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Chemical modification of fine paper base with amphiphilic copolymer

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KEYWORDS: ToF-SIMS, Paper Coating, Stearyl Methacrylate, Calendering

SUMMARY: A set of hydrophobically-modified water soluble methacrylate copolymers was synthesized for chemical modification of paper surfaces. Viscosity and water solubility of the polymers were tailored to different coating methods. Fine paper was coated by two different methods, either by using a blade coater or by using the polymer as an additive in a calendering process. Paper was coated with a very small amount of polymer, 0.16 g/m², which is much lower than the typical coating amount. Chemical surface analysis was used to confirm the uniform spreading of the polymer on the surface of the paper. An even distribution of the polymer on the surface was obtained and this was confirmed with ToF-SIMS. It was possible to increase the contact angle for the fine paper surface with a small amount of polymer.

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Paper surface coatings are typically mixtures that consist of different components including pigment, binder and different additives. Coating amount varies depending on the application but is generally rather high, about 15 g per m². (Järnström et al., 2010) After coating, the paper surface is typically calendered in order to improve, for example, gloss and surface smoothness. (Schuman, Wikström, & Rigdahl, 2004) The properties of calendered paper can be enhanced by wetting the paper surface prior to calendering, (Granberg, Nylund, & Rigdahl, 1996) and one way to further improve paper surface properties could be to use additives in the moistening water.

Several groups have reported hydrophobization of hydrophilic surfaces with water soluble amphiphilic polymers, and amphiphilic polymers containing poly[2-(dimethylamino) ethyl methacrylate] (PDM) have been reported to effectively hydrophobize surfaces (Nurmi et al., 2009). It has also been shown that it is possible to modify paper surfaces chemically with a small amount of water soluble amphiphilic polymers. (Ibrahim et al., 2006) Amphiphilic polymers are typically synthesized through block formation (de Banez, Robinson, &

Armes, 2000) but can also be made using long aliphatic grafts (Liu, Ni, Fang, & Zhou, 2009).

Polymers used in calendering water must be water soluble up to a few percent concentration since the amount of wet coating on the surface must be rather low, less than 10 g solution per square metre. (Granberg et al., 1996) Stearyl methacrylate polymers have been reported to be effective modifiers of boxboard (Vaha-Nissi, Kervinen, Savolainen, Egolf, & Lau, 2006) but there have been no reports on the use of stearyl methacrylate polymers in water solution. Also, polymers containing stearyl methacrylate and DMAEMA have been prepared previously, but they are not water soluble on their own. (Liu et al., 2009) However, stearyl methacrylate can be made water soluble by introducing ionic co-monomers. (Akay & Tong, 2001) Therefore, stearyl-based polymers could be used as coating polymers on paper surfaces. In order to be able to apply water soluble polymers on surfaces in conventional processes, the viscosity of the solutions must be sufficiently low at relatively high concentrations. (Di Cola et al., 2004; Jamieson & Telford, 1982; Lim, Cho, Kim, & Chang, 2007; McKee, Hunley, Layman, & Long, 2006)

Time of flight secondary ion mass spectrometry (ToF-SIMS) is surface-sensitive mass spectrometry (Michel & Castner, 2006) with a measuring depth of 1-2 nm. (Belu, Graham, & Castner, 2003) ToF-SIMS is widely used in biopolymer analytics (Belu et al., 2003) but it is also a practical tool to characterize paper surfaces. (Fardim & Durán, 2003; Fardim, Gustafsson, von Schoultz, Peltonen, & Holmbom, 2005; Kokkonen, Fardim, & Holmbom, 2004) The carbon in cellulose fibre gives a strong signal in analysis, and in order to identify components on the surface they have to have a molecular structure with a signal that deviates from that of cellulose. (Fardim et al., 2005) Many polymers used in paper applications contain a cationic group originating from ammonium ion, and in these cases nitrogen-containing components can be identified with ToF-SIMS (Fardim & Holmbom, 2005), for example, the amine present in cationic starch. Another good component to identify on paper surfaces is fluorine-containing molecules. (Cunha et al., 2007) A high tendency of fluorine to ionize makes it a good marker polymer. (Belu et al., 2003) One problem with ToF-SIMS can be its lack

of quantitiveness. The surrounding matrix affects the susceptibility to ionization but this is often not a big problem in polymer analytics and it can be taken into account by using internal standards. ToF-SIMS is not only used for identification of components but also for chemical imaging. In imaging, the resolution originating from the primary beam is 150 nm, (Belu et al., 2003) which is enough to be effective in measurements of surfaces wood fibres.

In this study, fine paper was coated with hydrophobically-modified water soluble polymers. A set of statistical co-polymers containing cationic [2-(methacryloyloxy)ethyl] trimethyl ammonium iodide (META1) and stearyl methacrylate (SMA) or fluorodecyl methacrylate (FMA) with varying hydrophobicities and solution viscosities were prepared with conventional radical polymerization. Solution viscosities were characterized with dynamic rotational rheometry. These hydrophobically-modified water soluble polymers were applied to paper sheets with two methods: with a blade coater at lab scale, and with a spray coater as an additive in the calendering process. The purpose of the belt calendering was to study the effect of calendering temperature on polymer behaviour. The aim was to make the paper surface less wetting with chemical modification with a very small amount of the copolymer on the surface without physically modifying the surface characteristics. Coating with pure water was done as a reference, because water itself can change the surface chemistry of a paper sheet. TOF-SIMS analysis of prepared paper sheets was done to study the spreading of polymers on the surface, and it was also used to confirm the presence of the polymer on the surface of the paper.

Materials and Methods

The chemicals used and their suppliers were: 2-(dimethylamino) ethyl methacrylate (DMAEMA), diphenyl ethylene (DPE), deuterated chloroform, D₂O, and deuterated acetone, Aldrich; basic alumina, methylene iodide (MeI), azobis isobutyronitrile (AIBN), and tetraethylene glycol dimethyl ether (TEGDME), Fluka; stearyl methacrylate (SMA), tetrahydrofuran (THF), hexane and acetone, BHD Prolabo; iso-octane, Rathburn; 3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,10-hexadecafluoro-1-decyl methacrylate (FMA), DuPont (commercial name Zonyl). DMAEMA was purified by removing inhibitor by filtration through basic alumina. Other chemicals were used without further purification. All chemicals were of reagent grade.

Uncoated wood-free base paper used in this study had the following specifications: The grammage was 81.5 g/m² and the moisture content was 5.7% (measured in standard conditions: T = 23°C, RH

50%). This uncoated fine paper base (FP) was supplied by Stora Enso Oulu Mill, Finland.

Nuclear Magnetic Resonance Spectroscopy (NMR)

NMR spectra were analysed with a 300-MHz Varian Gemini 2000 and the solvent used was deuterated chloroform (CDCl₃). Conversion during synthesis was followed with ¹H NMR spectroscopy as decrease in the height of vinyl peaks, and the structure was confirmed with ¹³C NMR. Formation of cationic segments through post-modification was measured in D₂O and in deuterated acetone by ¹H NMR.

Size Exclusion Chromatography (SEC)

Purified polymers were analysed with size exclusion chromatography (SEC) using chloroform with 2% triethylamine (TEA) as eluent. Elution speed was 1 ml/min through the following column system: PLgel pre-column and PLgel 10⁴ Å, 10⁵ Å, 10³ Å and 10² Å columns supplied by Polymer laboratories. Relative changes in molecular weight were determined with a Waters RI-detector (refractive index) against polystyrene standards.

Synthesis of water soluble copolymers

Methacrylate co-polymers were prepared with radical polymerization using AIBN as initiator. The molecular structures are presented in Fig 1. The amount of hydrophobic monomer was varied, and was the basis on which the resulting polymers were named (e.g. PFMA5Q contains 5 mol-% FMA). Both of the monomers (DMAEMA and SMA, or DMAEMA and FMA) and the initiator were weighed in a reaction vessel. A dry atmosphere was achieved with three vacuum-argon cycles. The polymerization was carried out at 60 °C. Conversion of the polymerization was followed with ¹H NMR. Polymerization was carried out for three hours or until the conversion reached 90%. The resulting polymer was precipitated in hexane or iso-octane depending on the content of hydrophobic segment. The molecular weight of the polymer was measured with size exclusion chromatography (SEC) against polystyrene standards. Molecular weight characterization was done before following the methylation reaction.

Cationic species were introduced to the copolymer with methyl iodide. A dilute solution (1g/100 ml) of methacrylate co-polymer and tetrahydrofuran was prepared at ambient temperature. Three equivalents of methyl iodide for each equivalent of DMAEMA were added while stirring, and the reaction mixture was stirred overnight at ambient temperature. Cationic polymer was precipitated from the solution during reaction when the amount of incorporated cationic subunits was high enough. The remaining

solution was filtered and washed with acetone. The quantitative reaction could be confirmed by the appearance of signal at 3.2 ppm in ^1H NMR.

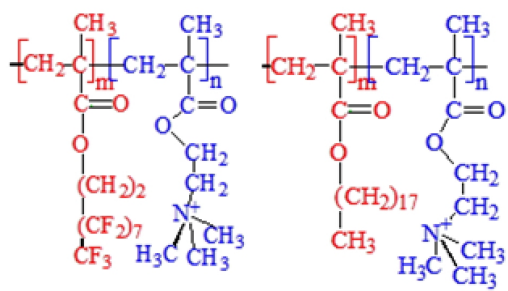


Fig 1. Repeating units of PFMAQ (left) and (PSMAQ) (right).

Stearyl methacrylate co-polymer with a lower molecular weight was synthesized otherwise in the same way except using diphenyl ethylene (DPE) as a molecular weight controller. Synthesis and detailed characterization of the resulting polymers are described elsewhere. (Vesterinen, Rich, & Seppälä, 2010)

Coating of papers at lab scale using a blade coater

Polymer was applied to the FP surface using a 1% solution diluted in distilled water containing 7.5 mmol NaCl to reduce viscosity and stabilize the ionic environment of the solution. The solution was applied to the surface by blade coating. The papers were dried in a heat circulating oven at 105 °C for one minute. The amount of solution applied was measured gravimetrically, and the amount of polymer on the surface was found to be about 160 mg/m².

Preparation of coating solution for belt calendering

Cationic PSMA co-polymer was dispersed in water by mixing with a magnetic stirring bar. In order to obtain a homogeneous mixture at 4% concentration, the mixture was heated to 90 °C while stirring. The solution was cooled down and the viscosity of the solution was measured.

Belt calendering

The web calender used is designed to study calendering phenomena on a laboratory scale. The calender nip was formed between a steel roll and a soft polymer roll (92 Shore D). The paper web length was 6 metres and web width 130 mm. The distance between the spray unit and nip was 1.5 metres. The paper web was fastened to form an endless loop by splicing the end with a piece of tape. The system identified the paper loop by recognizing the dark tape on the web. With the computer-guided system it was possible to adjust the running speed and nip temperature, choose the

number of nips, determine the sequence of nip loads, and set the spray treatments before the nips.

The spray unit was a UniJet 650044-TC and the orifice size was 0.43 mm, the pressure was 70 bar and the flow rate 0.9 l/min. The nozzle distance from the paper web was 100 mm and the fan width was the same as the web width (130 mm). Nip pressure was 100 kN/m and the number of nips was taken 4 times. The time delay between spray and calender nip was 0.2 to 0.6 s. Calendering temperatures were 120 and 170 °C and the calendering speeds 2.5, 5.0 and 7.5 m/s. Because the flow rate of the spray unit was constant, the amount of liquid applied to the paper was dependent on calendering speed. The transferred amount of liquid was approximated by measuring paper grammage before and after spraying, and the amount of transferred polymer was calculated based on the amount of transferred liquid. The surface temperature of the calendered paper was measured with infrared thermometer after the calendering nip, and at 120 °C nip temperature, the temperature on the paper surface was 55-60 °C, whereas at 170 °C the surface temperature of the paper was 60-70 °C, depending on the calendering speed.

Solution viscosity studies with rotational rheometry

Rheology of the polymer solutions was measured with a stress-controlled rotational rheometer (TA Instruments AR-G2) with a Peltier heating element and a circulated water cooling bath. Viscosities of blade coater solutions were measured according to the following procedure: Steady shear viscosity with continuous ramp was measured from 0.1 to 10 000 s⁻¹ shear rate. The measurement was performed at 23 °C with 40 mm parallel plate geometry using a 150 µm gap size. The viscosity of belt calendering solution was measured according to following procedure: Shear viscosity was measured from 0.002 to 1000 s⁻¹ using recessed end cylinder geometry with 14 mm and 15 mm rotor and stator radii, respectively.

Time of Flight Secondary Ion Mass Spectrometry (ToF-SIMS)

The ToF-SIMS spectrometer used in this work was a PHI TRIFT II (Physical Electronics, USA). High-mass-resolution spectra over a mass range of 0-2000 Da were acquired using a Ga primary ion source with an applied voltage of 15 kV and a primary ion current of 600 pA. The acquisition time for the samples was 10 min. The area used for the spectral measurements was 2.5 mm x 2.5 mm. Charge compensation with low energy electrons was used during the measurements. More details on the use of this measuring system are reported elsewhere. (Juhanaja et al., 2007; Tervahattu et al., 2005)

Contact angle and surface energy measurements

A CAM 200 goniometer system (KSV Ltd.) was used to perform contact angle, surface energy and polarity measurements. As model liquids, five solutions with known surface tensions and its components were used: water, ethylene glycol (EG), tricresyl phosphate, formamide, and diiodomethane. (Della Volpe & Siboni, 11 January 2000) A drop of liquid placed on a substrate was displayed on a monitor and the contact angle of the drop was measured by image analysis and reported as an average of three measurements. Surface energies were calculated from the contact angle data by the software by Fowkes' method. (Fowkes, 1964) Detailed description of the technique is described elsewhere. (Kontturi et al., 2009)

The method divides surface free energy into two components: dispersive (hydrophobic) and polar (hydrophilic), and uses the geometric mean approach to combine their contributors. When combined with Young's equation, the Fowkes' equation yields a form according to Eq 1.

$$\gamma_l (1 + \cos \theta) = 2 \left(\sqrt{\gamma_l^d \gamma_s^d} + \sqrt{\gamma_l^p \gamma_s^p} \right) \quad [1]$$

θ is the contact angle, γ_l is the surface tension of the liquid and γ_s is the surface tension of solid, i.e., the surface free energy. Superscripts d and p refer to the dispersive and the polar component, respectively. The total surface free energy is the sum according to Eq 2.

$$\gamma_s = \gamma_s^d + \gamma_s^p. \quad [2]$$

Results and Discussion

Tailoring polymer properties for surface treatment

PSMAQ and PFMAQ were prepared through radical polymerization with AIBN with or without DPE.

The resulting polymers and their properties are listed in Table 1. Molecular weights were measured before post modification. Molecular weights were over 200 000 g/mol for those polymers in which DPE was not used as controlling agent; using DPE reduced molecular weights down to < 100 000 g/mol. The pre-polymers were further modified with methyl iodide in order to get a cationic backbone and increase solubility in water.

Viscosities of the coating solutions were determined with rheometry. Viscosities of strong polyelectrolytes can be effectively reduced by adding salt, and the amount of salt needed was determined before preparation of the solutions. Solution viscosities of 1% solutions of PSMA5Q at different salt concentrations are reported in Fig 2. It is clear that viscosity decreases with increasing NaCl content. The biggest decrease occurs at salt levels between 1 and 10 mM. Solution viscosity was determined for all coating solutions, and the results are reported in Table 1. An intermediate salt concentration for 1% coating solutions was chosen, and thus a 7.5 mM NaCl solution was used in lab scale blade coating. It can also be seen here that the viscosities of these polymers strongly increase as the amount of hydrophobic graft increases.

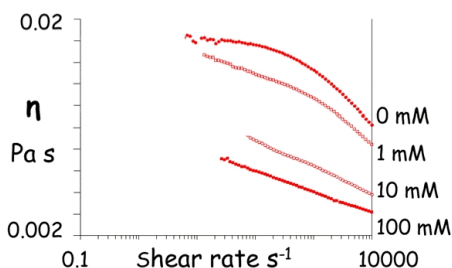


Fig 2. Effect of NaCl on viscosity of PSMA5Q. Salt levels are 0, 1, 10 and 100 mM.

Table 1. Properties of polymers and coating solutions.

Polymer	Hydrophobic	SEC	Coating solution			Coating method
	segment	M _n	Conc.	Salt (NaCl)	Viscosity **	
	mol %	kg/mol	mass-%	mM	mPas	
PFMA5Q	4.9	200	1	7.5	3.2	Blade
PFMA9Q	9.1	~200*	1	7.5	4.4	Blade
PFMA16Q	16.3	380	1	7.5	210	Blade
PSMA5Q	4.9	~200*	1	7.5	6.0	Blade
PSMA9Q	9.1	~200*	1	7.5	2300	Blade
PSMA13Q	13.0	51	4	0	4.1	Spray

* some crosslinking in the sample, measurement only indicative

** zero shear viscosity

At pilot scale, stearyl-containing copolymer was determined to be the most suitable polymer for this environment since it is commonly used in pulp and paper applications. It was also found to be suitable for quantification of coating amount, because of clear signals originating from the ammonium group. On the one hand, the aim was to modify the surface hydrophobicity using a polymer containing the highest possible content of hydrophobic segment that can be achieved without losing water solubility. On the other hand the amount of solution that can be applied to the surface in the moistening water is limited because of web break and low drying capacity. Therefore the polymer concentration should be as high as possible in order to minimize the amount of moistening water. The high molecular weight PSMA copolymers studied with blade coating were not suitable for the calendering process because the viscosity was too high; therefore viscosities needed to be lowered. It is not possible to add salt for modifying the solution viscosity in the calendering process so the viscosity of the solution had to be modified by modifying polymer properties.

In order to tailor the amount of polymer coating on the paper surface in the calendering process the concentration of the coating solution had to be as high as possible while maintaining appropriate viscosity properties for the process. The challenge was that increasing hydrophobicity in the copolymer increases the viscosity, especially at high concentrations, (Vesterinen et al., 2010) but solution viscosity of a polymer can effectively be reduced by decreasing molecular weight. (Jamieson & Telford, 1982) Solution viscosities are reported in Table 1 and it can be seen that the viscosity of the coating solution was effectively reduced by modifying the average molecular weight. The solution viscosity was studied with increasing concentrations of PSMA13Q copolymer and it was found that the polymer was soluble up to more than 20% mass concentration. A relatively modest increase in viscosity up to 5% concentration was observed, and therefore a 4% solution had sufficiently low viscosity and was prepared for use in belt calendering. (Table 1) A more detailed description of the solution rheology of PSMA13Q was published earlier by our group. (Vesterinen et al., 2010)

Characterization of paper surface after blade coating

Lab scale coating of fine paper base with hydrophobically modified water soluble polymers was done with a blade coater. The amount of added polymer on the surface was 160 mg/m². The approximate thickness of the polymer layer on an

even surface would be 160 nm. Typically, the amount of coating in conventional processes is much higher. Mass analysis was performed on the coated fine paper surface and an example of a mass spectrum is presented in Fig 3. In TOF-SIMS analysis the signals are detected at 1-2 nm depth. (Tokareva et al., 2007) From the wood-based surface only groups not present in cellulose can be identified. In the studied copolymers, such groups are nitrogen (Fardim & Holmbom, 2005) and fluorine-based (Cunha et al., 2007) segments, even though nitrogen compounds are also present in pure paper. A systematic set of signals with increasing mass, originating from the 3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,10-hexadecafluoro-1-decyl methacrylate graft, can clearly be identified. A cationic group originating from [2-(methacryloyloxy)ethyl] trimethyl ammonium iodide (METAI) can also be identified, and the main signal is the same as has been identified from cationic starch (Fardim & Holmbom, 2005) but also mass fractions containing an additional oxygen were found. Additionally, signals from the polymer backbone (Belu et al., 2003) can be identified in the higher mass region.

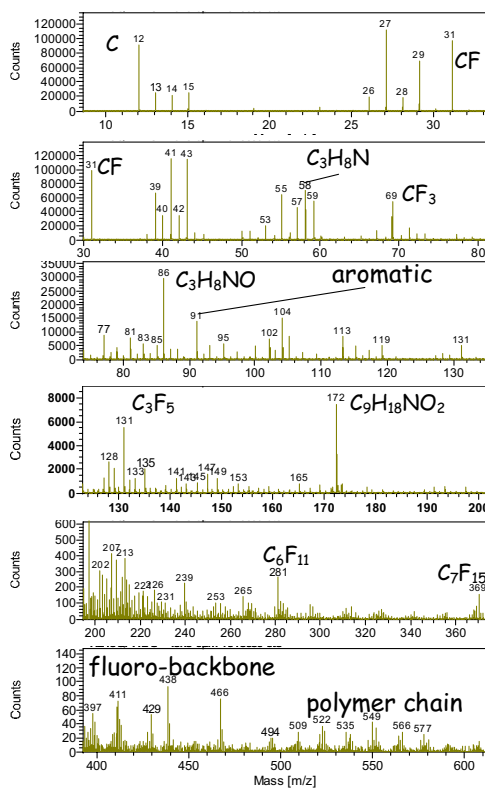


Fig 3. An example of a mass spectrum of FP base coated with PFMA9Q.

Table 2. Intensities of representative ions on blade coated surfaces.

Copolymer	Hydrophobic segment mol-%	Ions detected in ToF-SIMS a. u.							Relative amounts	
		C ₃ H ₈ N	CF	C	CH ₃	C ₂ H ₃	C ₃ H ₅	CF/CH ₃	C ₃ H ₈ N/ CH ₃	C ₂ H ₃ /CH ₃
PFMA5Q	4.9	85.6	15.9	16.6	10.6	42.0	4.6	1.5	8.1	4.0
PFMA9Q	9.1	58.2	48.4	49.5	14.8	59.4	4.2	3.3	4.0	4.0
PFMA16Q	16.3	53.0	84.1	69.9	15.8	53.6	3.1	5.3	3.4	3.4
PSMA5Q	4.9	64.8	0.3	1.9	12.5	59.8	8.2	0.0	5.2	4.8
PSMA9Q	9.1	51.3	0.2	2.8	15.5	85.7	7.3	0.0	3.3	5.5

Quantification of identified signals

Relative amounts of the most representative mass signals are listed in *Table 2*. The amount of CF increases with increasing molar amount of fluoro-containing monomer in the methacrylate polymer. The presence of fluorine can also be seen in the increase in the amount of C on the surface. At the same time, the amount of C₃H₈N decreases with increasing content of CF. Also the CF values relative to CH₃ signal increase. In all samples the C₃H₈N/CH₃ ration is decreasing with decreasing amount of ammonium ions in the polymer. Also a correlation between the amount of stearyl group and the ratio of C₂H₃/CH₃ was found. ToF-SIMS is not a method that is typically used for quantitative analysis and further conclusion about molecular orientation was excluded in this research.

Copolymer spreading on paper surface

Chemical imaging with ToF-SIMS was used to evaluate the spreading of the coating polymer on the paper surface. The resolution in imaging originating from the primary beam is 150 nm. (Belu et al., 2003) In *Fig 4*, the presence of nitrogen and fluorine on the surface of coated papers are visualized based on their characteristic signals. The variation in brightness observed in the surfaces originates from the topography of the paper surface. Nitrogen and fluorine compounds follow the topography variations caused by the sample and they are evenly distributed on the surface of the fibre, whereas calcium has an uneven distribution. It can be concluded that the very small amount of polymer applied to the surface has spread and then distributed on the surface fibers evenly – it did not form polymeric clusters, and the polymer was adsorbed on the surface.

Application with belt calendering

The copolymer was applied to the surface as a 4% solution. PSMA13Q copolymer did not cause any web breaks or sticking in the coating process. The maximum amount of water that can be sprayed on a surface is limited to about 10 g/m² because the belt calendering technique demands rapid drying of the surface. (Granberg et al., 1996) In this study the

amount of coating polymer was varied with speed and three different amounts of solution were transferred to the surface. Additionally, the effect of heat treatment on the coated surface was examined by carrying out the calendering at 120 °C and 170 °C. The calendering temperatures were chosen so that the upper temperature would be above and the lower one below the transition temperatures of the coating polymer.

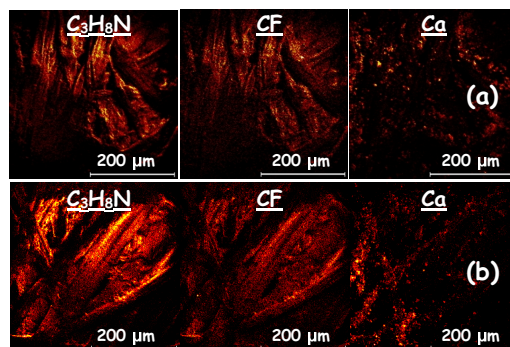


Fig 4. Distribution of C₃H₈N, CF and Ca on FP base surfaces shown by TOF-SIMS chemical imaging. (a) = PFMA5Q and (b) = PFMA9Q.

A change in the hydrophobicity of the paper can be estimated with contact angle measurements, and the results are presented in *Table 3*. It can be seen that water contact angle is strongly increased with polymer coating. Treatment with pure water also increases the contact angle but the effect is rather small. The lowest coating amount was enough to get less hydrophilic paper surface, and increasing the amount of coating did not have a significant effect on the water contact angle. The most effective modification was achieved when polymer coating was combined with heat treatment. It can be observed that the heat treatment further increases the contact angle of paper sheets coated with polymer solution. The same phenomenon has been observed previously by Nurmi et. al. in a study where a nanolayer coating of methacrylate copolymer on a silica surface was annealed, and annealing was found to enhance the chemical modification by increasing the contact angle of the surface. (Nurmi et al., 2010)

Table 3. Contact angle and TOF-SIMS quantification of PSMA13Q in belt calendaring.

Calendering Speed m/s	T °C	mass water g/m ²	mass polym. mg/m ²	Ions in ToF-SIMS a.u.				C ₃ H ₈ N/C ₂ H ₃	* WCA (°)	Surface Energy mN/m		
				C ₃ H ₈ N	C ₃ H ₈ NO	CH ₃	CH ₃ O			γ_s	γ_s^d	γ_s^p
7.5	120								29			
2.5	120								32			
7.5	170								29			
2.5	170								29			
7.5	120	3.3	0	8.52	0.93	5.28	7.67	0.4	34	58	33	25
2.5	120	14.7	0	9.78	1.13	5.05	8.05	0.5	47	54	35	19
7.5	120	3.3	140	24.11	5.82	6.75	2.96	0.8	65	48	38	9
2.5	120	15.5	650	20.95	5.16	4.56	3.69	1.2	57	49	35	14
7.5	170	3.3	0	9.69	1.12	4.34	6.55	0.5	38	57	33	23
2.2	170	14.7	0	10.38	1.36	5.41	7.26	0.5	50	53	35	17
7.5	170	3.3	140	33.07	5.76	6.98	2.39	1.3	82	45	42	3
2.5	170	15.5	650	33.66	6.92	7.06	2.46	1.3	85	44	42	2

* WCA = Water contact angle. The maximum deviation in the measurements was $\pm 5^\circ$.

Evaluation of changes in surface energy

The effect of the polymer coating was analysed further by calculating surface energy based on a set of different solvents. Surface energy in Table 3 is reported as total energy (γ_s), polar component (γ_s^p) and dispersive component (γ_s^d). γ_s^d is considered to describe the Van der Waals forces, of which the dispersive interaction is predominant component in condensed phase. γ_s^p describes electron donor-acceptor interactions. (Ogwu et al., 2005) The most significant effect was seen in the polar component of the surface energy, γ_s^p , where polymer coating decreased surface energy by half and temperature treatment further decreased this component to close to zero. A similar effect was already observed in the contact angle measurements with water where polymer coating was giving a strong increase in values.

Evaluation of changes in Effect of temperature and polymer amount in ToF-SIMS surface energy

Polymer behaviour in belt calendaring was also studied with ToF-SIMS, and the results are presented in Table 3. Previously it was found that the contact angle increases when papers are calendered at a higher temperature. When polymer coated samples are compared in ToF-SIMS, the increase in contact angle is seen as strengthening of the nitrogen signal. Intensities of high-temperature calendered samples are strengthened by 40% compared to paper calendered at a lower temperature. The chosen calendaring temperatures were rather moderate, and the surface temperature of the coated paper was well below the softening temperature of the chemical components present in wood fibre. (Schuman et al., 2004) It is obvious that

the possible mobile components in the polymer are stearyl graft and methacrylate backbone, in contrast to the cationic ammonium group, which is a salt. The stearyl group has a melting point of around 40 °C (Vesterinen et al., 2010), whereas methacrylate has no melting point but softens at a glass transition point. (Vesterinen et al., 2010) The higher calendaring temperature is already at the point where the stearyl group is softened. Mobility of the soft segment is seen as strengthening of the cationic group, and stearyl groups are more levelled and not as much on the surface.

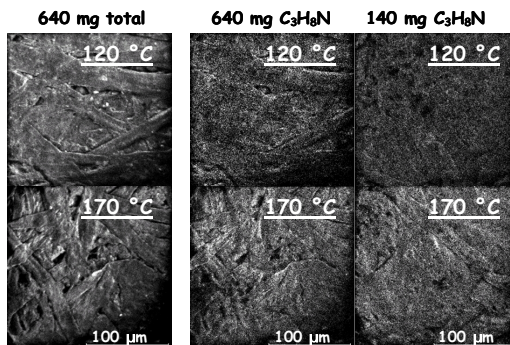


Fig 5. Chemical imaging of ToF-SIMS visualized as total ions (left) and C₃H₈N (right) from paper surface calendered at 120 °C (top) and 170 °C (bottom) and with two different amounts of polymer coating.

Chemical imaging was also performed for belt calendered samples. The C₃H₈N nitrogen group that is seen in ToF-SIMS measurements and originates from polymer was analysed and compared with total ion signal originating from the paper surface. Spreading on the surface can be seen in Fig 5. Just as previously reported for surface energies, there was only a minor difference in relative intensities of nitrogen signals when coating amounts were

compared but a clear increase in intensity is observed when the calendering temperature is increased from 120 °C to 170 °C, which can be seen as a brightening of the nitrogen signal (*Fig 5*).

It is very interesting that in the same samples where contact angle was increased, the nitrogen signal is strengthened, even though ammonium ion has hydrophilic nature. The most likely explanation for the increased contact angle is that the temperature treatment makes the surface more smooth, which has been observed also by Nurmi et al. (Nurmi et al., 2010) It is possible in these samples that the polymer molecules are flattened and no molecular orientation occurs, but actually no difference in polymer spreading was observed at the two different temperatures with ToF-SIMS imaging, and the polymer was evenly distributed on the surface. Here it must be pointed out that the resolution limit of this technique is 150 nm, and changes may occur that are under the resolution limit of this technique.

When the two coating methods, lab scale blade coater and spray coating in calendering, are compared, there is a difference in the level of intensity of the signals, e.g. the C_3H_8N signal is much stronger when using the blade coating method. The reason might be that the viscosity of the coating solution in spray coating is lower or that the molecular weight of the polymer is lower, so that the polymer does not penetrate the fibre pores as much as with spray coating. However, the reason for increased intensity in blade coating could be as well due to differences in chemical environments, namely because NaCl was used as a viscosity reducing agent in coating solutions.

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Conclusions

Hydrophobically modified water soluble polyelectrolytes having solution properties tailored for different coating methods were synthesized. An evenly distributed polymer layer with a thickness of approximately 160 nm could be prepared on a paper surface both with a blade coater and by using moistening water in belt calendering. The tailored polymers were completely soluble in water, had sufficient viscosity and they formed thin layers on the surface of the paper even though the coating amount was very small. An even distribution of polymer could be achieved and this was qualitatively confirmed with chemical imaging performed with ToF-SIMS. ToF-SIMS was also used to quantify the effect of the amount of coating used as well as that of the amount of hydrophobic graft in the coating polymer. The amount of hydrophobic segments on the paper surface increased as the molar composition of the corresponding segment increased.

In contrast to molecular composition, there was no correlation between the amount of polymer coating and the signal in mass spectrometry. Therefore, the lowest amount tested, 0.16 g/m², was sufficient for chemical modification of the fine paper base, resulting in nanolayer coating. This was also confirmed with contact angle measurements, where no correlation between contact angle and the amount of polymer coating was observed. However, contact angle could be increased by heat treatment of the paper surface. When the same samples are studied with ToF-SIMS, in those samples where the increase in contact angle is seen, the signal of the cationic ammonium group is strengthened.

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