Annual Report 2006-2007

Edited by Jarl B. Rosenholm and Christina Luojola

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FunMat Annual Report 2006-007

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Foreword

On 26.1.2005 Åbo Akademi University launched an internal competition for research groups to receive extra funding for three years, set into disposal by the Foundation for Åbo Akademi University to “create strong research environments of international standing”. Moreover, an option was set for maintained or altered funding for a fourth year and an extension to a fifth year after additional evaluation in 2008. A panel evaluated the preliminary proposals on the basis of creativity, sufficient critical mass and developed national and international network with cross-scientific character. Out of the 28 proposals 14 were selected on 28.4.2005 for further evaluation by an international committee, consisting of: Professor Bengt Ankarloo and Professor Ole Elgström, Lund University, Professor Gunnar Svedberg, University of Gothenburg, Professor Morten Søndergaard, University of Copenhagen, Professor Lars Bäckman, Karolinska Institutet and Professor Udo Zanders, University of Economy, Stockholm.

The Functional Materials Center (FunMat) for Printable Electro-, Magnetic-, Optical-, Chemical-, and Biofunctionanlities was selected on 17.11.2005 as one of the four Åbo Akademi Centers of Excellence.

The collaboration in materials science is not new, but was initiated already in late 1980-ties. The present strategy is, however based on recent market surveys conducted by Turku Science Park and Foundation for New Technology. The first action taken was the establishment of Knowledge Network of Printed Media in 2005 which was supported by two of the present FunMat partners and Turku Expertise Network of Printed Communication at Southwest Finland Centre of Expertise. The strategy outline is published as a separate brochure.

This report describes the organization and partners of and personnel at the FunMat Center, which has grown from the core financed by Foundation of Åbo Akademi University to nearly hundred researchers. The relevant projects active during the two first years of existence and the publications resulting from them are also included. It should be pointed out, that a large portion of the initial funds has been directed to the foundation of a Functional Printing (FunPrint) Laboratory. Although the primary aim is to produce advanced researchers training and research, the strategy of the FunMat Center is focused on materials functionalization through printing. The required advanced printer was not commercially available, but has been constructed in-house.

It is my sincere hope that this report convinces the reader that the activities have been of a high scientific standard and particularly successful. One proof of this is that FunMat Center received additional support from the Ministry of Education, starting 2007 and was awarded the Center of Excellence status at the Academy of Finland, starting 2008.
Moreover, the researchers training is supported by Graduate School of Materials Research (GSMR) of which most partners hold a share. The expanding activities will be described in future reports from the FunMat Center of Excellence.

Åbo, June 2008

Jarl B. Rosenholm
Professor, Chairman
1. **Organization of the Functional Materials (FunMat) Centre**

![Diagram showing the organization structure of FunMat Centre]

**Executive Board**

*ÅAU members:*
Professor Jarl Rosenholm (Chairman)
Professor Ronald Österbacka (Vice chairman)
Professor Carl-Eric Wilén
Professor Martti Toivakka
Professor Jouko Peltonen
Ass.prof. Mika Lindén
FunPrint Lab. manager Tapio Mäkelä

*External members:*
Mining Councillor Tor Bergman
Industry Councillor Heikki Huhtanen
2. Personnel in charge and funded by FunMat, 2006-2007

Department of Physical Chemistry

*Professor*  
Jarl B. Rosenholm

*Ass.professor*  
Mika Lindén

*Ass.professor*  
Jouko Peltonen (1.1-30.9.2006)

*Researcher*  
Per Dahlsten (1.4.2006-31.3.2007)

*Researcher*  
Yang Liu (1.4.2006-)

Laboratory of Polymer Technology

*Professor*  
Carl-Eric Wilén

*Researcher*  
Nils Kullberg (1.5.2006-28.2.2007)

*Researcher*  
Mia Koskinen (1.3.2007-)

*Researcher*  
Carl-Johan Wikman (1.5.2007-)

Laboratory of Paper Coating and Converting

*Professor*  
Martti Toivakka

*Professor*  
Jouko Peltonen (1.10.2006-)

*Researcher*  
Andreas Kass (3.5.2006-17.7.2007)

*Researcher*  
Hanna Koivula (1.6.2007-31.8.2007)

*Researcher*  
Jonna Teerimäki (25.9.2007 -)

*Researcher*  
Roger Bollström (1.10.2007-)

Department of Physics

*Professor*  
Ronald Österbacka

*Researcher*  
Nikolai Kaihovirta (1.1.2006-)

*Researcher*  
Daniel Tobjörk (1.1.2007-)

FunPrint Laboratory

*Laboratory manager*  
Tapio Mäkelä (1.3.2006-)

*Ass.lab.manager*  
Kjell-Mikael Källman

*Secretary*  
Christina Luojola

*Senior researcher*  
Harri Kosonen (10.1.2007-9.4.2007)
3. RESEARCH UNITS

3.1. Department of Physical Chemistry (DPC)

The overall goal for the fundamental research in physical chemistry is to formulate laws of nature and to experimentally examine their validity. If successful, the theoretical models based on simple systems are able to predict the behaviour and properties of more complex systems of interest, e.g. for life-, natural-, material-, and applied sciences. The basic framework is anchored in equilibrium and irreversible thermodynamics. However, more advanced models and simulation techniques are provided by quantum chemical or simulation methods describing small model systems.

Most of the advanced materials today are integrated, hierarchic or hybride composites, i.e. a mixture of monolith, fibrous and particular materials giving rise to synergistic properties. Nano-sized particles are synthesized exhibiting exceptional (optical, magnetic, electronic, catalytic, bio, etc.) functionalities which may be colloidally processed to larger mesostructures maintaining their particular properties. Alternatively surface- active molecules are self-assembled to mesoscopic structures holding comparable functionalities themselves or then these structures are used as templates for the processing of hierarchical porous structures. These materials find wide applications e.g. as catalysts, in advanced sensors, as biomaterials, in solar cells, etc. A particular goal is to find cost-efficient synthesis and processing methods utilising e.g. new printing techniques.

Publications:


Tanya Tsoncheva, Jessica Rosenholm, Mika Lindén, Freddy Kleit, Michael Tiemann, Ljubomira Ivanova, Momtchil Dimitrov, Daniela Paneva, Ivan Mitov, Christo Minchev: “Critical evaluation of the state of iron oxide nanoparticles on different mesoporous


Jessica Rosenholm:”Modular design of mesoporous silica materials: Towards multifunctional drug delivery systems.” (Dissertation) Department of Physical Chemistry, Åbo Akademi University, Åbo (2008).


3.2. Laboratory of Polymer Technology (LPT)

Laboratory of polymer technology is specialized in the design and synthesis of functional macromolecules and novel environmentally friendly plastic additives. The well-defined macromolecules with demanding chemical structures and polymer architectures are prepared from tailor-made monomers using in-house made organometallic catalysts or by utilizing advanced living radical polymerization techniques. In addition, new functional materials have also been prepared by modification through reactive processing in combination with specialty plastic additives. Also electron beam induced grafting techniques have successfully been used as a facile synthetic route to functional polymers. As of today, tailor-made polymer properties are requested in many demanding applications ranging from biotechnology and power supplies to advanced microelectronics.

Publications:


Andell, Ove; Penninkangas, Antti; Ge, Shaozhong:”Transition-metal metallocenes with mono- or bicyclic multi-siloxy-substituted cyclopentadienyl groups, their preparation and use as polymerization catalysts.” Eur. Pat. Appl. (2006), 20 pp. CODEN: EPXXDW EP 1640378 A1


Ge, Shaozhong; Andell, Ove S.; Penninkangas, Antti; Maaranen, Janne; Telen, Tuula; Mutikainen, Ilpo. :”The first synthesised examples of di-siloxyl-substituted cyclopenta-


Orava, Eeva; Korventausta, Joni; Rosenberg, Meri; Jokinen, Mika; Rosling, Ari:“In vitro degradation of porous poly(DL-lactide-co-glycolide) (PLGA)/bioactive glass composite foams with a polar structure.” Polymer Degradation and Stability **92**, 14-23 (2007).

Aubert, Melanie; Roth, Michael; Pfaendner, Rudolf; Wilen, Carl-Eric:“Azoalkanes: a novel class of additives for cross-linking and controlled degradation of polyolefins.” Macromol. Materials and Engineering **292** (6), 707-714 (2007).


Åström, Jan A.; Timonen, Jussi; Myllys, Markko; Fellman, Jacob; Le Bell, Jean:“Random networks of fibres display maximal heterogeneity in the distribution of elastic energy. European Physical Journal E **22**, 61-66 (2007).


3.3. Laboratory of Paper Coating and Converting (LPCC)

Coating and printing, specifically ink – paper interactions, is the major research focus area of LPCC. Within FunMat, an important goal is to understand setting mechanisms of novel inks that are used for printed functionality. Understanding of mechanisms and interactions between ink components and print substrates is needed for successful printability and utilization of fiber-based products for printed functionality. It is also essential to understand the compatibility between the ink solvents and the components in paper, and develop appropriate solutions for problems such as loss of surface strength caused by solvent absorption into latex binder in a pigment coating. Detailed and versatile characterization of surface chemical and topographical properties of the studied surfaces and interfaces is an important part of the research.

While there is a clear need for the compatibility of a fiber-based substrate for the required functionality, e.g. printable electronics, it is also important to exploit the inbuilt properties of substrate when possible. By including functionality into the paper or paperboard substrate itself (active paper) new types of product concepts can be developed. The pore structure of paper or its coating may be utilized to create controllable mass transfer properties that in combination with an active indicator layer could be used as a sensor device. One approach to improve substrate compatibility is to adapt techniques already in use for traditional surface treatment, e.g., pigment coating, surface sizing and calendering. In addition, nanoparticle-stabilized dispersions/emulsions will be utilized as compatibilizers and adhesion promoters of substrate coatings. One of the goals of LPCC is to understand the prerequisites for incorporating biofunctional coatings and sensor elements to printable electronic devices.

The instrumentation of LPCC has been actively upgraded with new test printers (IGT (offset, gravure, flexo)), ink-surface interaction testers (ISIT), contact angle instrumentation (KSV CAM 200 multidispenser) and microscopy (Ntegra AFM).

Publications:


steel analysed by field emission scanning electron microscopy and physicochemical methods.” Journal of Industrial Microbiology & Biotechnology (2008), accepted.


3.4. Department of Physics (DPh)

The research of the Department of Physics at Åbo Akademi University is focused around the clarification of electro-optical properties of disordered organic materials and to demonstrate novel solution processable electronic devices based on these materials. Especially \( \pi \)-conjugated polymers and related materials are promising candidates for novel electronic device applications such as field effect transistors, light emitting diodes, memories, etc. that can be printed on fiber or plastic based substrates.

A central theme today, is the development of tools for the characterization of charge carrier transport and dynamics, i.e. time-of-flight (TOF) and (photo-)CELIV (charge extraction in a linearly increasing voltage), dark injection current transients, photo-modulation spectroscopic techniques (both cw- and transient) as well as dielectric spectroscopy techniques, such as impedance and Kelvin probe spectroscopy.

In order to successfully make “intelligent packages”, there is a need to print at basically no cost power sources (i.e. batteries or photovoltaic cells), active components such as transistors and memory cells, as well as INPUT/OUTPUT units, all operating at low-voltages. This requires a totally new approach to electronics: simple device design and innovative solutions. Traditional organic electronics usually suffers from stability issues and high drive-voltages; especially for transistors. The use of ions usually offers robust performance at low voltages with less stringent needs for encapsulation, opening up a totally new field in device physics of organic electronics.

Publications:


4. Research projects
4.1. Introduction

The general aim for all research is excellence with a wide spectrum. The specific strategy for FunMat is to focus collective projects on assembling of communicative devices by printing on functionalized paper based substrates. The composite materials are intelligent which respond to external stimuli (only) upon request. In the booklet extended abstracts of ongoing projects with funding from Foundation for Åbo Akademi University have been written by the researchers. Moreover, other projects of relevance for FunMat Center are presented shortly. All contributions are collected under the following headings:

1. Abstracts by FunMat researchers, including FunPrint Laboratory
2. Materials including synthesis and physico-chemical modification
3. Functionalization by printing, coatings or laminated films
4. Characterization and modeling of precursor materials and structures
5. Utilization by demonstration of assembled structures, papers and boards

It is obvious that the topics overlap each other in a number of cases and thus the contributions should be considered as an unbroken chain. Moreover, an extensive characterization ensures the identification of predominant phenomena. As a result suitable analytical tools may be designed for manufacturing processes and predictive models may be designed to control them. The inter-relationships are described schematically in the back-coupled flow-diagram.

The projects do not fully match with those listed in the application, since a number of them has ended and are not relevant anymore. The project presentations follow the order from fundamental to targeted research and applications:
1. Foundation for Åbo Akademi projects  
2. Academy of Finland, including Graduate Schools and EU projects  
3. Finnish Funding Agency for Technology and Innovations (TEKES) projects  
4. Projects funded from other sources  

All refereed publications and theses for the years 2006-2008 are listed under the presentation of each research unit. Moreover, relevant publications are repeated under relevant projects. For additional information on the activities, the reader is referred to the homepage: www.funmat.fi with links to each partner.
4.2. Abstracts

In this section extended abstracts written by FunMat researchers are presented. Moreover, a comprehensive report on the development of the Functional Printing (FunPrint) Laboratory is provided.

Printing and deposit control of inkjet printed materials

Per Dahlsten, Yang Liu, Jarl B. Rosenholm, Mika Lindén
Department of Physical Chemistry

Inkjet printing can be used as a method for selective deposition of functional material. The printing method has some specific advantage compare to other used printing methods. Firstly it is a non-contact method with no printing roll/sheet in direct contact with the printed device. Secondly it can deposit materials in 3 dimensions and therefore be used for a variety of substrates. The advantages has in recent years lead to inkjet printing of a number of functional devices in different fields of science, such as printing electronics and printing in the field of chemistry and biology for different applications. The ability to control the deposit during the inkjet printing process is a key issue for successful printing of a functional device since the devices often are sensitive to misplaced material. The control is also important for printing of as high as possible resolution in order to minimize the printed devices. The control of the inkjet process relies on the three cornerstones of inkjet printing and those are the ink, the printer and the substrate. A change in any parameter (in any of the cornerstones) will likely affect the printing process in more than one way. Fortunately the process can be divided into different critical parts, starting with the ink followed by the ink ejection and droplet flight and thereafter ink and substrate interactions which will start with the droplet impact and end with the solidification of the ink on the substrate. An example of a scientific study in the ink ejection and droplet flight parts can be seen in [1]. The scientific work in the field of ink and substrate interactions during inkjet printing is extensive. The control of deposit from a single ink droplet is not an easy matter as seen in [2]. To start with, a typical inkjet ink droplet will bounce when it hit the substrate due to the kinetic energy of the droplet. This phenomenon will lead to both an advancing and a receding contact angle and an ink droplet with a maximum/minimum diameter and in the end an equilibrium diameter. The impact of water based ink droplets is dependent on kinetic energy and ink and substrate interactions. By selecting hydrophobic/hydrophilic substrate using water based ink, it is possible to control the equilibrium diameter closer or further from the maximum diameter (hydrophilic substrate will give equilibrium diameter closer to maximum diameter) [3]. The inkjet printing process will be even more complex since not only does an inkjet droplet need to hit its target in a controlled way but the droplet needs also to be control within the
droplet since there’s a transport of matter within the droplet caused by a surface tension and/or temperature gradient in the droplet. Methods for control of ink deposit within the ink droplet can be seen in [4, 5].

Firstly work has been focused on optimizing ink parameters aiming to a controlled inkjet printing of functional material. This has been done by using citric acid coated synthesized iron oxide nano particles in a dispersion optimized for inkjet printing. This part covers the inkjet printing process from the ink until the droplet hit the substrate. For a successful first part of the inkjet printing the droplet must hit its target with no redirected droplets caused by ink on the nozzle plate or satellite droplets. This is critical since a single redirected droplet can be enough to disable a printed electronic device to work. Some of the critical parameters for an inkjet ink will be (in the case of particle based ink) stability of the dispersion, pH, particle_aggregate size and its distribution, viscosity and surface tension of the ink.

Secondly work has been focused on controlling the ink on the substrate interactions and this will cover the inkjet printing process continuously from the first part of the work. This has been done with a commercial PEDOT: PSS ink. The main controlling parameters have been the surface tension and the viscosity of the ink. The substrate during the work has been polyimide and antistatic PET. Compared to paper substrates, the influence of surface roughness is small and no absorption of ink occurs.

Stabilization of iron oxide nanoparticles optimized for inkjet

The requirements on an inkjet ink are rather heavy. A particle based inkjet ink needs low viscosity, pH neutral, no sedimentation, mono-dispersed particle sizes and optimized surface tension and its properties needs to be constant for a long period of time (3-5 years). Dependent on printing conditions the requirements can vary. The sedimentation depends on particle size and specific density. Larger density differences between particles and carrier fluid requires smaller particles for continuous stability. Normally the size of the particles is also limited by the size of the nozzle orifice diameter. As a general rule the size of the particles should not be larger than 1/100 of the nozzle orifice diameter. A typical ink for inkjet printing has a particle size of 40-100 nm (both larger and smaller particles sizes exist). The major issue in the inkjet ink is normally not that the particle size from the beginning is too large but that aggregates forms in the ink. To prevent aggregates to form the ink needs to be stabilized. Two major methods are used for stabilizing the ink. Firstly a polymer can be coated on the particle surface and by that a steric stabilization can be achieved. Secondly, and the method used in this work, the stabilization can be achieved by charges on the particles. In dispersions an electrical double layer will form (in low electrolyte concentrations) and the particle will be shielded by a surface potential at a distance out from the particle where the first layer of non-stationary ions are found. The surface potential is often referred to as the ζ-potential when characterized. The ζ-potential can be useful for analyzing the stability of the dispersion. Dispersions with a larger positive or negative ζ-potential will in the case
of a collision between two or more particles/aggregates be less likely to see an adhesion between the particles/aggregates. This seen in the respect of the numbers of collisions occurring in a dispersion will give the stability of the dispersion where larger ζ-potential values will be more stable and form less aggregates than small ζ-potential values.

Since an inkjet ink should have a neutral pH a pure iron oxide surface is a disadvantage with its i.e.p. in neutral pH (i.e.p. → ζ-potential = 0). It is also desired to boost the ζ-potential and increase the stability. In order to increase the stability of the iron oxide nanoparticles a coating with citric acid was made. This was done by using 2.5 g of synthesized particles in 200 ml de-ionized water. Thereafter a diluted citric acid solution was added to the dispersion and the dispersion was vigorously stirred for 80 minutes in 70°C. The pH was kept at 8±0.1 by adding of NH₄OH.

The coating process was investigated by measuring the ζ-potential as a function of pH and this method is sensitive to a change in the particle surface structure in the dispersion. Different concentration of citric acid was used during measurements. The characterization of the ζ-potential was done by micro-electrophoresis using a Malvern Nano ZS. The instrument measure the electrophoretic mobility of the particles in the dispersion and results were thereafter converted to ζ-potentials by the use of Smoluchowski equation. Result can be seen in figure 1.

![Graph showing ζ-potential as a function of pH](image)

Figure 1: Zeta-potential as a function of pH for different citric acid concentrations in a 30 wt% glycerol/water mixture.

The dispersion was measured in a mixture of 30 wt% glycerol/water since this mixture was suited for inkjet printing. The non-coated iron oxide indicates an i.e.p. value of a bit higher than pH 5. With a concentration of citric acid 2.6 mmol/dm³ citric acid a small decrease in i.e.p. could be seen. The use of even lower concentrations did not give a change at all. The 2.6 mmol/dm³ concentration did not change the absolute value of the ζ-potential. 13 mmol/dm³ citric acid concentrations gave an i.e.p. value less than pH 3.
This result clearly indicates a change in the surface structure and the decrease in i.e.p. is expected. The absolute value of the higher citric acid concentration is also increased in neutral pH and this corresponds to a higher stability in the dispersion. To further investigate the influence of the ζ-potential in the dispersion the hydrodynamic size was characterized by the use of dynamic light scattering using the same instrument as for the ζ-potential measurements. The hydrodynamic size was first measured for different citric acid coatings. The pH during measurements was about 2.5 pH steps higher than the i.e.p. for pure iron oxide. Result from the measurements can be seen in figure 2.

![Figure 2](image_url)

Figure 2: Hydrodynamic size distribution as a function of citric acid concentration in water.

The result demonstrates the volume size distribution of the particles/aggregates for non-coated and citric acid coated iron oxide nanoparticles. A non-coated surface gave large aggregate size scattered over a broad size range. Particle sizes in the range of the non-coated iron oxide will experience a fast sedimentation and the received size distribution peaks will change fast. For a 2.6 mmol/dm³ concentration of citric acid the distribution was seen in a large peak between 15-100 nm and a small peak between 100-300 nm. The 13 mmol/dm³ concentration of citric acid gave only one size peak between 15-100 nm. In this result it can be seen that it is possible to use both citric acid coated dispersion for inkjet printing and the most suited dispersion is the higher concentration of citric acid. This concentration also meets the requirement of sizes less than 1/100 of the nozzle orifice diameter since the diameter on the test printer used was 21.5 µm. A final tuning was made on the most suited citric acid concentration when the size distribution as a function of pH was analyzed. Result can be seen in figure 3.
Figure 3: Hydrodynamic size distribution as a function of pH for iron oxide dispersions in a 30 wt% glycerol/water mixture.

As expected and in agreement with result found during ζ-potential measurements, the hydrodynamic sizes are smallest in neutral pH. They remain stable with a small change at pH 4.40. A pH close to i.e.p. will give a weak electrostatic repulsion and forming of aggregates. This can be seen in the pH 3.38 and also this is in agreement with expectations.

**Inkjet printing of stabilized iron oxide nanoparticles**

An aim for the inkjet printing was to be able to control the printing in a way that all droplets should hit its target (no misplacement of ink or other related problem). For the printing, iron oxide nanoparticles coated with a citric acid concentration of 13 mmol/dm³ was used in neutral pH. The particles were dispersed in a mixture of 30wt% glycerol/water. In order to achieve controlled inkjet printing Dodecylbenzene sulfonic acid (DBS) was used to decrease the surface tension. The printer parameters such as acoustic wave and ink temperature were optimized. A critical part of the optimization was the amount of added surfactant. No added surfactant was very difficult to eject and not suitable to print. A too high concentration surfactant caused the ink to flood on the nozzle plate with the effect of limited and re-directed ink during printing. This can be seen in figure 4a.

Figure 4a, b and c: Inkjet printing of iron oxide nanoparticles.
The individual inkjet droplets can be seen as black points on a paper substrate. The diameter of the droplet printed on a paper substrate is about 35 µm. In figure 4a a surfactant concentration of 1.0*10^{-3}M was used. Such high concentration leads to misplacing an uneven printing. In figure 4b and c a surfactant concentration of 6.5*10^{-4}M has been used. This concentration enables controlled printing of 35µm sized droplets with an error estimated to ± 5µm.

References


*Preparation of core-shell latexes for paper coatings*

*Mia Koskinen and Carl-Eric Wilén*

*Laboratory of Polymer Technology*

Core-shell latexes, composed of a core covered by a shell, can be prepared by a two-stage emulsion polymerization or seeded emulsion polymerization. Colloidal stability can be difficult to obtain in a core-shell polymerization because the composition of the surface and the bulk change dramatically during the polymerization process itself. The advantage of core-shell latexes though is their ability of having a composition of different monomers in core and shell, and thereby giving the particle tailor made properties for each application. Via core-shell polymerization it is also possible to get otherwise incompatible monomers into one particle or to add functionality either into the core or shell. One way of modifying plastic pigments is the use of crosslinking
agents. Crosslinking generally improves physical properties of the polymer. Improvements are most significant above the glass-transition temperature. For example thermal expansion and heat capacity are lowered and heat distortion temperature, tensile strength and refractive index are raised. Glass-transition temperature increases with increasing crosslink density.\textsuperscript{5-7} Latex with high degree of crosslinking in paper coating colour tends to reduce porosity and blister resistance, on the other hand, binding strength when latex is used as binder, increases and coating strength properties such as dry pick, wet pick and wet rub resistance will improve.\textsuperscript{4} Another way of adding value to the paper is incorporation of optical brightening agents (OBA) or fluorescent whitening agents (FWA). They can be used either in the pulp or in the coating. They absorb UV light and radiate the absorbed energy in the range of visible light thereby increasing the degree of whiteness experienced. The most common OBAs used in paper coating are derivatives of diaminostilbene.\textsuperscript{8-10}

Experiment

Novel core-shell latexes with a partially crosslinked hydrophilic polymer core and a hard hydrophobic shell of polystyrene were prepared in order to improve printability. Core-shell latexes were prepared by sequential addition of a monomer mixture of styrene, \textit{n}-butylacrylate and methacrylic acid using different crosslinkers to form the polymer core and styrene in the second stage to form the hard shell component. In addition, attempts were made to further improve optical properties by introducing a new polymerizable optical brightener 1-[(4-vinylphenoxy)methyl]-4-(2-phenylethylidencyl)benzene during polymerization either into the core or shell. The prepared core-shell latex particles were used as specialty plastic pigments for paper coating together with kaolin as the primary pigment. The runnability of paper coating formulation by either using a laboratory scale Helicoater or pilot scale JET-coating machine was very good. The produced coated papers were printed on both sides employing a heat set web offset (HSWO) printer in order to study the quality of image reproduction in terms of print gloss, print mottle, print through, etc. Overall the core-shell latexes improved the print quality. Furthermore, the results demonstrated that by optimizing polymer composition one can affect optical properties of coated paper whereas the type of cross-linker has a less pronounced influence on coated paper properties under investigation.

Core-shell latexes were prepared by a two-stage polymerization of styrene (S), butyl acrylate (BA) and methacrylic acid (MAA) in the core and styrene alone in the shell. Pre-emulsions were prepared of the monomers and they were fed into a 1L jacketed reaction vessel one after another and reacted under agitation at 80°C for 6 h. The tested crosslinking agents used in the core were ethylene glycol dimethacrylate (EGDMA), N,N–methylene bisacrylamide (MBA) and 1,1,1-trimethylol propane triacrylate (TMPTA). An optical brightening agent, 1-[(4-vinylphenoxy)methyl]-4-(2-phenylethylidencyl)benzene,
was synthesized of trans-4-hydroxystilbene and vinylbenzylchloride in the presence of potassium carbonate in acetone and washed and dried before mixing with the pre-emulsion. The synthesized core-shell latexes were used in coating colour preparation with kaolin as primary pigment. Coating trials were carried out on both laboratory scale with Helicoater and on pilot scale with a JET coating machine. Coated samples were calandered and conditioned before analysis.

Results

A series of core-shell latexes with varying compositions were synthesized. In the first series ten latexes were prepared and their particle sizes varied in a range of 113 to 283 nm depending on the composition of the synthesized latex. From selected latexes coating colours were prepared and as a reference one coating colour that did not contain any additional core-shell latex was used. Then the coating colours were used to coat (10 g/m²) LWC-paper on one side using a laboratory scale Helicoater and their paper performance characteristics were analysed. The results are summarized in Table I. Most of the core-shell dispersion formulations exhibited an improvement in gloss, IGT surface strength and surface roughness compared to the reference. We examined the effects of polymer composition contributing to paper properties such as gloss. The results from polymer composition indicate same kind of behaviour that is seen with styrene-butadiene latex investigated by Taber et al.¹¹ e.g. increase in gloss with increasing fraction of styrene units. On the contrary, decrease in butyl acrylate units leads to higher gloss. Consequently, having a high fraction of styrene units in the core-shell dispersion has a beneficial impact on paper gloss.

Table I. Latex compositions and particle sizes and paper properties for papers laboratory coated with sample latexes.

<table>
<thead>
<tr>
<th>Sample</th>
<th>S in shell g</th>
<th>BA in core g</th>
<th>MAA in core G</th>
<th>Particle size nm</th>
<th>Gloss %</th>
<th>PPS 10 µm</th>
<th>K&amp;N</th>
<th>IGT m/s</th>
</tr>
</thead>
<tbody>
<tr>
<td>Reference</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>58.4</td>
<td>1.10</td>
<td>8.2</td>
<td>0.28</td>
</tr>
<tr>
<td>Latex 1</td>
<td>60</td>
<td>20</td>
<td>2</td>
<td>209</td>
<td>70.0</td>
<td>0.91</td>
<td>8.3</td>
<td>0.35</td>
</tr>
<tr>
<td>Latex 2</td>
<td>60</td>
<td>20</td>
<td>6</td>
<td>113</td>
<td>69.2</td>
<td>0.95</td>
<td>5.9</td>
<td>0.33</td>
</tr>
<tr>
<td>Latex 3</td>
<td>90</td>
<td>30</td>
<td>6</td>
<td>184</td>
<td>68.7</td>
<td>0.98</td>
<td>7.0</td>
<td>0.37</td>
</tr>
<tr>
<td>Latex 4</td>
<td>60</td>
<td>40</td>
<td>14</td>
<td>155</td>
<td>63.3</td>
<td>0.98</td>
<td>6.2</td>
<td>0.33</td>
</tr>
<tr>
<td>Latex 5</td>
<td>75</td>
<td>40</td>
<td>2</td>
<td>275</td>
<td>68.9</td>
<td>0.98</td>
<td>7.3</td>
<td>0.34</td>
</tr>
<tr>
<td>Latex 6</td>
<td>75</td>
<td>30</td>
<td>14</td>
<td>125</td>
<td>70.0</td>
<td>0.98</td>
<td>5.8</td>
<td>0.26</td>
</tr>
<tr>
<td>Latex 7</td>
<td>90</td>
<td>30</td>
<td>2</td>
<td>283</td>
<td>68.3</td>
<td>0.93</td>
<td>7.0</td>
<td>0.35</td>
</tr>
<tr>
<td>Latex 8</td>
<td>90</td>
<td>20</td>
<td>14</td>
<td>166</td>
<td>70.4</td>
<td>0.92</td>
<td>6.2</td>
<td>0.30</td>
</tr>
<tr>
<td>Latex 9</td>
<td>75</td>
<td>40</td>
<td>10</td>
<td>166</td>
<td>67.1</td>
<td>0.96</td>
<td>6.0</td>
<td>0.27</td>
</tr>
<tr>
<td>Latex 10</td>
<td>90</td>
<td>20</td>
<td>10</td>
<td>140</td>
<td>71.1</td>
<td>0.91</td>
<td>6.6</td>
<td>0.29</td>
</tr>
</tbody>
</table>

Next we wanted to correlate the type of crosslinker used to various paper properties such as gloss, PPS surface roughness, brightness, K&N ink absorption and IGT surface
strength. The following three cross-linkers were tested in the core: ethylene glycol dimethacrylate (EGDMA), N,N –methylene bisacrylamide (MBA) and 1,1,1-trimethylol propane triacrylate (TMPTA). In all cases the amount of crosslinker used to partially crosslink the core was 0.33 wt-% of the total weight of all monomers in the recipe and the results are shown in Table II. The best gloss, brightness and smoothest surface were achieved with EGDMA, while the surface strength was weakest for EGDMA. TMPTA had the lowest gloss whereas MBA had the roughest surface. In general EGDMA seemed to exhibit the best balance of properties and was therefore chosen as the lead candidate for further testing in pilot trials.

<table>
<thead>
<tr>
<th>Crosslinker</th>
<th>Gloss %</th>
<th>PPS 10 μm</th>
<th>K&amp;N</th>
<th>IGT m/s</th>
<th>Brightness %</th>
</tr>
</thead>
<tbody>
<tr>
<td>EGDMA</td>
<td>61.20</td>
<td>1.20</td>
<td>12.1</td>
<td>0.14</td>
<td>75.9</td>
</tr>
<tr>
<td>MBA</td>
<td>60.30</td>
<td>1.40</td>
<td>11.1</td>
<td>0.17</td>
<td>69.2</td>
</tr>
<tr>
<td>TMPTA</td>
<td>56.80</td>
<td>1.27</td>
<td>12.3</td>
<td>0.17</td>
<td>69.9</td>
</tr>
</tbody>
</table>

Based on the aforementioned preliminary test series Latex 10 was modified to KALA 10 and up-scaled for coating, calendering and printing pilot scale trials. Two concentrations were tested: 4 pph (parts per hundred parts of main pigment by weight) and 8 pph. The reference contained no additional core-shell latex. Figure 1. Shows a scanning electron microscopy (SEM) image of coated paper from the pilot trial coated with KALA 10 (8pph) after calendering. Spherical latex particles are approximately of size 290 nm in diameter. Pseudo-hexagonal plates larger than 1 μm in the micrograph are delaminated Nugloss kaolin pigments.

![SEM image of coated pilot trial sample KALA 10 (8pph).](image)
The pilot trials proceeded without any fault occurrences and the overall runnability was very good. Z-strength (Scott Bond), PPS-surface roughness, gloss, mottling, print through and print density were analyzed. Selected results are presented in Table III. Z-strength diminished compared to the reference when we added 4pph KALA 10 latex whereas it was increased in the case of using 8 pph the same. PPS and print gloss were improved for the core-shell latex irrespective of concentration used, however, now the improvement was greater for the paper with lower concentration of KALA 10 latex. The loss of gloss in papers with 8pph compared to papers with 4pph could partially be attributed to its rougher surface – too high particle concentration cannot any more even out the surface. The optimal concentration of the sample latex is therefore dependent on the desired effects.

Table III. Some paper characteristics of papers from the pilot test.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Z-strength J/m²</th>
<th>PPS 10 µm</th>
<th>Print gloss %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Reference</td>
<td>346</td>
<td>1.90</td>
<td>63.8</td>
</tr>
<tr>
<td>KALA 10 (4pph)</td>
<td>341</td>
<td>1.74</td>
<td>66.6</td>
</tr>
<tr>
<td>KALA 10 (8pph)</td>
<td>354</td>
<td>1.81</td>
<td>65.5</td>
</tr>
</tbody>
</table>

Finally we wanted to further modify KALA 10 by incorporating an optical brightening agent within. The effect of 1-[(4-vinylphenoxy)methyl]-4-(2-phenylethylene)benzene as an optical brightener on paper coating was tested in two latexes: in Optikala 1 OBA was polymerized into the core and in Optikala 2 into the shell. Latexes with incorporated OBA improved brightness, although very little. Also gloss was improved. The results are seen in Figure 2. Though the improvement of brightness is small, we also get an advantage in reducing the need and cost for OBA carrier in paper coating colour when the OBA is already bound to the latex particle.

Figure 2. The effect of optical brightening agents on gloss and brightness.
Conclusions

We were able to prepare partially cross-linked core-shell latexes that improved printability. High styrene concentration and low butyl acrylate concentration in the latex resulted in good gloss. Different cross-linkers: ethylene glycol dimethacrylate (EGDMA), N,N –methylene bisacrylamide (MBA) and 1,1,1-trimethylol propane triacrylate (TMPTA), also affected paper properties to some extent. Best balance of properties was achieved with EGDMA. The latex performed well also in pilot scale trials. Additionally we were able to incorporate a novel optical brightening agent, 1-[(4-vinylphenoxy)methyl]-4-(2-phenylethylene)benzene into either core or in shell of the core-shell latex. By modifying paper coating we can either create a more favorable paper surface for functional printing or directly add functionality to it.

References


**Modification of Polymeric Films – Ion- and Electron Conducting Materials**

*Carl-Johan Wikman and Carl-Eric Wilén*

*Laboratory of Polymer Technology*

The central themes during the year 2007 have been electron beam irradiated polymeric films as substrates for grafting, electrochromic polymeric materials and electron conducting and semiconducting polymeric materials.

The goal of the electron beam irradiation experiments has been

- to understand the factors governing the grafting of irradiated films in order to control their properties;
- to create a set of materials with hydrogen- or ion-conducting properties for use in for example fuel-cells, separation techniques and sensors.

The electron beam equipment has been used to irradiate different polymer films (for example PE, PP, PVDF, ETFE). The radicals formed on the surface and to a depth of about 250 μm are either reacted with ambient oxygen to form peroxides and hydroxyperoxides or used for direct radical polymerization in an inert atmosphere. The latter technique is more demanding as ambient oxygen must be excluded completely. The peroxide path is interesting because the irradiated films are stable for months when stored in a freezer.

Grafting reactions with different vinyl monomers have been carried out, for example with styrene, vinyl benzyl chloride (VBC), and acrylic acid (AA).

The degree of grafting (weight increase as percent of starting weight) is dependent on the film, solvents, monomers, reaction temperature, and other factors. The grafting parameters of different systems have been investigated.

The grafted polymer film in itself does not necessarily have ion-conducting properties. Grafted AA is one example of the contrary, but the acid is a weak acid and the proton conducting properties are not good. Grafted AA can on the other hand be used as a starting point for further grafting reactions, polyaniline is one example. Two ways to achieve ion-conduction have been investigated. VBC grafted PVDF films were quaternized with trimethyl ammonium chloride (TMA), leading to Cl⁻ conduction, and styrene grafted PVDF was sulfonized with chlorosulfonic acid, leading to H⁺ conduction.

Within the FunMat project the paper as a substrate is important. Cellulose in itself has been used as a carrier for active conducting components, and research along this line is ongoing. It is more likely though that the paper will be used as a substrate for active components. Then the paper surface has to be modified by suitable coatings. One route apart from the more traditional paper coating is lamination of the paper with a polymeric film. The film can be modified prior to or after lamination as described above.
The other themes during 2007 are more directly inspired by outspoken FunMat goals. We have been working with some conducting polymers with the long term goal to produce polymers of specific properties. These include conductivity, color change upon change in red-ox state or pH, and solubility. The solubility characteristics are important in ink formulations and therefore in printing processes. Within FunMat so far, commercial conducting printing inks have been used, but at some point we may need to make tailor-made polymers for novel ink-formulations.

We have made some experiments to produce electron conducting materials:

- PEDOT-ferritosylate polymerized in situ on PVDF and PET; this leads to highly conductive films by a simple process where reactants are spread on a film sheet which is then heated in an oven;
- PVDF-g-AA further grafted with PANI; this was seen as a route to covalently bound PANI.

A conducting viologen doped with methyl iodine was also prepared. The work is continuing with new grafting methods and other possible routes to ion-conducting membranes.

*  

**Adding functionality by coating and printing to paper based substrates**

Roger Bollström and Jouko Peltonen  
**Laboratory of Paper Coating and Converting**

Compared to normal graphical printing where the visual properties of the final print are the most important parameters we now have to focus on the functionality. As every rotating printing method is based on dots this is a problem when printing functionality, for example conducting materials, to get a homogenous and even layer. Other important properties for paper based substrates are good barrier properties especially against water and vapor since water is a conductor itself and therefore affects the conductivity of the final print. The most critical parameters regarding printing on the substrates are the roughness parameters at different length scales and surface properties like surface energy, contact angle and wetting of substrate.

Several different printing methods can be used to build up our final devices and for each method the rheology and tack parameters have to be adjusted. The solvent used in the inks are also important, by choosing different solvents the surface energy, wetting and drying can be adjusted.
As a first study the rheology of Pedot solution was adjusted to meet the requirements for offset print method, but unfortunately with poor results. The first objective was to find methods to increase the viscosity of the polymer solution. Different amounts of CMC were tested to achieve a viscosity high enough. The problem with the CMC was the low tack; the ink spreading was not possible when the rolls slipped during the spreading. Slipping also occurred during the print, especially on the coated papers. Printing on copy paper and Yupo film seemed to be possible. Different alcohols, ethanol, iso propanol and ethylene glycol were also mixed with the polymer solution in different amounts to achieve a higher tack. The alcohols reduce the surface tension and made the ink spreading work better, but when adding high amounts of other stuff in the solution, it makes the already low polymer concentration even lower. This again means that a higher amount of the “ink” has to be put on the printing roll, but a high amount is not possible since it will not penetrate into the paper but will be pressed to the sides of the printing roll. The best way to increase the viscosity seemed to be evaporation of the water. By evaporating away the water also the polymer concentration becomes higher and allows a lower amount of ink on the printing roll.

Conductive silver ink was also printed with inkjet on different substrates, Mylar and PET plastic films, coated paper, lacquered paper and glass. The conductivity was measured as a function of roughness but also as a function of sintering temperature. To achieve the best conductivity of printed silver the silver has to be sintered which means that the particles are melt together. High temperatures are not possible to use on paper substrates and therefore the effect of temperature in a region 0-120° for different times were studied. The print results and roughness were analyzed with AFM. Detailed results are available on request.

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Use of Confocal Laser Scanning Microscopy and Computer Model to Understand Ink Cavitation and Filamentation

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In an offset printing process, the ink film splitting event has some relationship to the tack forces experienced by the paper and has an important impact on formation of ink filaments. Already in 1962, Fetsko and Zettlemoyer \cite{1} concluded that the most important ink factor for the gloss and uniformity of prints is the size of ink filaments during the ink splitting when ink is transferred from printing rolls to paper. The filament
remains on the paper surface are the starting point for ink leveling and setting, print gloss and eventually the basis for the quality of the prints. However, ink filaments are difficult to image due to their short life time and fine length scale. Limited work has been reported on the parameters that influence filament size and methods to characterize this size. The direct observation of filaments, even on a laboratory scale, is challenging because of the fine length scale and the high speeds. Attempts of filament observation using high speed cameras or video have been reported in the literature [2, 3]. However, the filament “remains”, what is left after the filaments break, are easier to characterize.

This work attempts to image ink filament remains and to quantify some of their characteristics such as height and diameter as other parameters, such as printing speed, ink amount and fountain solution type are changed. Printed samples were prepared using a laboratory printability tester at varying ink level and operating settings. Influence of printing speed, ink grammage and fountain solution were probed. Rhodamine B dye was incorporated into fountain solutions to aid the detection of them. The prints were then imaged with a Confocal Laser Scanning Microscope (CLSM) and images were further analyzed.

Materials and methods

The ink used in this study was a heat set cyan ink, ACPC1059, provided by Sun Chemicals. Two different fountain solutions were tested to make ink emulsions for printing. The first fountain solution was alcohol-free Varn Majesta 635 Fountain (Day International, Inc.). The second fountain solution is alcohol (isopropanol) containing Adit Mouillage (10A1/000093) Fountain Solution (Siegwerk). In order to characterize the fountain solutions with CLSM, they were marked and made fluorescent by adding a dye, Rhodamine B (Wako Pure Chemical Industries, Ltd). 5 mg of Rhodamine B was added to 20 ml of fountain solution. The ink and emulsions were printed using qa CRK laboratory printability tester (Model MPT800, Kumagai Riki Kogyo Co. Ltd., Tokyo, Japan) on smooth Mylar film in order to mimic a smooth coated paper surface but at the same time to restrict the absorption and penetration of the ink into the substrate. The emulsification process for fountain solutions was as follows: Predetermined amount of ink was measured onto rolls and inking was started to spread the ink evenly on rolls. After 30 seconds of ink distribution, the fountain solution was added in drops within 30 seconds. Then a time of two minutes was allowed for the emulsification to take place. After this, the emulsified ink was transferred onto a printing roll and then printed. The transfer time of printing roll on the laboratory printability tester is about 1 minute. Constant pressure of 1000N was used while making the prints, as earlier research suggests that the nip loading does not have a significant effect on filament size or the size distribution [2].
Printing parameters were varied as to see the influence of these changes to filament remain size. The three main parameters to vary were fountain solution, ink grammage and printing speed as shown in Table 1.

Table 1. Varied printing parameters.

<table>
<thead>
<tr>
<th>Fountain solution 50% added on rolls</th>
<th>Ink grammage g/m²</th>
<th>Printing speed m/s</th>
</tr>
</thead>
<tbody>
<tr>
<td>No fountain</td>
<td>2</td>
<td>1</td>
</tr>
<tr>
<td>alcohol free</td>
<td>4</td>
<td>4</td>
</tr>
<tr>
<td>Alcohol containing</td>
<td></td>
<td>8</td>
</tr>
</tbody>
</table>

Another variable used in this study was the influence of blanket roughness on ink splitting and filament remain size. A green blanket with relatively rough surface and hardness of 77-78° Shore A, supplied by Day International, Inc., was used to print on a smooth film. The blanket material was imaged with an Environmental Scanning Electron Microscope (ESEM) (Electroscan E3) to show the surface texture, Figure 1. Magnification was x1000 was obtained for the image. The samples did not require any pretreatment before imaging on ESEM. The image clearly shows that the surface is uneven with high and low points occurring. The surface seems to have some porosity, which will allow air to be present in the nip and contributes to the compressibility of the blanket in the printing nip.

![ESEM image of green blankets surface. The white scale bar at the bottom of the image is 10 μm.](image)

After printing the samples were taken to be imaged with Confocal Laser Scanning Microscopy (CLSM, Leica TCS SP2 Confocal microscope) to obtain images and quantify surface roughness characteristics. The time between printing and imaging was about 15-20 minutes. This was the shortest possible delay time due to physical restrictions.
Results and discussion

Addition of a fountain solution, either type, does not have a significant effect on filament remain size. Figure 2 shows a typical image. In these figures, the blue region with “contours” are the ink film surface with contours. A number of hills are apparent in various shapes. The length scales of these hills do not change as fountain solution used in the ink. Red spots of Rhodamine B dye in the images seen in Figure 2 b) indicate where the fountain solution is located. Some of the fountain has probably evaporate and just left open bubbles/cavitations behind. A number of drops are found throughout the ink.

Figure 2. Samples printed using printing speed 1 m/s resulting 2 g/m² of ink on film : Emulsion made with alcohol containing fountain solution b) A blown up image where red spots of Rhodamine B dye used as marker in the fountains is clearly visible. The white scale bar at the bottom of the image is 150 μm.

Figure 3. Effect of printing speed to filament remain size from left to right and 8 m/s.

Figure 3. shows that higher speeds seem to increase the filament size. The 1 to 4 m/s is not as clear as it is from 4 to 8 m/s. Slightly more ink, 0.03 c