Investigation of Ink-Substrate Adhesion in LEP Printing

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Abstract

Understanding of ink-paper adhesion in LEP printing through interface investigation is presented. Relationship between macroscopic time dependent work of adhesion measurement, polar content of paper and ink surfaces, and interfacial acid-base interaction is revealed. Direct observation of the ink-paper interfacial interaction through ATR-FTIR measurement is described and C-O stretching band around 1152 cm^{-1} is shown to indicate acid-base interaction. Papers with high polar content exhibit strong intensity as well as reduction in the band location of the C-O stretch. Intensity ratio of C-O stretch around 1152 cm^{-1} and a neighboring C-C stretch at 1168 cm^{-1} is shown to have a linear relationship with the total work of adhesion immediately after printing.

Introduction

Adhesion of materials to a substrate plays an important role in many processes, ranging from biological systems[1] to industrial applications.[2] Interfacial physico-chemical interactions are known to affect the desired outcome of a process.[3]

With respect to advanced digital printing technology[4], an excellent interfacial adhesion between a marking material, typically an ink particle, and a substrate, generally a paper or a plastic, can provide important print and page attributes – visually pleasant image quality, typically represented by high print durability for rub resistance, water and smear fastness, and overall throughput of a printing process. With the advent of high-speed digital commercial printing based either on the liquid- (L)[5] or dry- (D) electrophotographic (EP) printing processes[6], this becomes critical.

Significant efforts have occurred to facilitate good adhesion of ink particles on a wide range of substrates. For example, thermal-induced fusing via mechanical interlocking of ink particles onto a substrate is known to facilitate reasonably good adhesion.[5] Besides, tailoring of interfacial electrostatic and van der Waals interactions have been demonstrated to enhance ink adhesion to substrates.[7] In addition, coating of a polymer which acts as a primer on a substrate to facilitate hydrogen bondings (HBs) and or acid-base interactions (A-BIs) has been shown to noticeably improve ink-substrate adhesion, and hence the so-called paper gamut.[8,9]

In particular, the HBs and or A-BIs are thought to play critical roles in a LEP printing process (Figure 1), and are clearly iterated by the total reversible work of adhesion[10], WA, as: $WA = W_{ab} + W_d$ where WA is defined as the energy required to break a unit area of an adhesional contact. In this case, it is a measure of the 'fundamental' adhesion between an ink layer and a substrate. Here, W_{ab} denotes the acid-base interaction component while W_d denotes the dispersion component. The later typically involves Lifshitz-van der Waals interaction.[11]

For most polymer-fiber systems, W_ds are comparable and have been shown to not being able to account for the considerable adhesion strength (i.e. 'practical' adhesion) differences observed. On the other hand, promoting W_{ab} by increasing the electron-donor capability at the interfaces generally results in an increase of both the fundamental and practical adhesion.[11] However, its distinctive transient role in such an interfacial interaction is poorly understood, particularly for polymeric ink-paper interactions. Since ink-paper interactions in LEP are essentially a surface phenomenon and occur across a narrow interfacial boundary, probing of the interfacial interactions pose a significant challenge. Although surface-sensitive techniques such as attenuated-total-reflectance Fourier-transform infrared spectroscopy (ATR-FTIR) and X-ray photoelectron spectroscopy have been reported to successfully investigate various interfaces[12-16], probing of ink-paper interfaces remains a significant challenge. Two major showstoppers are the interferences coming from the non-uniformity of the ink layer and the uneven surface topography of the printed papers, especially for cellulose-based papers.

We show here that intricate transient behavior pertaining to interfacial A-BI of ink particles and papers can be readily revealed via the ATR-FTIR spectroscopic technique upon careful control of the ink thicknesses on the paper. Correlations with adhesion strength of an ink layer with various substrates, more specifically cellulose-based papers, agree well with the enhancement of A-BIs.

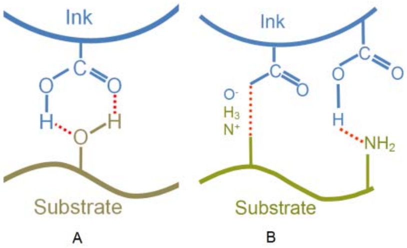

***Figure 1**. Pictorial description of ink-substrate interaction. The figure on left (A) shows H-bond, while the figure on right (B) shows A-BI and H-bond.*

To mimic the acid-base interactions between an ink particle and a paper as depicted in Figure 1, we have adopted an ink particle which is a controlled blend of polymers like methacrylic acid (MAA) and acrylic acid (AA) copolymers with polyethylene and several other additives.[17] The copolymers provided the desired carboxylic groups (-COOHs) while the hydroxyl groups (-OHs) and the amine groups (-NH, -NH2 or –NH3) were derived from four representative papers featuring varying concentrations of the latter two (Table 1). Common sources of C-OHs include polyvinyl alcohol, polyethylene glycol, starch and carboxymethyl cellulose. One common source of amine in paper industry is polyethyleneimine which is often found to include primary, secondary and tertiary amines. These are typically used as binders or co-binders in the paper manufacturing process to be added to the coating pigments.[8] When a spatially accessible -COOH on the ink particle's surface comes in close proximity to a surface –OH or -NH of a paper, either hydrogen bonding or acid-base reaction is anticipated to occur.

Experimental

I. *Liquid electro-photographic printing*

Liquid electrophotography (LEP) is a variation from the conventional dry electrophotography (DEP).[5] LEP uses a liquid toner for printing instead of the conventional dry toner particles typically used in DEP. As depicted in Figure 2, in a regular printing process, a photoconductor is first charged uniformly by a charging unit and is then followed by exposure to a laser beam (i.e. via a laser writer) to create a latent image on the photoconductor. A liquid toner which contains ink particles suspended in an isoparaffinic oil, is subsequently developed onto the photoconductor in a controlled fashion to form an uniform ink layer. The ink layer thickness on the photoconductor can be controlled by changing the electric fields in the developer units. The ink layer is then transferred to a so-called intermediate transfer medium which is maintained at an elevated temperature (~ 90˚C) before printing onto a piece of paper.

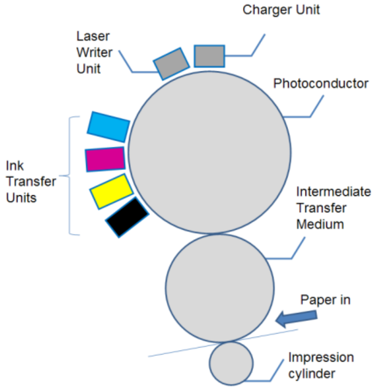

***Figure 2**. Schematic of a LEP printing system. All measurements were done on a HP/Indigo 5000 LEP digital press.*

II. *Sample configurations and X-ray photoelectron spectroscopy*

Table 1 lists four commercially available papers used in the present study. P1 and P2 are uncoated (UC) papers while P3 and P4 are coated (C) papers. One of the major differences between P1 and P2 is a treatment of polyethyleneimine (PEI) on P2. In general, all of these papers exhibit acceptable or enhanced levels of practical adhesion for LEP printing.

Surface elemental compositions were obtained via X-ray photoelectron spectroscopy (XPS) using the PHI Quantum 2000 system. A monochromated Al K_α 1486.6 eV X-ray source was used for probing the surfaces. An analysis area of ~ 1300 by 300 µm was used for the XPS measurements. All XPS data were quantified based on respective relative sensitivity factors. The relative percentage of the total polar components' concentration on the paper top surface is also provided, as this ratio is sometime taken as an indication of the polar reactivity between ink and paper.

III. *Attenuated-total-reflectance Fourier-transform infrared spectroscopy (ATR-FTIR)*

ATR-FTIR spectroscopy was used to characterize the ink-paper interface as well as the surfaces of papers and ink particles. All measurements were done on a Nicolet Nexus 870 spectrometer equipped with a liquid nitrogen cooled mercury cadmium telluride (MCT) detector. A single reflection Harrick Scientific Germanium IRE with an incident angle of 65° was used. Nitrogen was used as the purging gas. A resolution of 1 cm^{-1} with a total of 64 scans was used for all the measurements.

	Total C atomic %	Total O atomic %	Total N atomic %	(O+N)/C %
P1 (UC)	61.5	35.5	0.9	59.2
P2 (UC)	66	23.5	8.5	48.5
P3 (C)	53.5	33.2	0.0	62.1
P4 (C)	45.6	40.1	0.3	88.6

***Table 1**. Atomic percent ratio of elemental carbon, oxygen and nitrogen among the four papers.*

IV. *Adhesion Strength Measurement*

We have adopted a method similar to that as reported by Zhao *et al*.[18] First, a pressure-sensitive 3M half-inch tape (no. 401B) was pressed onto an ink layer and then pulled with a specified transversal speed using a ChemInstruments AR1000 adhesion tester at an angle of 180°. When measurable detachment of ink particles was detected visually, the pulling force and the traversal speed (TS) of the pulling tape were recorded. For measurable ink particle detachment, we have assumed a 10% ink layer surface damage (i.e. the ink detachment may not be total) as the threshold. A graph of the work per unit area of the tape versus the pulling speed was then plotted. To compensate for the input energy needed to deform the tape and the paper, the effective adhesion strength is determined from the intercept of y axis at TS = 0 ms^{-1}. Use of linear scale of TS was seen effective as compared to logarithmic reported by Zhao et al.[18] High repeatability was routinely obtained using a similar set of measuring and preparing tools.

Results and Discussion

I. *Importance of Ink Layer thickness control*

To probe the intricate interfacial interactions between an ink layer and a paper surface via the surface-sensitive ATR-FTIR spectroscopy, we have used a LEP printing process to controllably derive continuous thin films of ink particles with desired thicknesses of ~ 0.5 and ~ 5 µm. The importance of ink layer thickness control can be understood by considering the penetration of the evanescent wave in an ATR-FTIR measurement.[16] A thin, smooth and continuous ink layer is needed for successful and unambiguous probing of the ink-paper interface layer by the evanescent wave. Trial and error of the printing process and a judicious guess of the refractive index of the black ink used in printing here determined the appropriate ink thickness of around 0.5 µm. With an ink layer thickness higher than this critical thickness, one measures solely the bulk ink characteristics (bulk ink is denoted as thick ink in subsequent discussion) and does not probe the ink-paper interface whereas a thinner ink layer imposes practical implementation difficulty due to discontinuity of the printed layer. Figures 3A and B show cross-sectional SEM images of both ink layers on a paper. We also noted the relative smoothness of both ink layers which is conducive towards investigating the interfacial physico-chemical interactions via ATR-FTIR spectroscopy by facilitating enhanced optical contact while suppressing undesirable signal scatterings.

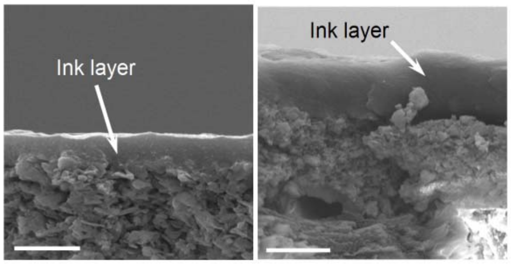

***Figure 3**. Left (A) thin ink, and right (B) thick ink. Scale bar is 2µm.*

II. ATR-FTIR measurement of four papers, thick ink and thin ink

Figure 4 shows the ATR-FTIR spectra of the four paper samples as shown in Table 1 and also that of a thick ink as shown in Figure 3B. Major signature peaks are seen from either the paper coating or the filler materials: $CaCO_3$ at 1444 (broad), 1796, 874 and 713cm^{-1}, Kaolin Clay at 1007, 1036, 1111, 913, and its twin bands of 3696 and 3621 cm^{-1}.[19] The thick ink (~ 4 µm in this measurement) shows a characteristic carbonyl (C=O) peak at 1700 cm^{-1} and –CH2 stretching bands at 2920 and 2850 cm^{-1}. Of particular importance is a narrow region marked with a dashed circle as shown in Figure 4B and further explored in Figure 5.

The importance of controlling ink layer thicknesses towards revealing key signature peak which is indicative of A-BI is clearly seen in Figure 5A. We observe two distinctive bands for both ink layers, one commonly centered at ~ 1169 cm^{-1} and the other at ~ 1156 cm^{-1} and 1152 cm^{-1} respectively for the thick and thin ink layers. To elucidate the origins of these vibrations, we have acquired individual FT-IR spectra of the ink particle's components, namely polyethylene, MA and AA copolymers. It is obvious that these two bands have no direct associations with polyethylene and the paper P4 (i.e. having the highest polar component concentration of among the four papers employed in this study). By Gaussian-Lorentzian curve fitting of these profiles after respective baseline corrections, we assign the bands centred at ~ 1169 cm^{-1} to the carbon-carbon stretching vibrations while the bands at ~ 1156 cm^{-1} to the O-C-O bond of the carboxylic group.[21] Unlike in the case of the thick ink layer, a downshift of ~ 4 cm^{-1} to ~ 1152 cm^{-1} is noted for the thin ink layer. In addition, we observe a relative increase in intensity of C-O stretching vibration (sv), as compared to the nearby C-C sv. While assigning the C-O sv intensity as IR_2 and that of the C-C sv as IR_1, the ratio, IR_2/IR_1, increases from 0.9 (for the thick ink) to 2.5 (for the thin ink). Taking into consideration penetration depth of the IR evanescent wave, we strongly believe that we have successfully probed the ink-substrate interface and that the downshift is likely due to acid-base interaction of the –COOH with –OH of the underlying paper. It is important to note that similar trends were observed for the other three papers (Figure 6 A, B and C) even though their –OH or –NH concentrations are lower than that of P4. Further evidence of such an A-BI is provided by suppression of the dimeric –COOH band intensity at around 3100 cm^{-1} and the slight appearance of monomeric –COOH at ~ 3500 cm^{-1}.[21] Although it has been reported in some cases that a dehydration reaction between -OH and -COOH could occur[22], we failed to observe such a reaction in this work. This is likely due to the relatively short duration (~ 150 µs) of the nip contact, i.e during the transfer of the heated ink particles from the ink transfer medium to the paper at ~ 90°C. Further supporting evidence is given by the band centered at 1700 cm^{-1}, which coincides with those of MAA, AA and the thick ink layer, and suggests presence of carbonyl group of -COOH.

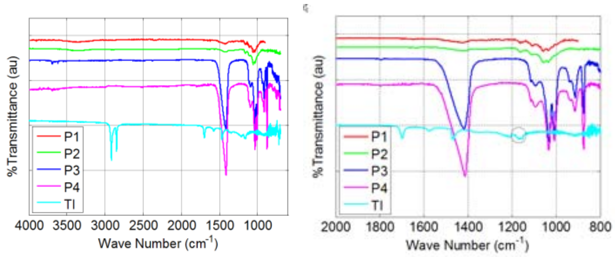

***Figure 4**. Left (A), right (B). ATR-FTR spectra of paper and thick ink.*

III. Temporal Evolution of Acid-Base Interaction

Next, we studied temporal evolution of the transient A-BI between a thin ink layer and a paper surface. Immediately upon printing the ink layer onto P4, we tracked changes of the signature peaks at both 1169 cm^{-1} and 1152 cm^{-1}. As shown evidently by the band position at ~ 1152 cm^{-1} in Figure 5B, within the first 4 min after printing, more than 80% of the A-BI has taken place, as compared to that of Figure 5A which was acquired after an hour of printing. Interestingly, we observe that ~ 15 min after printing, near complete A-BI has occurred. On the other hand, no noticeable changes were seen for the bands centered at 1169 cm^{-1}.

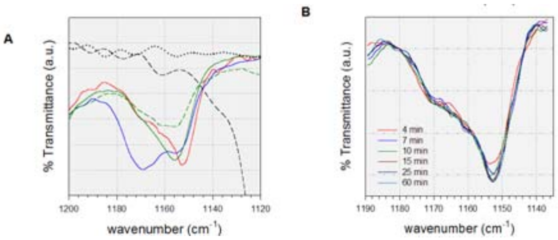

***Figure 5**. Left (A): 1-hour after printing and right (B) as a function of time.*

IV. Macroscopic Adhesion Strength and A-B Interaction

More importantly, we have consistently observed that the transient A-BI behavior manifested itself through macroscopic measurement of the adhesion strength, or the 'practical' adhesion.

It should be pointed out that typical experimentally measured adhesion strength values reflect the interfacial adhesion indirectly, and are influenced not solely by physico-chemical interfacial interactions but also mechanical properties of the paper matrix.[11] We observe that for each profile, the adhesion strength increases exponentially to a near-flat plateau in less than 20 minutes. Based on the relative strength and kinetics of acid-base and van der Waals interactions[23] and the transient A-BI behavior as shown in Figure 5B, we suggest that at time t = 0 s or soon thereafter (measured at regular intervals after printing), A-BI dominates the ink-substrate interaction. However, contribution of van der Waals interaction to the adhesion strength should not be completely ruled out. During the transfer of ink particles onto the paper surface, minute amount of isoparaffinic oil (i.e. liquid carrier of the ink solution) is likely to be carried over and trapped in between the ink-paper interface. As the liquid carrier wicks away from the interface, van der Waals interaction is expected to take effect.

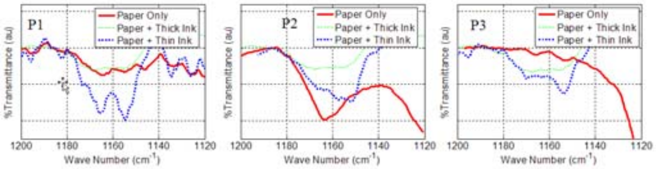

***Figure 6**. Tracking of A-BI in P1, P2 and P3.*

Hence, it is reasonable to divide the profiles into two working regimes. In regime 1, the adhesion strength increases rapidly and is governed mainly by A-BI. In regime 2, van der Waals interaction dominates the practical adhesion. A transition should exist between regimes 1 and 2, where the incremental dispersion component is higher than the incremental A-BI component. The exact duration of this transition is expected to be a strong function of the paper surface porosity and surface roughness. It is thus logical to assume that if the adhesion strength versus time profiles are extrapolated to T = 0 s, the A-BI component of W_A could be obtained as shown in Figure 7B (i.e the blue-colored profile). The almost perfect linear fit is striking and reinforces the supposition that short time adhesion is dominated by the A-BI between ink and paper. Figure 7B shows the final adhesion strength obtained with these four papers versus the A-BI component (the blue-colored profile). The difference between the red and blue profiles represents the van der Waals component of the adhesion strength.

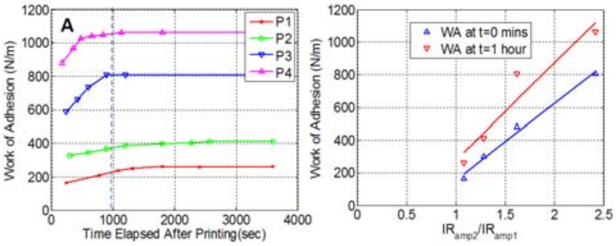

***Figure 7**. Macroscopic WA measurement and its correlation with A-BI growth.*

Conclusion

In conclusion, we show the important role of A-BI towards enhancing ink-paper adhesion strength. The LEP printing process has been demonstrated to be an ideal approach of laying down high-quality continuous smooth thin films of ink particles, and could serve as an appropriate test bed for investigation of advance material sets for future high speed digital printing.

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Biography

Manoj K. Bhattacharyya received his Ph.D in Electrical and Computer Engineering from Carnegie Mellon University in 1984. He has been with the Hewlett-Packard Laboratories since his graduation and works in a variety of fields including magnetics, magnetic recording and digital commercial printing.

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