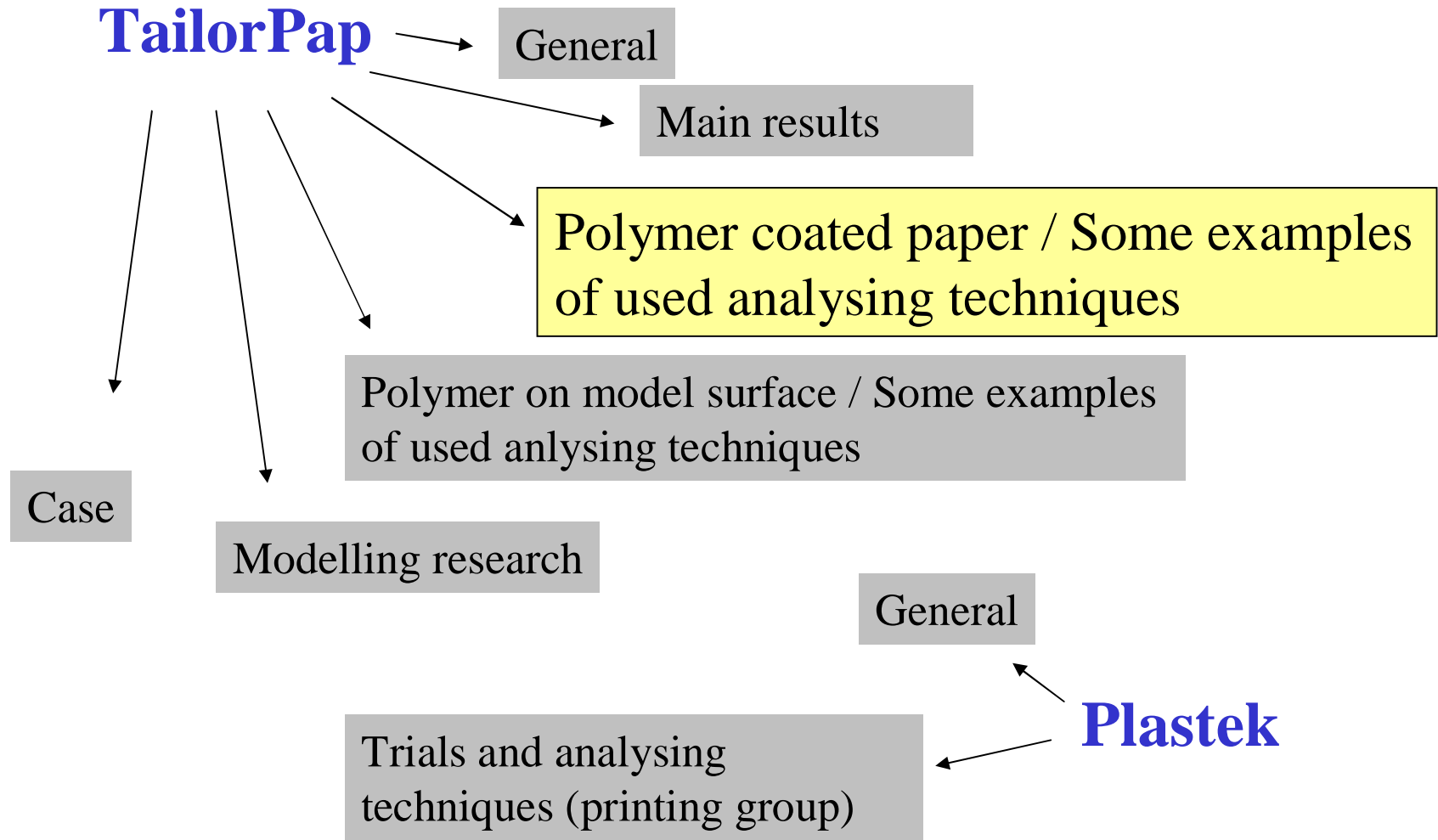


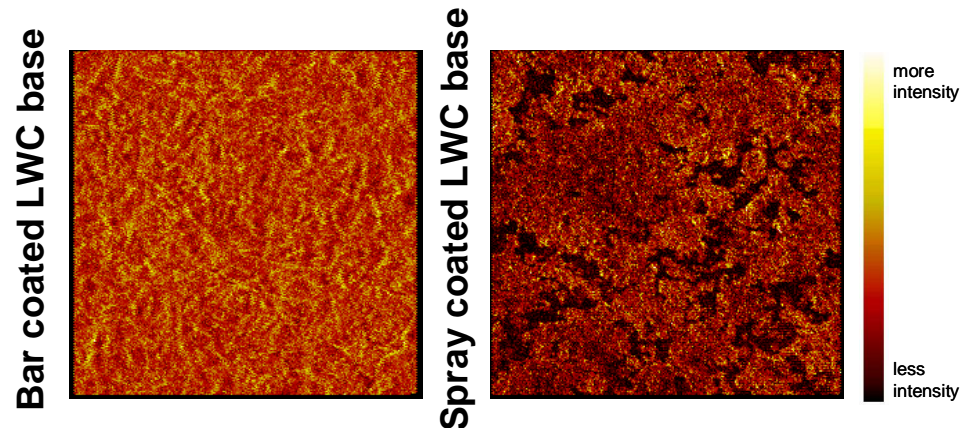
Figure 1. IGT gravure test results.

*Note that LWC end product has mineral coating 12,5g/m<sup>2</sup>/side compared to N3 polymer 0,3 g/m<sup>2</sup>.*

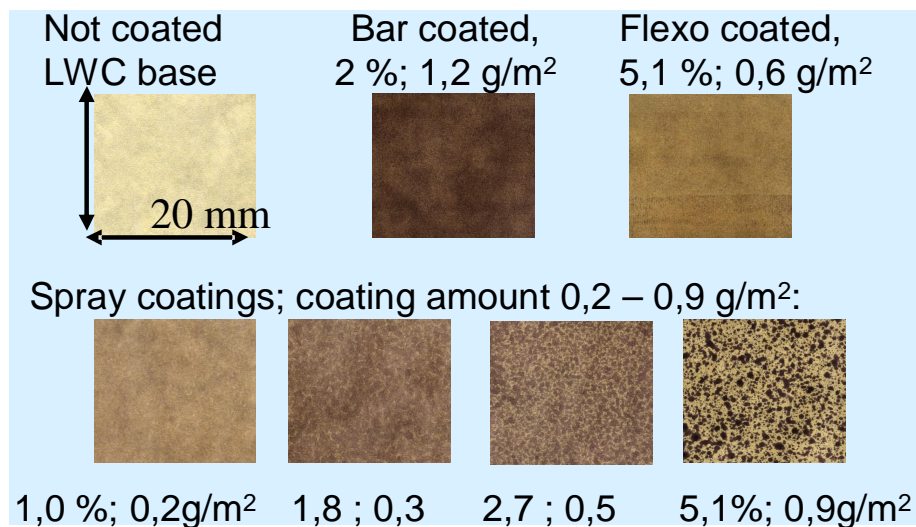
- Possibility to control heterogeneity of paper surface chemistry



# TailorPap System development



**Figure 3.** Large scale ToF-SIMS imaging maps of 43 Da, which represents starch coating. Area is 2,5 mm x 2,5 mm. The coating is substantially more uniform of the bar coated sample (coating covers the surface). Bar coating  $\sim 3 \text{ g/m}^2$ , spray coating  $\sim 0,7 \text{ g/m}^2$ .



**Figure 4.** Evenness of anionic starch A2 coating. Starch dyeing technique. Percentages are referring to concentration of coating solution.

# TailorPap

## Polymer size and chemical structure vs. penetration and surface properties

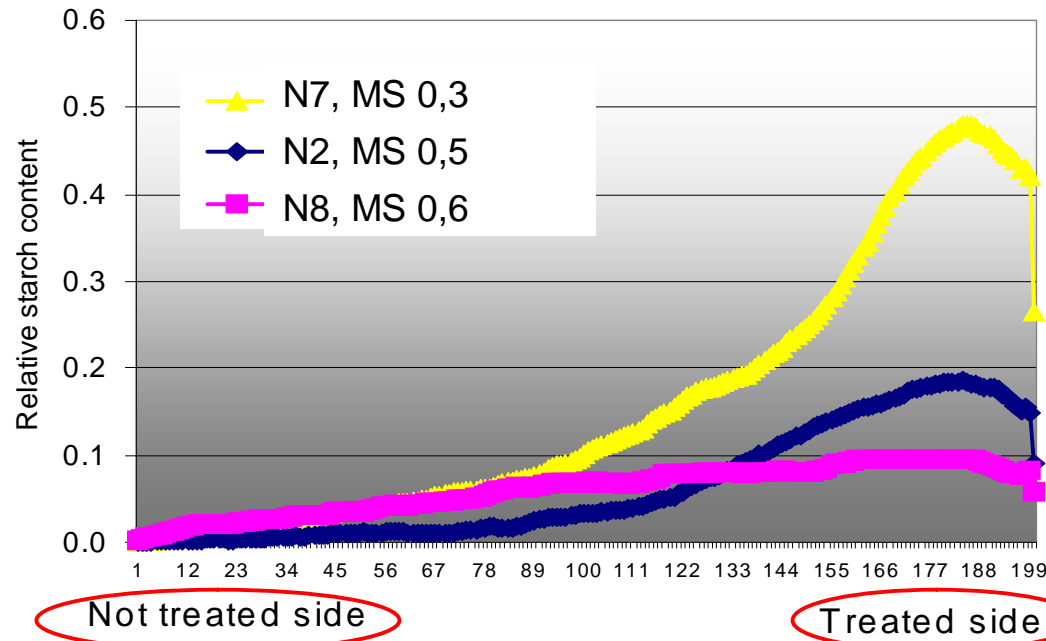


Figure 7. The effect of the degree of substitution on z-directional starch distribution.

MS (N7) = 0.3, viscosity 12 mPas, SCSS = 91 %.

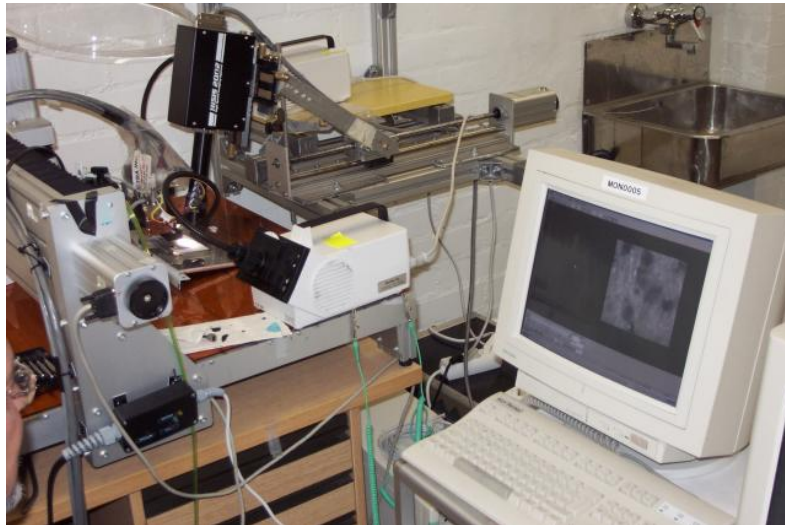
MS (N2) = 0.5, viscosity 169 mPas, SCSS = 88 %.

MS (N8) = 0.6, viscosity 106 mPas, SCSS = 67 %.

(SCSS = starch content on sprayed side)

# TailorPap

## Ink jet interactions



Measurement of dynamic interactions of treated paper samples with ink jet droplets and high speed camera.

Clear ink jet interactions have been detected. Distinctly sharper edged dot can be received. Delayed penetration of ink drop (after 300 ms) can also be detected.

**NETCOAT**

*Results by Pertti Moilanen/VTT*



# TailorPap

## Ink jet interactions

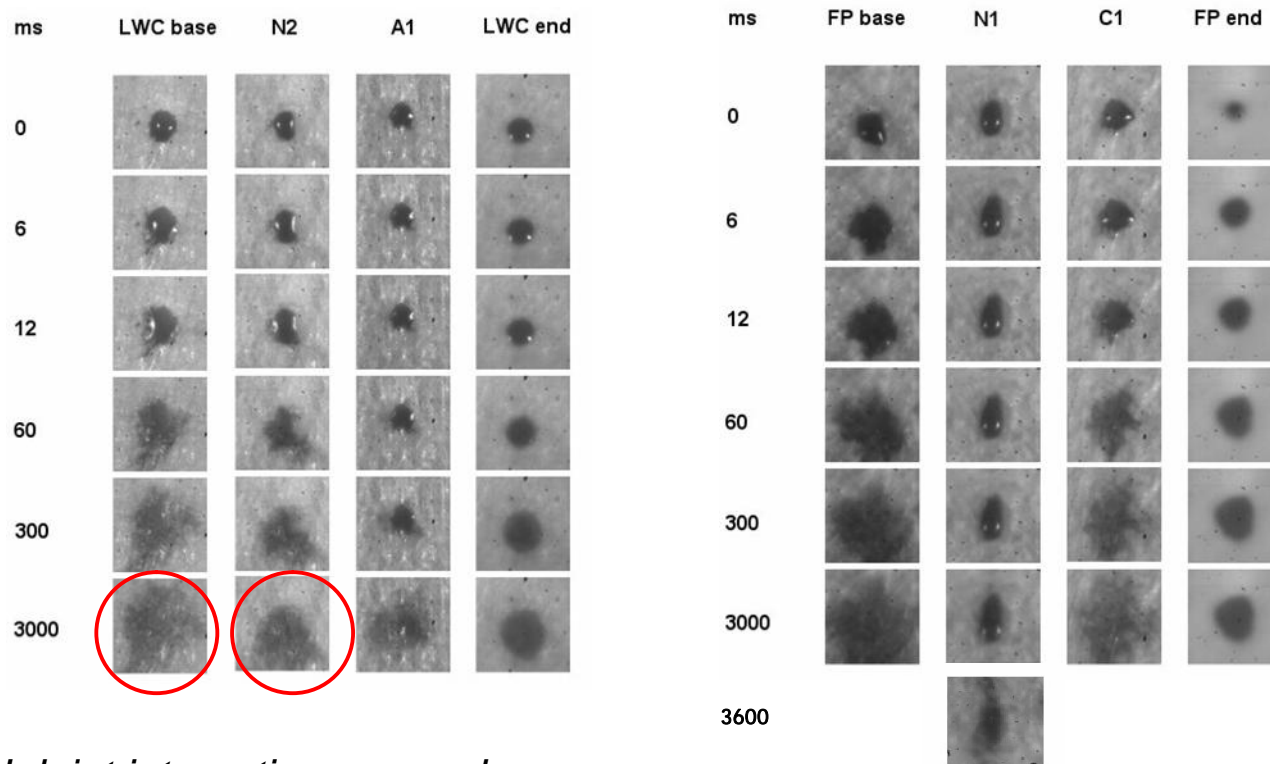
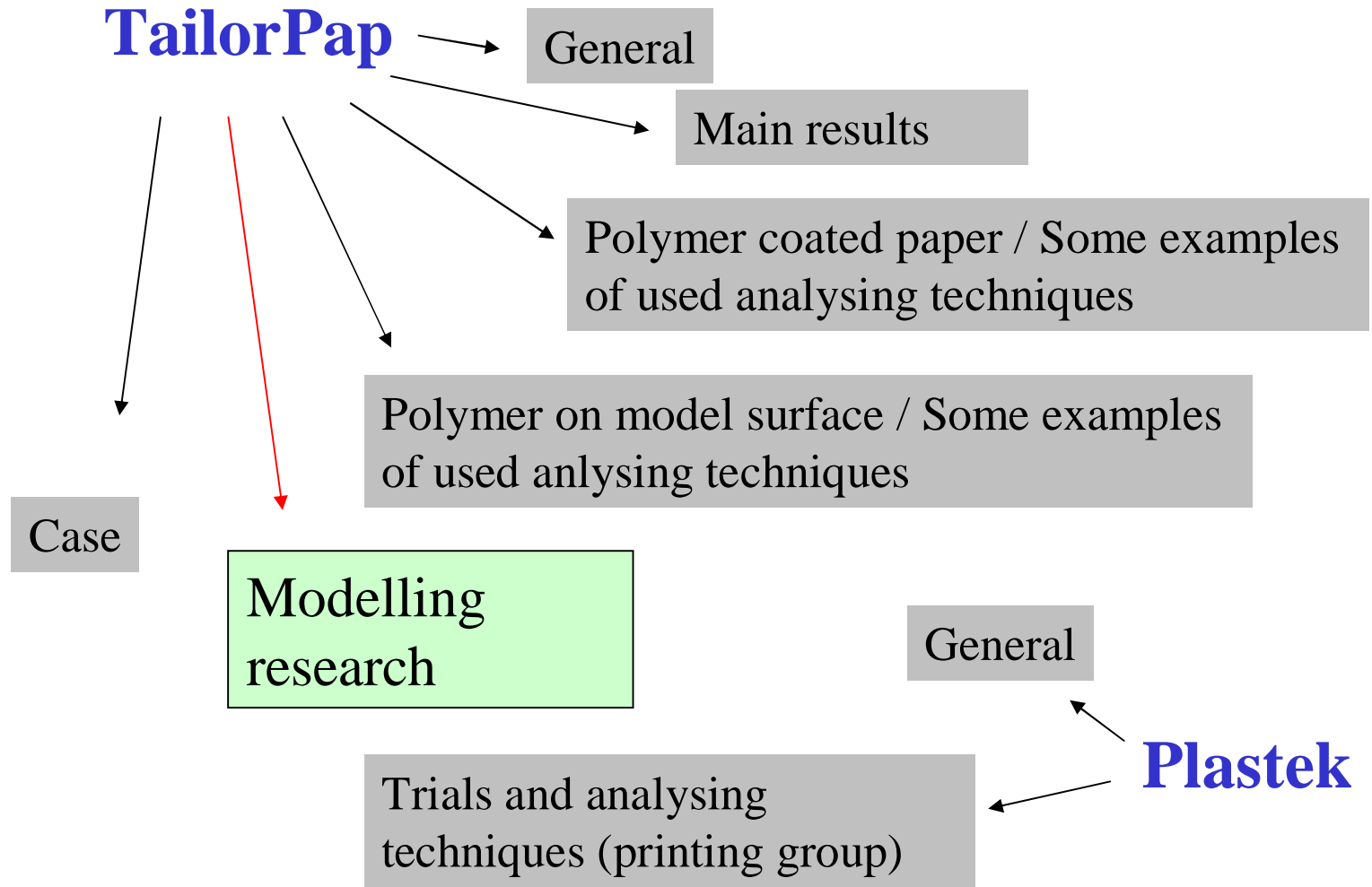


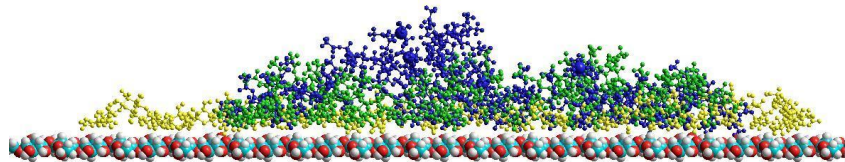
Figure 8. Ink jet interaction research.

(FP end product has mineral coating  $16\text{g/m}^2/\text{side}$ , and LWC end product has mineral coating  $12,5\text{g/m}^2/\text{side}$ .)

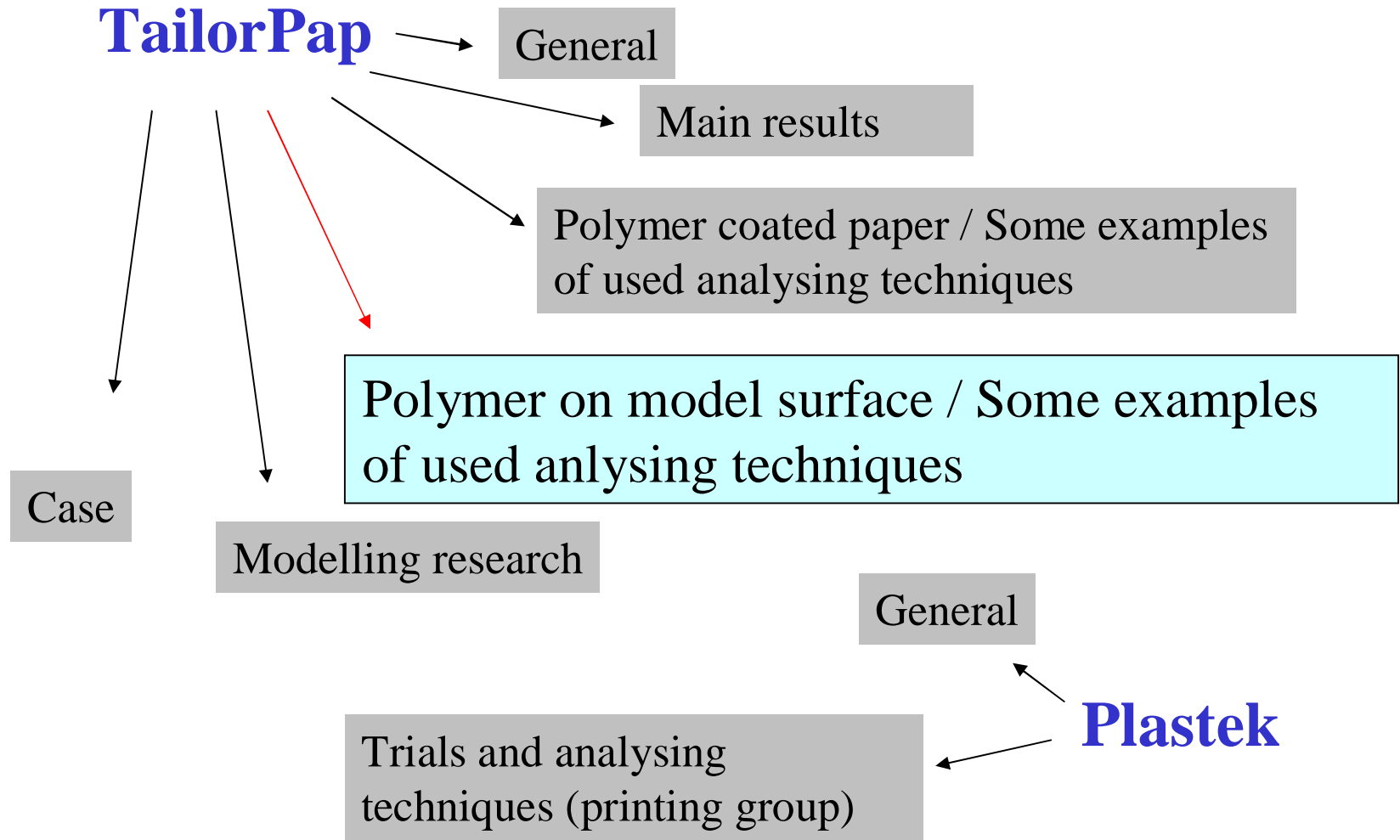


## Modelling research

Modelling research with starch polymers on cellulose have showed among other things, that the settlement of anionic typed amylose derivative on the cellulose surface is more uniform than the settlement of nonionic amylose derivative, which is more uniform than the settlement of cationic amylose derivative.



**Figure 9.** Cationic (blue), neutral (green) and anionic (yellow) amylose chains on the model surface simulated by BIO+ method in vacuum.



## Model surface research

- developing model surface research environments

Several types of model surfaces

- hydrophilic, hydrophobic, cellulose

Analytical methods

- Contact angle measurement
- Atomic force microscopy (AFM)
- QCM-D (quartz crystal microbalance with dissipation)
- ESCA

SiO<sub>2</sub> crystal

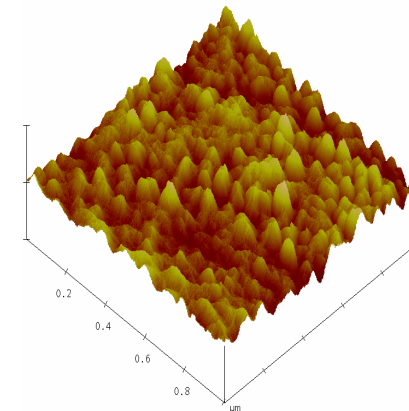
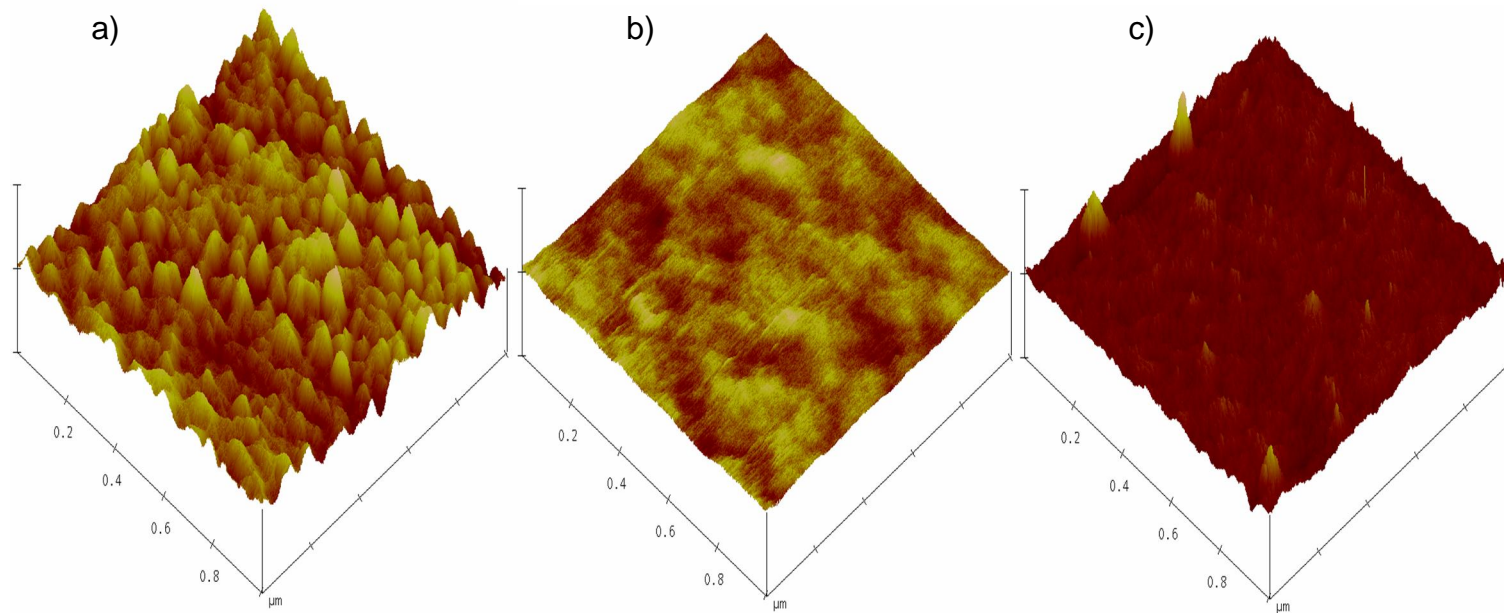


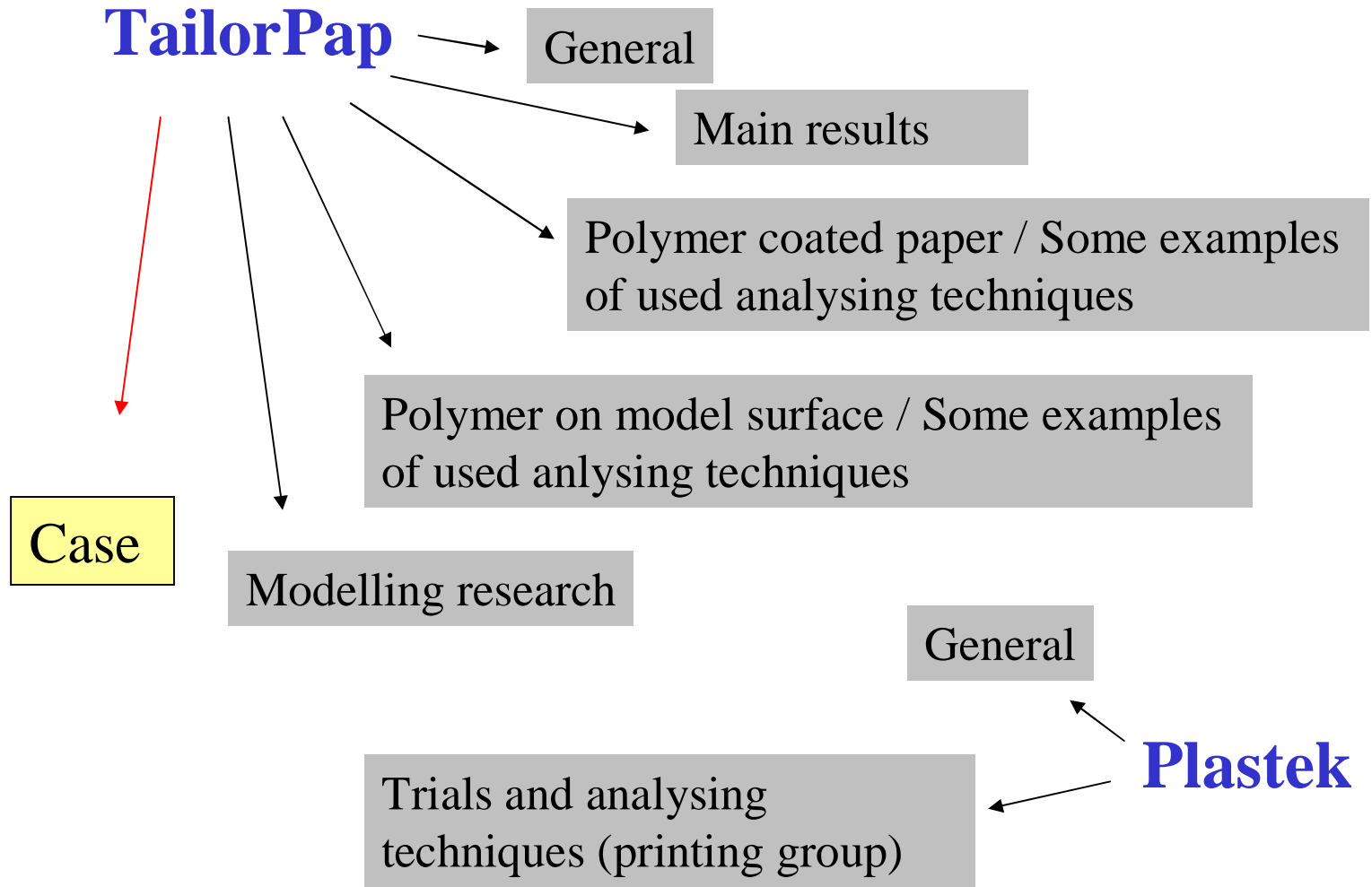
Figure 10. AFM of polymer P3 on QCM-D crystal

## Model surface research (continued)

Interactions of polymers on model surfaces: Interesting interaction patterns have been found out. Some examples:



*Figure 11. AFM images of dry amphiphilic polymer P3 layers adsorbed on QCM-D crystals a) SiO<sub>2</sub> crystal, b) polystyrene crystal and, c) cellulose coated crystal.*



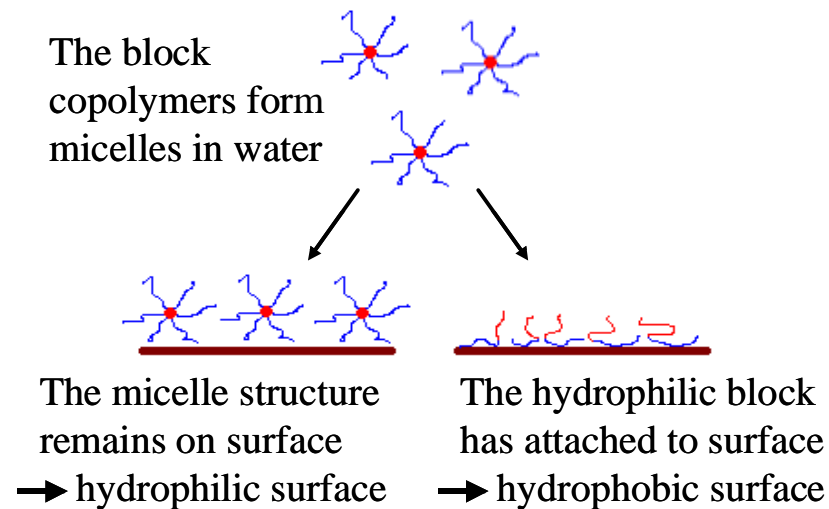
# TailorPap

## Case

### CONCLUSIONS

#### According to model surface experiments

- The hydrophobicity of the surface is not only influenced by the polymer but also by the application method



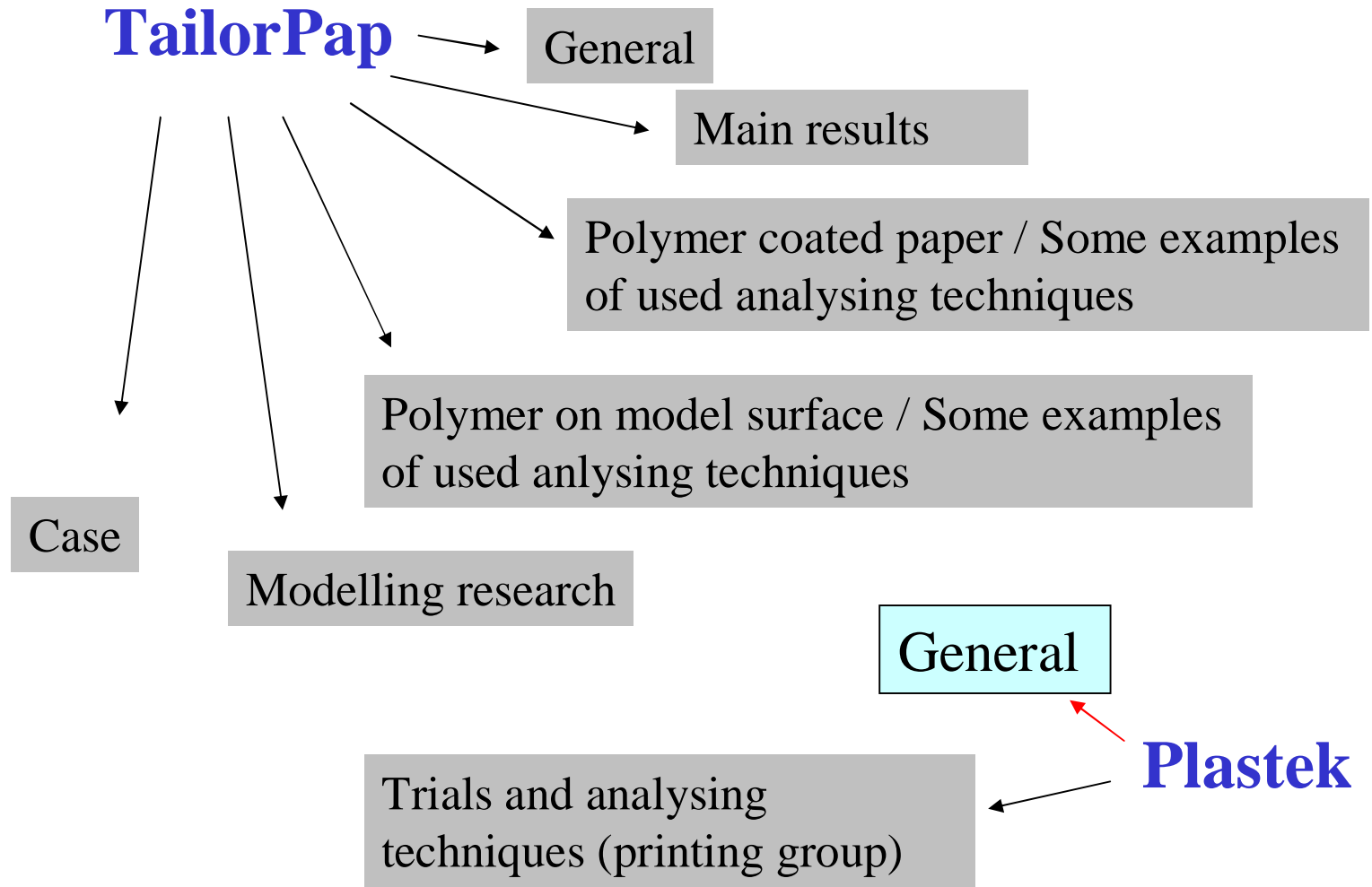
TailorPap

EU project?  
Contact: [kirsi.kataja@vtt.fi](mailto:kirsi.kataja@vtt.fi)

**NETCOAT**

*Results by Susanna Holappa and Leena Nurmi/HUT*



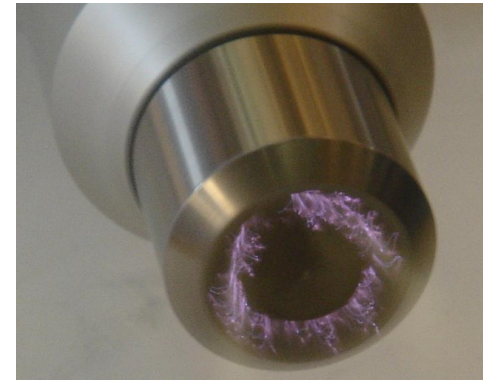
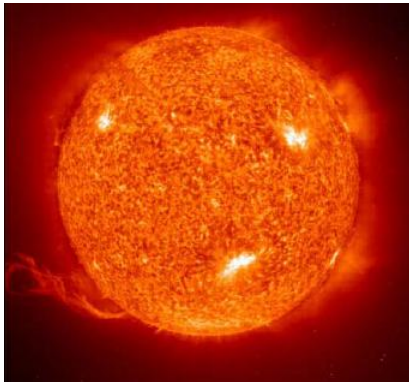


# Plastek project

11/2005-12/2009

Project coordinator: Kalle Nättinen, VTT  
(kalle.nattinen@vtt.fi)

- General objectives: Surface modification of substrates with plasma and corona techniques



# Research partners

## Printing group

- VTT
  - Print surfaces
  - Functional printing
  - Nature resources and environment
- Tampere University of Technology
  - Institute of Paper Converting
  - Institute of Fiber Materials Science
- Åbo Akademi University
  - Laboratory of Paper, Coating and Converting
- Funding by Tekes (National Technology Agency of Finland), VTT and industrial partners Stora Enso Oyj, UPM Oyj, Millidyne OY, Vetaphone A/S

# Plastek:

## Surface modification with plasma and corona techniques

### Substrates:

Plasma treatment is applicable to a wide range of materials: fiber materials (paper, cardboard, non-wovens), plastics, laminates, metals.

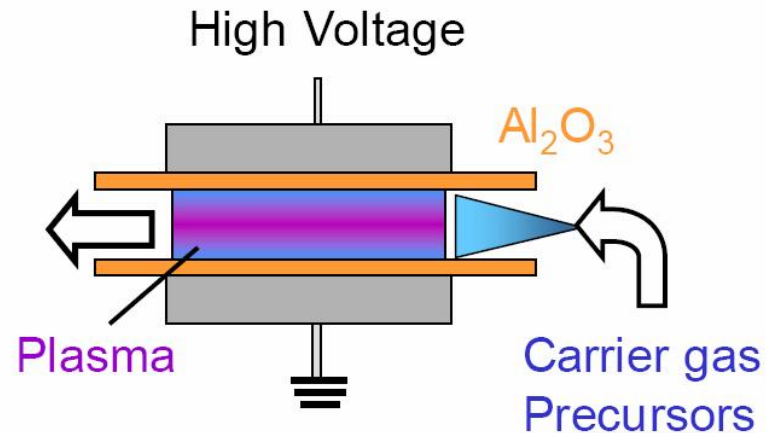
### Targets and benefits of plasma treatment vs. corona:

- Enhanced power of treatment
- Permanence of the effect: longer shelf life
- Tailored activation by depositing active substances
- Coating with desired precursor

# Objectives

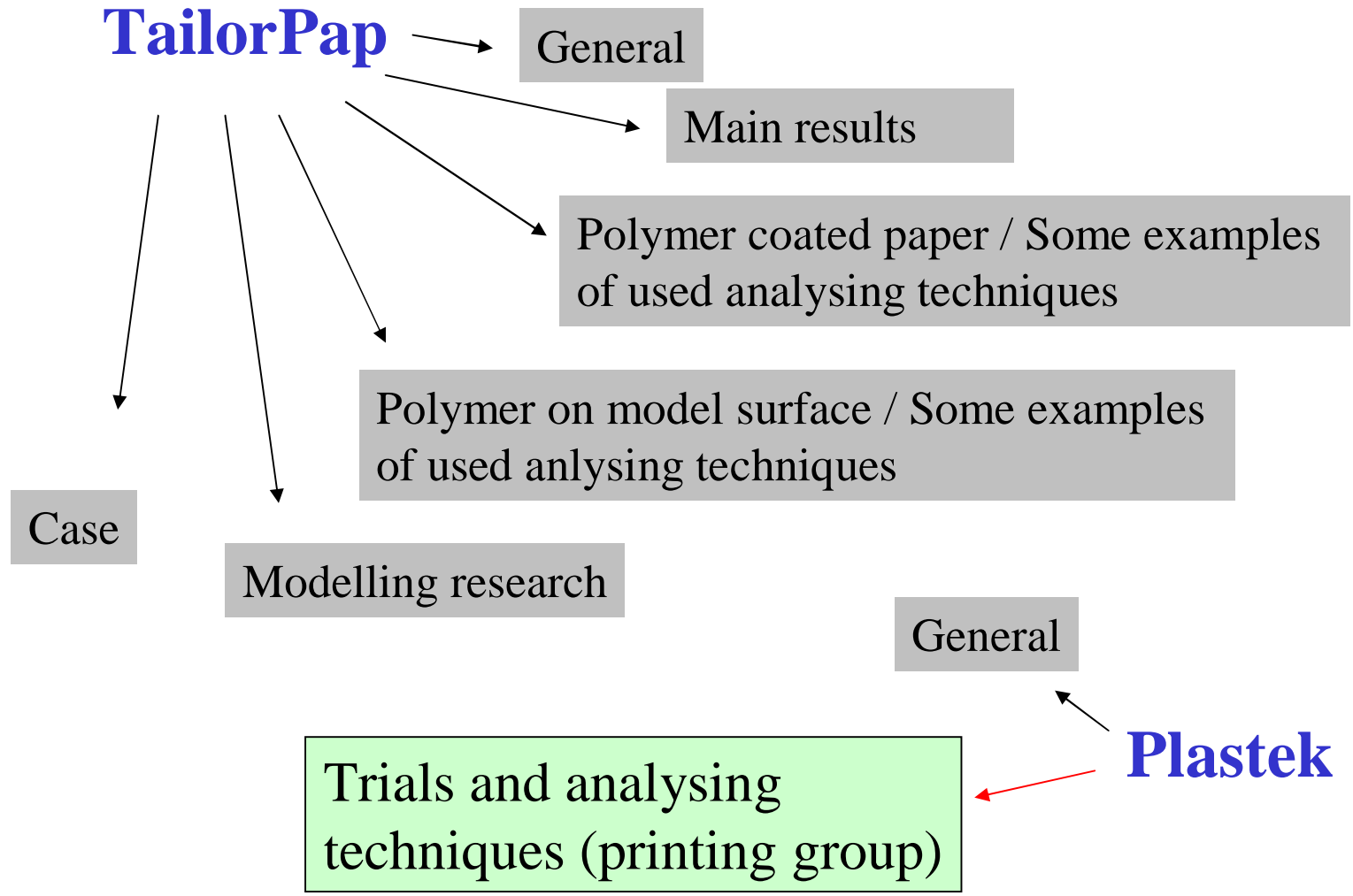
Printing group of the project

- Improved printability through atmospheric pressure plasma treatment.



- Plasma treatment increases the surface energy of the substrate, however the role of surface energy and chemistry in printability is not fully understood.

Slides by Otto-Ville Kaukonieni, Henna Sundqvist and Kalle Nättinen / VTT



# Trials 2006

- Pilot scale plasma and corona treatments using nitrogen and helium gases at Tampere University of Technology
- Printability testing of treated paper substrates at VTT
  - Pilot scale gravure and flexo printing trials
  - Inkjet printing trials

# Surface analysis methods

- Surface energy determination
- ISIT (Ink Surface Interaction Tester)
- ESCA/XPS
- AFM
- Image analysis (TAPIO printability tester)
- Dynamic interactions in inkjet printing



Thank You!

Contact information:

[kirsi.kataja@vtt.fi](mailto:kirsi.kataja@vtt.fi)