

Nanoclay Plating of Cellulosic Fiber Surfaces

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ABSTRACT: A basic problem in making cellulose-reinforced composites is achieving a dispersion of cellulosic fibers in an often olephinic polymer matrix. Drying cellulosic fibers results in the formation of fiber flocs/nodules because of their strong interfiber bonding, and this makes the hydrophilic cellulosic fibers difficult to disperse in a hydrophobic matrix material. One common approach to alleviate floc formation is to adsorb cationic surfactant onto anionically charged cellulose, which reduces the interfiber bonding, decreases floc formation and gives better compatibility with the matrix. In this report, a different approach is taken, namely to adsorb nanoclays onto the cellulosic fibers, and thereby reduce the natural hydrogen-bonding affinity between fibers. In a second report, the same technology will be shown to be advantageous to decrease floc formation in olephinic composites reinforced with cellulosic fibers. This article summarizes experiments aimed at optimizing the chemistry of deposition of montmorillonite clay onto fiber surfaces. The aim was to optimize the chemical conditions for the heterodeposition of the anionic clay onto

cationically charged fluff pulp. The experiments were designed to provide a theoretical framework for the deposition of the nanoclay onto the pulp fibers. High M_w p-DADMAC and an exfoliated clay (achieved by passing the clay through a homogenizer) were used. As expected, a certain degree of charge overcompensation by adding an electrolyte was necessary to bring about deposition. The adsorbed amount of clay could be calculated from the charge balance between the overcompensated charge and the net clay charge, constituting the theoretical framework for nanoclay heterodeposition. As expected, montmorillonite clay greatly destroyed the joint strength between fibers (determined by evaluating the strength of paper made from treated fibers). The surface coverage (determined by ESCA) was shown to be a linear function of the attached amount of clay, and ~3% clay was required to fully cover the fiber surfaces. © 2008 Wiley Periodicals, Inc. *J Appl Polym Sci* 108: 887–891, 2008

Key words: deposition; montmorillonite; cellulose fiber; composite; nanocomposite; surface modification

INTRODUCTION

Cellulose composites have a long history. Already at the beginning of the 20th century, Baekeland prepared composite materials, for the fabrication of large quantities of sheets, tubes, and pipes for electrical purposes, usually fiber-reinforced phenol–formaldehyde or melamine–formaldehyde resins. There is also a long history of reinforced composite materials derived from fibers such as jute, flax, and hemp.

Today there is a renewed interest in the use of natural fibers for the reinforcement of technical plastics and coatings for the automotive and packaging industries. These are two widely different segments to which considerable research and development efforts are being devoted today.

The resurgence of interest in composite materials during the 1990s is due to the increasing costs of plastic materials and the environmental advantages of using renewable materials.

Composite technology utilizes the high stiffness and high strength of filamentary materials, of which cellulose is the only example. Cellulose composites include everything from straw-reinforced clay materials to cellulose fibers in radial tyres. There are, however, a number of technical challenges related to both the processing and the end-use performance of such composites, associated with the use of cellulosic fibers. These problems include fiber flocculation, moisture sensitivity, fiber–matrix adhesion, and cellulose degradation at high processing temperatures. Surface engineering of fibers may alleviate some of these problems through chemical/biochemical methods. This particular field was also recently reviewed by Lindström and Wågberg.¹

The field of nanocomposites literally exploded when Toyota researchers successfully developed nanoclay/nylon nanocomposites for under-the-hood applications for the automotive industry.² Bio based nanocomposites are a more recent addition to the field.^{3–5}

In this contribution, it will be shown that wood fibers can be plated using nanoclays. In this way, the natural hydrogen-bonding affinity between fibers can be significantly reduced, enabling nanoplated

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fibers to be used in various applications such as improving fluff pulp quality.⁶ The idea is to use nanoplated cellulosic fibers in polymer composites and this will be reported separately.⁷

The principle of nanoplating is to recharge (charge over-compensation) cellulosic fibers with a cationic polyelectrolyte and then adsorb a negatively charged nanoclay. Critical issues such as the influence of type of electrolyte and the electrolyte concentrations necessary to achieve a workable process will be outlined and discussed.

MATERIALS AND METHODS

Materials

The pulp used in the experiments was Vigorfluff A from Korsnäs, Nordic softwood with traces of birch: 65% pine, 35% spruce; kraft pulping process; bleaching sequence: OOD(EO)DD. This pulp was extracted with acetone to remove extractives, after which the pulp was washed with 0.01M HCl for 30 min followed by deionized water, 0.001M NaHCO₃, and deionized water again. The reference pulp, treated with montmorillonite, was the Korsnäs Vigorfluff S.

The swelling clay used was Kunipia F. This clay was swollen for 24 h in deionized water, disintegrated at a concentration of 4 g/L and finally homogenized in a high-pressure homogenizer, Mini-lab type 8.30H (APV Homogenizer group). The clay was then allowed to settle and a clear aqueous phase (clay concentration = 3.8 g/L) was collected and used in the subsequent experiments. The supernatant phase was always transparent and did not scatter light. Hence, homogenization appears to be an efficient means of achieving exfoliation.

Some experiments were also performed using the clay used at Korsnäs, Hydrocol MD (CDM). In the experiments with this clay, the clay was allowed to swell for 24 h and then directly used.

Methods

Charge determination on pulp and clay

The total charge of the pulp was determined using conductometric titration on a 702 SM Titrino (Metrohm), and the surface charge was determined by polyelectrolyte adsorption⁸ on a 665 Dosimat (Metrohm), in deionized water, with a high-molecular weight poly-DADMAC ($M_w \approx 500,000$). The adsorption of poly-DADMAC was also measured at various electrolyte concentrations to determine the degree of charge overcompensation.

The charge ratio is defined as the measured charge divided by the total charge, and it was determined at different electrolyte concentrations.

The charge of the montmorillonite clay was determined with a charge reversal experiment in the Mütek PCD 03-titrator (Mütek Analytic GmbH, Germany) with a low-molecular weight poly-DADMAC ($M_w \approx 60,000$). The cationic demand to the zero point of charge was taken as the total charge of the clay.

Adsorption isotherms of poly-DADMAC on montmorillonite clay and of clay on cellulosic fibers

To determine the maximum amount of poly-DADMAC, which it is possible to adsorb onto the fiber surface, an adsorption isotherm was prepared. To aliquots of 0.5% fiber slurry, poly-DADMAC ($M_w \approx 500,000$) was added in different amounts. The mixtures were stirred for 30 min and then filtered through a no. 3 filter paper (Munktell). The amount of poly-DADMAC not adsorbed onto the fibers was measured in a charge reversal experiment (Mütek PCD 03-titrator). Adsorption isotherms were prepared for different electrolytes and different electrolyte concentrations.

The adsorption isotherm of bentonite clay onto the cellulosic fibers was obtained in the same way as the poly-DADMAC isotherm. The fibers were pre-adsorbed with 1.5 mg poly-DADMAC per gram fiber and the clay adsorption was carried out with process water at Korsnäs Paper Mill during a contact time of 10 min.

Surface analysis with electron spectroscopy for chemical analysis

Three fiber samples with different amounts of bentonite clay attached (2, 10, and 20 mg/g), a sample with clean fibers, and a clay sample were sent to YKI (Institute for Surface Chemistry) for electron spectroscopy for chemical analysis (ESCA). The method measures the different amounts of chemical elements present at the surface of the sample (5–10 nm deep). The aim of the analysis was to investigate how much of the fiber surface could be covered with the clay. The analysis was performed on an AXIS Integrated Imaging XPS.

RESULTS AND DISCUSSION

Adsorption of poly-DADMAC on pulp fibers

The idea behind this investigation was to recharge the negatively charged fibers using poly-DADMAC and then adsorb the negatively charged nanoclay. Hence charge overcompensation is a prerequisite to obtain a cationically charged fiber. Poly-DADMAC interacts with cellulose through charge interaction,⁸ and in deionized water the adsorption is stoichio-

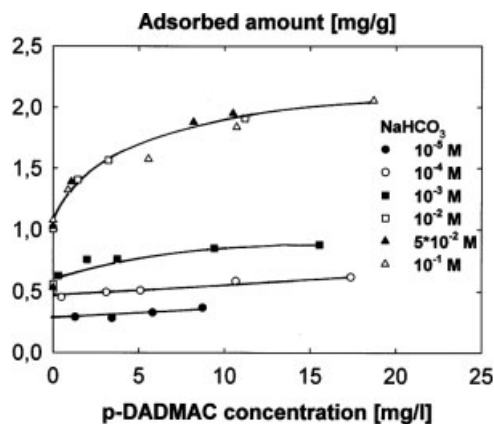


Figure 1 Amount of poly-DADMAC adsorbed onto the pulp at different concentrations of NaHCO₃.

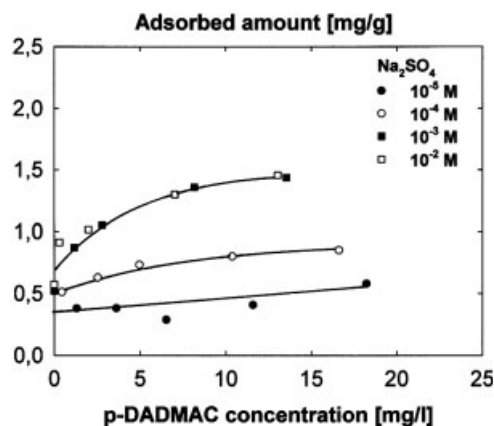


Figure 3 Amount of adsorbed poly-DADMAC onto the pulp at different concentrations of Na₂SO₄.

metric with respect to the accessible charges on the fibers and the poly-DADMAC. In the presence of an electrolyte, the adsorption increases, leading to charge overcompensation, and finally the adsorption decreases to zero at high electrolyte concentrations. It was therefore important to determine the adsorption of the poly-DADMAC at different electrolyte concentrations in order to be able to assess the optimum conditions for adsorption of poly-DADMAC and hence the conditions for adsorption of the nanoclay. Another objective was to investigate the stoichiometry of the nanoclay adsorption.

The adsorption isotherms of high *M_w* (0.5 MDa) poly-DADMAC onto the used pulp at different concentrations of CaCl₂, NaHCO₃, and Na₂SO₄ are shown in Figures 1–3. This poly-DAMAC is of sufficiently high *M_w* not to penetrate the cell wall of swollen cellulose fibers.⁸

To determine the surface charge density of the cellulose fibers, the adsorption isotherms are extrapolated back to zero polymer concentration (to com-

pensate for swelling of the polymer on the fiber surface at higher polymer concentration).^{8,9}

From the extrapolated isotherms, the charge adsorption and the charge ratio (ratio of surface charge to total charge) were determined for the different electrolytes and the charge ratios thus calculated are given in Figure 4. The total charge of the pulp was determined by conductometric titration to be 35.2 μequiv/g. The surface charge is 0.05 times this value (see Fig. 4), i.e. 1.76 μequiv/g.

Hence, Figure 4 gives the charge overcompensation at different electrolyte concentrations.

Adsorption of nanoclays onto cationized cellulosic fibers

In the next series of experiments, adsorption isotherms were obtained for the Kunipia F nanoclay onto fibers which had been cationized with high *M_w* poly-DADMAC under various electrolyte conditions.

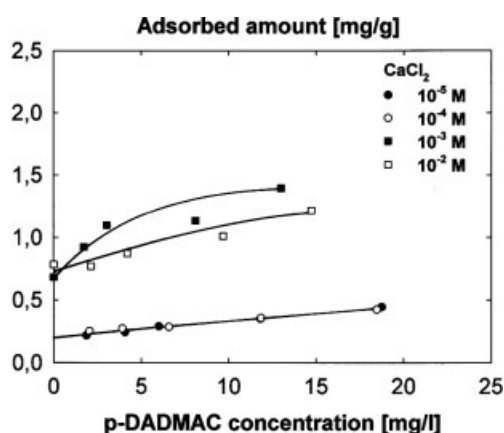


Figure 2 Amount of adsorbed poly-DADMAC onto the pulp at different concentrations of CaCl₂.

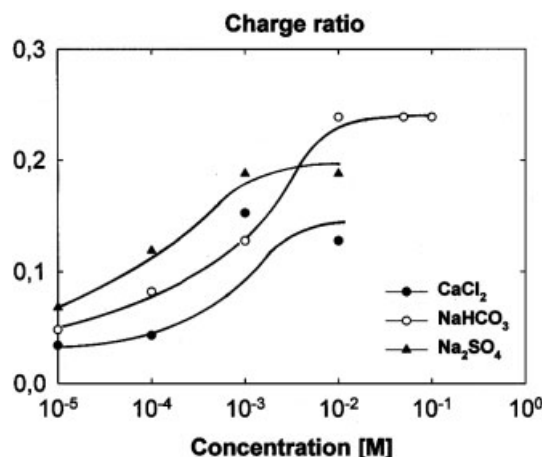


Figure 4 Charge ratio for adsorption of high *M_w* poly-DADMAC on the pulp at different electrolyte concentrations for various electrolytes.

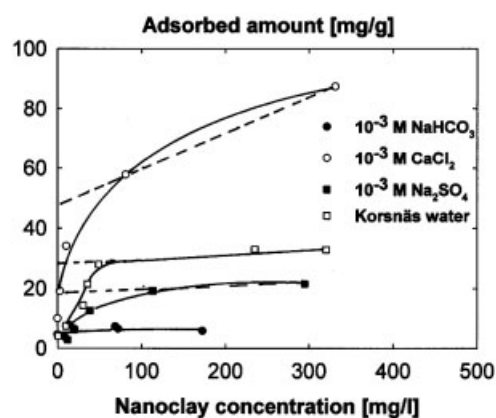


Figure 5 Amount of Kunipia F adsorbed onto Vigorfluff VFS treated with 1.7 mg/g p-DADMAC in 0.001M NaHCO₃, 0.001M CaCl₂, and 0.001M Na₂SO₄ and in process water from Korsnäs Paper Mill.

After adsorption of the poly-DADMAC, the fibers were washed with an excess of the corresponding electrolyte to remove the polymer in the supernatant solution. The adsorption isotherms for pulps treated with 1.7 mg/g poly-DADMAC in 0.001M NaHCO₃, 0.001M CaCl₂, and 0.001M Na₂SO₄ are given in Figure 5.

The second item of information needed to make a comparison of the stoichiometric relationships is the charge of the Kunipia F nanoclay at different electrolyte concentrations. This was determined using a charge reversal titration with a poly-DADMAC with a M_w of 60,000. The results are given in Table I.

It is obvious that the charge determined in this way decreases with increasing ion concentration. Theoretically, it is not expected that the charge would decrease with increasing electrolyte concentration (monovalent ions) as the charge of the clays is determined mainly by isomorphous substitution in the clay lattice. It is therefore probable that charge condensation takes place, because of the high surface charge density of exfoliated clays.

TABLE I
Charge of Kunipia Nanoclay at Different Electrolyte Concentrations

	Charge (μ equiv/g)	Theoretical deposition (mg/g)	Experimental deposition (mg/g)
NaHCO ₃ (M)			
0.00001	380		
0.0001	262		
0.001	257	10	5
0.01	190		
CaCl ₂ (M)			
0.001	107	42	48
Na ₂ SO ₄ (M)			
0.001	246	18	20
Korsnäs water	163	42.5	30

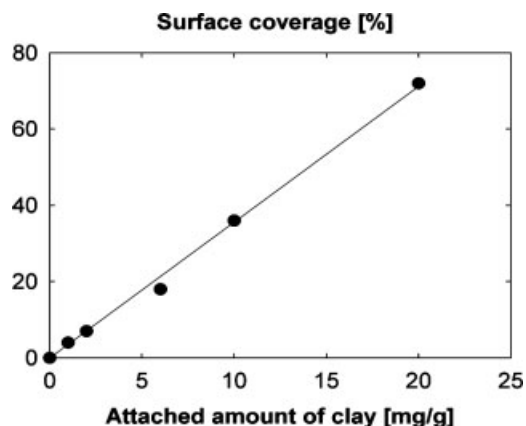


Figure 6 Surface coverage of fibers, as determined by ESCA vs. adsorbed amount of clay.

The amount of adsorbed clay was then compared with the theoretical amount calculated on the basis of the charge conditions in the various systems. These calculations were done as follows—exemplified with 0.001M CaCl₂.

When the total amount of added poly-DADMAC was 1.7 mg/g, the adsorbed amount was about 1.0 mg/g (Fig. 2). The charge density of poly-DADMAC is 6.2 μ equiv/mg.

The excess charge is therefore 6.2–1.76 μ equiv/g = 4.44 μ equiv/g. The charge of Kunipia F in 0.001M CaCl₂ is 107 μ equiv/g. Therefore, assuming stoichiometry 4.44/107, a maximum deposition of 42 mg is expected. This may be compared with the value of about 48 mg/g shown in Figure 6, determined by back extrapolating the adsorption isotherm.

The charge of Kunipia in Korsnäs water is 163 μ equiv/g. Amount of poly-DADMAC adsorbed in Korsnäs water was 1.4 mg/g. The excess charge was 8.68–1.76 μ equiv/g = 6.92 and the theoretical adsorption was therefore 6.92/163 g/g = 42.5 mg/g, compared with the value of 30 mg/g determined experimentally, Figure 5. In the same way, the theoretical adsorption capacity under other conditions was calculated and the results are given in Table I. Overall, these calculations show that there is a qualitative agreement between the theoretical values calculated in this way and the experimental data.

Paper handsheet properties

To assess the influence of montmorillonite on fiber-fiber bonding, handsheets were made with different amounts of Kunipia F nanoclays added in 0.001M CaCl₂. The results are summarized in Table II. As expected, the strength of the sheets was severely reduced when Kunipia F was adsorbed onto the fibers, because the clay prevents hydrogen bonding between the fibers. From the ESCA-measurements

TABLE II
Strength Properties of Paper Made from Kunipia F
Nanoclays-Treated Pulps

Added (adsorbed) amount of Kunipia (mg/g)	Sheet density (kg/m ³)	Tensile index (Nm/g)	Elongation to rupture (%)	Work to rupture (mJ/g)	Tensile stiffness index (kNm/g)
Reference paper	438	12.8	1.4	129	2.23
2(2)	433	11.4	1.2	95.8	2.13
5(5)	427	10.5	1.0	75.9	2.11
20(15)	465	3.75	0.5	11.7	0.9

(see below), it is obvious that the deterioration in strength is related to the degree of which the surface is covered with clay.

ESCA-investigations

ESCA measurements on fibers treated with Kunipia F nanoclay are given in Figure 6. ESCA is a surface selective analysis, that determines elemental composition with a typical analysis depth of 2–10 nm.

Fibers pretreated with poly-DADMAC were treated with different dosage levels of the clear aqueous phase of exfoliated montmorillonite clay.

ESCA measurements give the relative elemental composition of the fiber surface and the ratio between the Si signal/Al signal (markers for clay) and

the C3 signal (O–C–O or C = O types of carbon, a marker for cellulose). The surface coverage was calculated taking the mean value of the Si/C3 signal and the Al/C3. The results are displayed in Figure 6, which reveals there is a linear relationship between the adsorbed amount of clay and the surface coverage.

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