MOLECULAR INTERACTIONS BETWEEN MODEL CELLULOSE SURFACES AND INK – INFLUENCE OF SURFACE ENERGY AND SURFACE STRUCTURE ON ADHESION

Jennie Forsström¹, Malin Eriksson² and Lars Wågberg²

¹TetraPak R&D AB, Ruben Rausings gata, SE-22186 Lund, Sweden
²Department of Fibre and Polymer Technology, Royal Institute of Technology, (KTH), SE-10044 Stockholm, Sweden

ABSTRACT

The influence of surface roughness and surface hydrophobicity on ink detachment of water-based flexographic ink was studied. It was shown that increased surface roughness and an increased surface hydrophobicity both had a negative effect on ink detachment. The increased surface roughness was suggested to increase the molecular contact area between ink and cellulose and thereby also to decrease ink detachment. Ink cellulose interaction was evaluated from interfacial energies and contact angle measurements. A new technique in which the adhesion properties between ink and the model cellulose surface were directly measured using a Micro Adhesion Measurement Apparatus (MAMA) was also used. Upon increasing the hydrophobicity of the model cellulose surface it was shown that the work of adhesion between ink and model cellulose surfaces decreased. At the same time the interfacial energy between cellulose and ink increased, as did the inter-
facial energy between cellulose and water resulting in a lower degree of ink detachment.

**INTRODUCTION**

Surface interactions between cellulose and printing ink are of importance during printing, as a smooth surface gives a more uniform print, and during ink removal in paper recycling as a high adhesion between ink and cellulose might cause problems during ink detachment. With the rapid development of progressively accurate model surfaces for fibers it is becoming easier to study interfacial interactions between cellulose and other substrates [1–3].

Over the years it has been debated what mechanism controls the adhesion between ink and cellulose. In this respect, surface energy has a central role, as the wetting of cellulose by the ink is important for the final ink-cellulose interaction. Another component influencing the overall interaction is the molecular contact area. A larger molecular contact area allow for a larger interdiffusion and entanglement of binder molecules of the ink and molecules from the amorphous part of the cellulose. A large molecular contact area also increases the probability for chemical reactions between ink and cellulose.

According to Israelachivili and Kendall [4, 5] the total energy change, $W_{cw}$, associated with the separation of cellulose ($c$) and ink ($i$) in water ($w$) can thermodynamically be described by:

$$ W_{cw} = W_{ci} + W_{ww} - W_{cw} - W_{iw} = \gamma_{cw} + \gamma_{iw} - \gamma_{ci} = W_{ci} - \gamma_w (\cos \theta_{cw} + \cos \theta_{iw}) $$

where $W$ represents the work of adhesion or cohesion for the different components, $\gamma$ is the interfacial or surface energy and $\theta$ is the contact angle between water and the respective components. If the work of adhesion and cohesion are the only determining factors for ink release, $W_{cw} < 0$ would indicate spontaneous ink detachment from cellulose.

Andreasson and Wågberg [6] studied ink-cellulose interactions between model cellulose surfaces and offset ink by determining the interfacial energies from contact angle measurements and the Lifshitz-van der Waals acid/base approach [7, 8]. They concluded that decreasing the surface energy of the model cellulose surface had a negative effect on the ink detachment efficiency. There are drawbacks with this technique, as interdiffusion, entanglement and chemical bond formation are not taken into account. Also, porous substrates such as cellulose are difficult to evaluate via contact angle measurements.
In recent years, development of a new class of novel experimental methods allows for measurement of the intrinsic strength of an adhesive joint between solids. These methods, broadly classified as JKR-type (Johnson, Kendall and Roberts) experiments, are based on the JKR – theory of contact mechanics [9]. Several investigators have employed this method to measure the work of adhesion $W$ between elastomeric materials [10–12], in which a hemispherical cap is brought into contact with a smooth surface and the changes in contact area (i.e. contact radius $a$) are recorded as a function of the applied load ($F$) as described in Equation (2).

$$a^3 = \frac{R}{K} \left[ F + 3\pi WR + \sqrt{6\pi WRF + (3\pi WR)^2} \right]$$  \hspace{1cm} (2)

where $K$ is the elastic constant of the system and $R$ is the equivalent radius of the non-deformed sphere, for the arrangement with a sphere pressed against a flat surface. Upon separating the surfaces, a pull-off finally occurs. The load required to separate the surface from contact is called the pull-off force, $F_s$, and from a measurement of this force the pull-off work of adhesion, $W_{\text{min}}$, can be calculated, Equation (3):

$$F_s = \frac{3}{2} \pi RW_{\text{min}}$$  \hspace{1cm} (3)

The most commonly used surfaces are silicon oxide wafers, mica and glass [11–18] and the modifications of these surfaces have been numerous. Rundlöf et al. [19] also applied this technique to cellulose systems in experiments where a PDMS cap was contacted with a mica surface upon which 10 layers of cellulose had been deposited in order to evaluate the interaction between cellulose and PDMS.

Crosslinked poly(dimethylsiloxane) (PDMS) caps, developed by Chaudhury and Whitesides [11] are the most frequently used hemispherical surfaces. Recently, modified caps have also been developed in which the cap is coated with a polymer [10]. This gives a unique possibility to study the adhesion properties between almost any two substances as long as they both fulfill requirements such as smoothness, elasticity, cleanliness, and the coated PDMS cap maintaining its original elastic properties.

In the present study, the surface energy of the model cellulose surfaces was varied before printing and ink detachment studies. The influence of surface roughness was also studied by preparing cellulose surfaces from solutions of different concentration. A new technique to evaluate ink-cellulose
interactions is presented and direct adhesion measurements between ink and cellulose were conducted using MAMA, allowing both the thermodynamic work of adhesion and the receding work of adhesion to be determined.

MATERIALS AND METHODS

Materials

Model Surfaces – Model cellulose surfaces were prepared by spin-coating a solution of dissolved cellulose onto either a transparent glass slide or an oxidised silicon wafer according to an earlier outlined method [3, 20]. Surfaces were stored in a desiccator before use. To obtain model surfaces with different surface roughness, cellulose solutions of various concentrations were spin-coated onto the supporting material. Different surface energies were obtained by treating the cellulose surfaces with propyltrichlorosilane (98 %, Aldrich) in a gas phase reaction under vacuum, as described by Chaudhury and Whitesides [7]. To ensure that treating the treatment did not alter the surface roughness the surfaces were investigated using AFM.

Ink – The flexographic ink used was 82 Aquajet black ink (~15 wt% Pigment (CI PB 07), ~25 wt% Acrylate (Joncryl 90), ~2 wt% Defoamer, ~1.5 wt% Poly Ethylene wax) from A/S Torda Fabrikker, Lierstranda Norway. The corresponding ink varnish for 82 Aquajet black ink (pigment free ink) was also used. Joncryl 90 is a styrene-acrylic copolymer emulsion with the following specifications; Mol. mass (wt.av.) >200000, Viscosity (25°C) 260 mPa.s, T_g 110°C and it contains of 50–60 wt% deionised water 40–45 wt% styrene acrylic latex and 2–5 wt% ammonium hydroxide according to the supplier.

PDMS caps – PDMS hemispherical caps were prepared from poly(dimethylsiloxane) (182 silicon elastomer, Dow Corning, USA) and a curing agent (182 curing agent silicon elastomer, Dow corning USA). Curing agent (1 parts by weight) was added to (10 parts by weight) under vigorous stirring. Droplets of the reaction mixture were placed on a glass slide treated with fluorodecyltrichlorosilane (Aldrich) and then cured for 1h at 105°C, producing caps with a radius of approximately 1 mm. The cured caps were extracted in heptane for about 12 hours to remove unreacted monomer. To obtain ink coated PDMS caps, the surfaces of the cured and extracted PDMS caps were oxidised in air plasma for 15 minutes using a plasma cleaner (Model PDC 002, Harrick Scientific Corporation, New York, USA). Ink varnish, ~10 μl (20 wt%), was then spin-coated onto the plasma modified PDMS surface to ensure a uniform thin layer of ink varnish, as evaluated with AFM. The elastic constant, K, of the system was unaffected, as evaluated with MAMA.
Methods

Printing Technique – Flexographic ink (rastered pattern covering approximately 35% of the model surface) was printed onto the cellulose surfaces using an IGT Printability Tester F1, IGT, Amsterdam, Netherlands (Anilox force 75 N, Printing force 125 N, Speed 0.30 m/s).

Ink Detachment from Cellulose Surfaces – The printed cellulose surfaces were mounted in a liquid filled impinging jet cell and impinged with an alkaline water solution (pH 10) at room temperature. The volumetric flow rate was kept at 1 ml/s during all trials, corresponding to an average velocity of 0.3 cm/s. The deinking efficiency was analysed according to the procedure outlined in [17] where 100 % deinking efficiency defines detachment of all ink and 0 % deinking efficiency means that no ink was detached. All experiments were repeated 4 times, giving a variation coefficient of 6 %.

Micro Adhesion Measurement Apparatus (MAMA) – Measurements were performed according to the method outlined in [19]. PDMS caps were fixed to a rigid support that was mounted on a micrometer driven translation stage. The model cellulose surfaces were glued onto a rigid support that was placed on an analytical balance and the hemispherical cap was compressed against the flat surface. The changes in contact area (recalculated to the cube of the contact radius (a^3)) were recorded as a function of applied load during loading and unloading. All measurements were performed in 50 % relative humidity at 23°C. All experiments were repeated 5 times to ensure good reproducibility, a variation coefficient of no more than 8 % was obtained.

Contact Angle – Contact angle measurements were performed with a Dynamic Absorption Tester (Fibro DAT 1121/1122) using water, glycerol and methyleneiodide. The contact angles were measured in advancing mode. All experiments were repeated twice giving a variation coefficient of 6 %.

Atomic Force Microscopy (AFM) – Surface roughness, defined as the root mean square (RMS) over a 1 μm^2 area, was measured for model cellulose surfaces, non-coated and ink-varnish-coated PDMS caps from the height image in tapping mode with the aid of a Pico Force SPM (Vecco Inc. USA). Phase images of ink-varnish-coated silicon wafers were also measured.

Ink Detachment from Cellulose Surfaces – The printed cellulose surfaces were all stored in black plastic bags at 25°C over night, after which they were impinged with an alkaline water solution (pH 10) at room temperature in a liquid filled impinging jet cell. The volumetric flow rate was kept at 1 ml/s during all trials, corresponding to an average velocity of 0.3 cm/s. The detachment of one dot of the rastered pattern was monitored by images that
were collected every second and analysed by a software developed at SCA-Research (Sundsvall, Sweden) according to the procedure outlined by Forsström et al. [20]. All experiments were repeated 4 times, giving a variation coefficient of 5%.

RESULTS

Deinking efficiency from model cellulose surfaces

The effect of out of plane surface roughness and surface hydrophobicity on ink detachment from model cellulose surfaces is shown in Figure 1. Ink detachment diminished by approximately 33 % as the RMS roughness changed from 3 to 13 nm.

Lowering the surface energy, i.e. making the cellulose surface more hydrophobic, decreased the ink detachment. At a maintained surface roughness of 4 nm, the ink detachment efficiency decreased by almost 65 %.

Figure 1  The effect of surface roughness and surface hydrophobicity on deinking efficiency from model cellulose surfaces. The lines are merely a guideline to the eye.
**Cellulose and ink characteristics**

Surface roughness obviously has an effect on the contact area between ink and cellulose. The RMS surface roughness of model cellulose surfaces and the structural properties of ink were therefore evaluated using AFM. In Figure 2 AFM height images of cellulose with different surface roughness and phase images of non-treated and heat-treated ink varnish are shown.

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**Figure 2** Tapping mode, height images (1 × 1 μm) of a model cellulose surface with RMS surface roughness of 4 nm (a) and a model cellulose surface with RMS surface roughness of 10 nm (b). The z-scale in both (a) and (b) is 50 nm. Tapping Mode, phase images (1 × 1 μm) of non-treated (c) and heat treated (d) ink varnish spin-coated onto silicon wafers.
Increasing the surface roughness from 4 to 10 nm in the cellulose structure created more irregularities, still on a nanometer scale possibly facilitating a larger contact area between ink and cellulose. The spherical structures observed in non-treated ink are most likely latex particles. Upon heat-treating the ink at 105°C, the spherical structures disappeared, probably due to an annealing effect of the latex and consequently a film formation of the binder.

**Interfacial interactions between ink and model cellulose substrates**

The adhesion properties between ink and cellulose were determined using the JKR-methodology outlined by Chaudhury and Whitesides [11] and applied to cellulose following the work of Rundlöf et al. [19]. The elastic constant, $K$, of the ink-varnish coated PDMS cap was determined to ensure that coating the cap did not alter the elastic properties of the system. To ensure that the PDMS cap was sufficiently coated the RMS surface roughness, as determined by AFM, of non-coated and ink-varnish coated PDMS caps was also compared. Both uncoated and coated PDMS caps had a $K$-value of 3 MPa, which is comparable to values earlier found by Rundlöf [22]. It was also found that coating the PDMS cap increased the RMS surface roughness slightly from 4 to 6 nm.

In Figure 3 the loading and unloading curves for ink-varnish coated PDMS caps contacting a model cellulose surface and a hydrophobic model cellulose surface are shown.

The work of adhesion upon loading ($W_{\text{load}}$) and the adhesion energy at minimum load ($W_{\text{min}}$) was calculated using Equations (2) and (3) respectively. As can be seen in inset in the figures both $W_{\text{load}}$ and $W_{\text{min}}$ decreased slightly as the cellulose surface was made more hydrophobic. Rundlöf has previously noted this behavior in adhesion properties between hydrophobic cellulose and PDMS. From the work of adhesion and contact angle measurements the total energy change ($W_{\text{cwi}}$) connected with the separation of flexographic ink ($i$) from the cellulose ($c$) in water ($w$) was calculated using Equation (1). The results are shown in Table 1.

The total energy change calculated from work of adhesion upon loading had negative values, suggesting that the ink detachment occurred spontaneously, however the total energy change was much less negative for a hydrophobic cellulose surface than for a cellulose surface indicating a less spontaneous ink release from a hydrophobic cellulose surface. The total energy change, calculated from adhesion energy at minimum load, was positive and decreased slightly upon making the surface more hydrophobic. In Table 1 the interfacial energies between cellulose and ink and cellulose and
water are also shown. It can be seen that upon making the cellulose surface more hydrophobic both the interfacial energy of cellulose/water and of ink/cellulose increased.

Figure 3 The cube of the contact radius ($a^3$) as a function of the applied load for adhesion between a PDMS cap coated with ink varnish and a model cellulose surface (upper figure) and a model cellulose surface with covalently bonded C$_4$-tails (lower figure).
DISCUSSION

The influence of surface roughness was investigated and it was shown that ink detachment was more difficult when making the surface rougher. When comparing Figures 2a and 2c it becomes obvious that the latex particles are within a size range to fit into the irregularities present in the model cellulose surface. When increasing the surface roughness larger ink penetration into the nanometer-sized roughness of the cellulose surface might occur, thereby lowering the deinking efficiency via physical interlocking. This is possible since the binder latex is small enough to allow for a migration of the latex particles into the irregularities of the cellulose surfaces allowing for a mechanical interlocking upon film formation. Due to this matching of sizes the contact area between the ink and cellulose is increased. Generally it should be stated though that there is a balance between surface and surface modulus.

It has previously been shown that upon heat-treating water based flexographic ink chemical changes occur in the varnish as an extra peak at 1710 cm\(^{-1}\) in a ATR-FTIR spectra occurs, indicating either an oxidative reaction or a hydrolysis [23]. In the present study it was shown that structural changes occurred in the varnish after storage at elevated temperatures due to annealing and film formation. Annealing of latex particles has also previously been shown [24, 25]. The annealing and the chemical reactions that take place upon storage at elevated temperatures can clearly be the reason behind the difficulties in deinking surfaces stored at higher temperatures as previously shown by [20].

The effect of interfacial tension and adhesion properties between ink and cellulose are clearly of importance for ink detachment, as previously shown for offset ink by Andreasson and Wågberg [6]. These authors showed that a hydrophobation of the cellulose surfaces decreased the offset ink detachment from the surfaces. In the present study it has been shown that the work

<table>
<thead>
<tr>
<th>Model surface</th>
<th>θ (°)</th>
<th>γ(_{ci}) (mN/m)</th>
<th>γ(_{cw}) (mN/m)</th>
<th>W(_{load}) (mJ/m(^2))</th>
<th>W(_{cwi}) (mJ/m(^2)) from loading</th>
<th>W(_{cwi}) (mJ/m(^2)) from min. load</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cellulose</td>
<td>22</td>
<td>6</td>
<td>−9</td>
<td>34</td>
<td>−69</td>
<td>350</td>
</tr>
<tr>
<td>Hydrophobic cellulose</td>
<td>94</td>
<td>40</td>
<td>30</td>
<td>27</td>
<td>−4</td>
<td>340</td>
</tr>
</tbody>
</table>

Table 1  The contact angle (θ), interfacial energy (γ), work of adhesion upon loading (W\(_{load}\)) and the total energy change (W\(_{cwi}\)) calculated from loading for different model systems using Equation (1). Contact angle of ink water was 60°.
of adhesion between ink and cellulose can be directly determined using the MAMA methodology. Coating the PDMS cap with ink varnish facilitated direct adhesion measurements between ink and cellulose as an even coating was obtained and since the elastic constant of the system was not altered.

Increasing the hydrophobic nature of the cellulose surface decreased both the work of adhesion upon loading and the adhesion energy at minimum load, i.e. at pull-off. A possible explanation is that the amount of available OH-groups on the hydrophobic cellulose is lower, diminishing the possibility for hydrogen bonding between cellulose and ink [22]. An alternative explanation can be a decreased contact induced molecular rearrangement across the interface [26]. Migration of components across the interface between ink and cellulose is thereby lowered, decreasing the adhesion between the surfaces.

When calculating the total energy change for estimation of ink detachment in water using the work of adhesion upon loading, the negative values obtained indicated spontaneous ink release, both from cellulose surfaces and hydrophobic cellulose surfaces. However, the $W_{cw}$ value for hydrophobic cellulose was larger, i.e. less negative and rather close to 0, indicating that the spontaneous ink release would take place less readily. Calculating the total energy change using the adhesion energy at minimum load indicated a non-spontaneous ink release both from cellulose surfaces and hydrophobic cellulose surfaces. The difference in $W_{cw}$ values calculated from adhesion upon loading or from the adhesion energy at minimum load emanates from the fact that the adhesion at minimum load was far greater than adhesion upon loading. At minimum load, the ink had been in contact with cellulose for a long time. This facilitated possibilities to establish more stable bonds across the interface and to allow for molecular rearrangements, i.e. diffusion, across the interface. This can clearly be the reason for the much higher adhesion at minimum load and the observed hysteresis between loading and unloading [10].

The adhesion properties upon loading and unloading both decreased upon making the cellulose surface more hydrophobic as shown in Table 1. However, ink detachment studies showed that ink detachment was rendered more difficult from hydrophobic surfaces than from hydrophilic surfaces. The explanation to these seemingly contradicting results is most likely that upon making the surface more hydrophobic the interfacial energy between water and cellulose increased, as seen in Table 1, i.e. water wet the hydrophobic surface to a lesser extent. All this taken together concludes that ink detachment becomes more difficult from a hydrophobic cellulose surface than a non-hydrophobic cellulose surface.
CONCLUSIONS

It has been shown that the change of the in plane surface roughness for model cellulose surfaces of the order of 10 nm will affect the ink detachment from these model cellulose surfaces. The latex particles present in the ink are within the size range to fit into these irregularities present in the cellulose surface. Heat-treating the ink causes film formation, which renders ink detachment even more difficult. MAMA measurements have proven to be a useful technique when evaluating the adhesion properties between ink and cellulose. It was shown that making the cellulose surface more hydrophobic decreased the adhesion between ink and cellulose, but at the same time the interfacial energy between cellulose and water increased, making ink detachment more difficult. This was supported by actual studies of ink detachment from hydrophobic cellulose surfaces. In future studies it is suggested that the technique used when coating the PDMS cap should be further examined and in order to arrive at a complete description of the ink-setting mechanism, the wetting of cellulose by liquid ink should also be determined. This was, however, beyond the scope of the present work.

ACKNOWLEDGEMENTS

Jennie Forsström thanks SCA AB and the Fibre Science and Communication Network (FSCN) at Mid Sweden University for financial support. Malin Eriksson thanks KTH for financial support. A/S Torda Fabrikker, is thanked for supplying the ink samples. Gustavo Gil Barros at STFI-Packfors is thanked for providing help with the use of the IGT printer.

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¹TetraPak R&D AB, Ruben Rausings gata, SE-22186 Lund, Sweden
²Department of Fibre and Polymer Technology, Royal Institute of Technology, (KTH), SE-10044 Stockholm, Sweden

Glyn Jones Arjo Wiggins

You have done some work with flexographic inks. How applicable is this for toner inks, inkjet inks and digital inks?

Jennie Forsström

If you are referring to the ink attachment studies, I would say that you would probably have to modify the impinging jet cell somewhat. Four years ago Lars Wågberg made a presentation on offset ink. Studying offset ink in that type of equipment is not possible, as it is right now, because you need to have a water-filled system and then you are not going to get any ink attachment. If you are referring to the MAMA measurements, I would say that it is definitely applicable.

Theo van de Ven McGill University

It is nice to see you using the impinging jet technique, which we invented over
Discussion

20 years ago. The question I have with the impinging jet experiments is: do you have the whole surface covered with ink or is only part of the surface covered with ink?

Jennie Forsström

No, it is a raster pattern as was shown in the figure, so it consists of dots. However, when you are evaluating your system, you are focusing on a few small dots and then from that you can calculate ink attachment.

Theo van de Ven

Can I have another question? In your wetting model, you have the interfacial free energy between the ink and the cellulose and between the ink and the water as a parameter, but ink is really a multi-component system. Is it realistic to model this with one single interfacial parameter?

Jennie Forsström

No, most likely not. However, we had problems finding a model ink that we had more knowledge about and so we used a commercial ink. It is a very good question especially since studying these things most likely requires a model system, so if anyone has any nice model inks that we could use that would be very interesting.

Theo van de Ven

A final question if I may. You separate out the electrostatic components, $\gamma^+$, $\gamma^-$, from the interfacial free energy and I guess in doing so you used the geometrical mean rule where the total interaction is the square root of the product of both. This geometrical mean is known to work very well for dispersion interactions, but it is not very reliable for electrostatic interactions, which has been shown many years ago by people like Fowkes and others who are world experts in wetting. So you should be very careful when reporting those values.

Jennie Forsström

Yes that is true, thank you.
Bob Pelton

How do you make the hydrophobic cellulose?

Jennie Forsström

That was made by taking the cellulose surfaces and putting them above propyltrichlorosilane, so it was a diffusion reaction in which propyltrichlorosilane actually diffused up onto the surface and then you could evaluate the surfaces by using AFM, for example, and see that you had full coverage.

Anders Åström Aylesford Newsprint Ltd

I understand this is a very idealised model system you are using and the impact in a real system is a lot more complex than in this. I was just wondering whether you can tell anything or get any indication on the size of the particles that get detached because that is an important parameter when you subsequently remove them from the system?

Jennie Forsström

Yes the size of the ink particles is very important, however we used a water-based ink, meaning that the particles that do come out are very small. We have tried to evaluate it but the amount of water needed to get these particles out was just too much so the particles disappeared meaning we were unsuccessful.