

Toner Layer Structure and Toner Adhesion on Coated Paper

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Abstract

In electrophotography the toner adhesion to paper is an important quality parameter. All main components of printing - toner, paper and process - have an effect on the adhesion level. The objective of this study was to clarify the role of coated paper properties in adhesion. According to previous studies, both mechanical and chemical adhesion phenomena are involved when paper is the receiving layer.

The sample set included electrophotographic prints on coated papers, where the ratio of different coating pigments was varied. The series contained both uncalendered and calendered samples. Alterations in coating pigments and calendering caused the samples to have different surface properties. Variations in roughness and porosity together with the surface energy induced changes in toner layer formation on different types of coatings. Vibrational spectroscopic methods, i.e. FTIR and Raman measurements, were used to study the structure of the layer of the polyester toner and the chemical phenomena in more detail. FTIR-ATR measurements made from the very surface and depth profiling with Step-scan PAS proved that the molecular structure of the polyester toner layer changes as a function of depth. The confocal Raman technique was used to examine the composition of the toner-paper interface further.

Introduction

In electrophotographic prints the most important quality parameters are considered to be print evenness (lack of mottle) and toner adhesion to paper, in addition to normal optical quality parameters. In this study the focus is on toner adhesion. The fusing degree or toner adhesion is determined by the combination of properties of the fuser system, the toner and the paper.

Polyester toners are used as toners because they have low minimum fixing temperatures but also low hot offset temperatures. Branching, crosslinking and grafting can improve polyester resin properties. Unsaturated modified polyesters are also reactive in two different areas: unsaturation sites (double bonds) along the polyester chain and other functional groups in the polyester such as carboxyl and hydroxy.^{1,2}

Polyester toner resins usually have etherated phenols as a base component and aromatic acids as the main acid component. Bisphenol A derivatives are commonly used as the alcohol monomer because of their good toughness and thermal properties. In addition to the basic alcohol and acid components, alkyl-substituted dicarboxylic acids or alkyl-substituted diols are used as soft segments in the polyester backbone. The function of the two soft segments is to lower the fixing temperature and improve humidity resistance, which is quite poor because of the hydrophilic functional groups in the ester.^{1,2,3}

Toner pigments do not have specific affinity to the paper surface, so the main factor in the toner-paper interface is the toner resin. There are a few main theories for explaining the principles of adhesion on polymeric materials, but they have not been directly structured for toner adhesion. The general theories entail both mechanical and chemical adhesion. When paper is the receiving layer, both types of adhesion are involved.

In mechanical adhesion the polymeric molecules penetrate into the voids of the paper and interlock with both themselves and the solid surface. Mechanically formed adhesion is relatively weak and depends upon the degree of intermingling. Smaller polymer molecules give relatively high bond strength since they can mingle with the crevices of the paper more easily. The adhered area is a mixture of intermingled polymer chains and substrate fibers. Since the polymer chains in cellulose are longer than the ones in the adhering polymer, they are less strongly bonded together and will break before the shorter adherent bonds to the substrate.^{4,5}

There are various theories behind chemical adhesion, such as adsorption, electrostatic, diffusion, molecular dispersion, chemical reaction and thermodynamic adsorption. The most applicable chemical adhesion theory is the adsorption theory. In this theory it is assumed that intimate contact is needed between the two components in order to achieve attraction. Wetting of the substrate, and thus the surface energetic properties, have an important role and have also been linked to toner adhesion by Lee⁶. In addition, there are some other weak bonds involved. For example the hydrogen bond itself is a very weak bond, but on cellulose-based surfaces it is often the main force in the interaction.^{4,5}

From the chemical viewpoint, besides rheological and thermal properties of the toner resin, the toner adhesion is believed to be affected by both the physical and chemical properties of the paper. On uncoated papers the unmelted toner particles in the voids do not adhere as well as particles on the peaks of the profile, so paper roughness contributes to the adhesion level. Porosity and swelling of the fibers also have a certain effect.⁷ On pigmented and coated papers the surface chemistry is believed to have a stronger effect. Variability in the adhesion level has been related to variations in the surface energy of the substrates. Sanders⁸ et al. claim that the only significant connection between fixing and the chemical structure of uncoated paper involves the dispersion component of the paper surface energy. If surface energy is too low, the toner does not fix to the paper surface properly. Paper surface properties can be influenced for instance with surface sizing. The surface energy of the print depends on intermolecular forces, which form a bond between toner and paper.

The study of the inter- and intramolecular forces in the toner/paper interface requires a more analytical approach than the normal optical methods can provide. Since information on the molecular level is sought, vibrational spectroscopic methods are a good option and have proved to be applicable to electrophotographic print studies.⁹ In the study of toner adhesion and toner layer structure, depth profiling methods are of special interest.

Step-scan photoacoustic spectroscopy has been previously used for depth profiling of latexes, polyolefins and other polymers. With phase analysis capabilities, information about the interactions between individual components can be extracted. With ATR FTIR it is possible to analyze the first few micrometers of the sample surface. ATR has been used as a depth profiling method by varying the incident light angle to study for example stratification of components in organic coatings. By changing the crystal material and thus the refractive index, the penetration depth can be modified.¹⁰ Confocal Raman measurements have been applied to the study of interdiffusions, interactions and adhesions at polymer-polymer interfaces.¹¹

The object of this study was to determine the main paper properties affecting to toner adhesion level on coated papers. The formation of the toner layer structure with polyester toners was also examined.

Methods

Paper Properties

The papers used in this study were obtained from an experimental coated printing paper series, not optimized to non-impact printing. The series contains a base paper on which five different coatings were made. Kaolin was the main pigment in all coatings. Two other pigments were added in different relations to vary the paper surface properties. The sample set included both uncalendered and calendered papers.

The common physical paper properties were measured, including PPS roughness, micro-scaled roughness (measured with a profilometer) and porosity (measured with a mercury porosimeter). In addition, surface energies were measured from the papers with the test set-up developed in the laboratory, allowing measurement to be made at elevated temperatures. In the experiments for this study, surface energy was measured at 23 and 50°C.

Print Analysis

Compact yellow surfaces were printed on the paper samples with the OKI 8 four-color electrophotographic printer. The process conditions were normalized for each sample. Toner adhesion was measured with a crease test. The outcome was analyzed both by densitometric values and with a CCD camera attached to a microscope.

FTIR spectra were collected with a Bio-Rad FTS6000 FTIR spectrometer. For the ATR measurements the device was equipped with germanium and diamond crystal detectors attached to an UMA-500 microscope. The refractive index of the diamond crystal (2.4) is smaller than that of the germanium (4.0) and thus the penetration depth of the measurement is deeper according to the Rosenzweig theory.¹²

Step-Scan PAS measurements were accomplished with a helium-purged MTEC300 photoacoustic cell. Data processing was done with Win-IR Pro software with the integrated step-scan operation PAS DSP technique and G2D correlation algorithm.

With SS-PAS the amount of each component signal present in the toner layer was determined as a function of depth. This is accomplished by varying the modulation frequency. When phase modulation is used, two spectra can be obtained: in-phase (I) and in-quadrature (Q). Combination of these two gives a magnitude spectrum (M), which comprises signal data from the bulk and surface of the sample.¹⁰

$$M = \sqrt{I^2 + Q^2} \quad (1)$$

The penetration of the IR beam and thus the probing depth is determined by the modulation frequency in question. For this sample set-up, the following frequencies were used: 100, 300, 500, 700 and 900 Hz. For polymeric samples, the estimated depth range at these frequencies is from 13 to 5 µm.

The Kaiser Raman Hololab series 5000 dispersive Raman spectrometer, equipped with a 785 nm laser and Olympus microscope, was used in the confocal mode. With this set-up it is possible to get good spatial resolution along the optical z-axis.

Results and Discussion

Paper Properties vs. Adhesion

Different paper properties were correlated with the adhesion measurement results. From the physical surface properties PPS roughness in relation to toner adhesion is illustrated in Fig. 1. Base paper is used as a reference. The deviation originating from the nature of the crease test was in the same range for all samples.

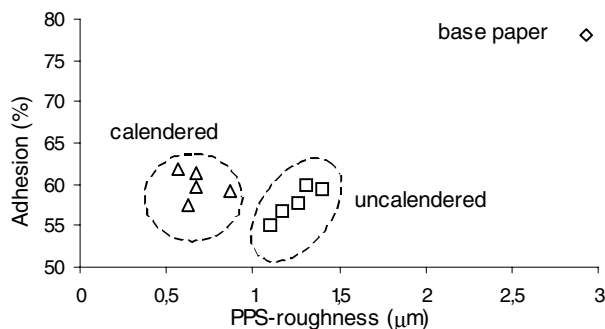


Figure 1. Effect of PPS roughness on adhesion.

It can be seen that PPS roughness correlated well with adhesion on the uncalendered paper set. On the other hand, surface roughness does not seem to explain the adhesion level on the calendered and thus smoother papers. Other roughness variables such as the average surface profile slope had similar correlations.

The correlation between the total pore volume of the coating and adhesion was not meaningful on the uncalendered samples, but on calendered samples an increase in pore volume was found to lower the adhesion level. Similarly, an increase in dominating pore radius increases the adhesion on calendered samples.

Surface energy has previously proved to be an important factor in toner adhesion. Figure 2 shows the toner adhesion as a function of the surface energy.

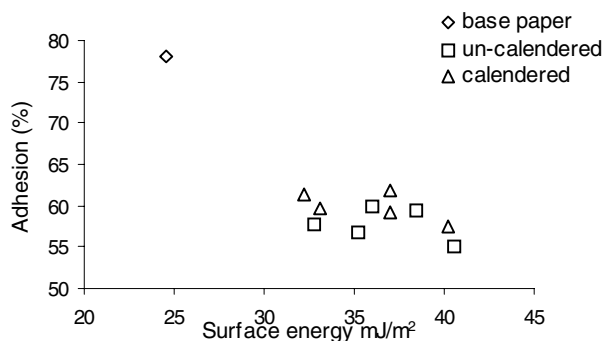


Figure 2. Paper surface energy vs. toner adhesion.

As was previously mentioned, it has been shown that an increase in surface energy increases the adhesion strength on surface sized papers.⁷ In the experiments for this study, the results were the opposite. The measurements in question were made at 50°C. The polarity component degree of the surface energy showed a similar trend. This is probably due to the nature of the coatings. An increase in the kaolin amount in the coating increases the surface energy and polarity degree.

An increase in the kaolin amount also has a direct effect on the toner adhesion level. Figure 3 shows an example of two sets of calendered paper samples. It is clear that when the kaolin amount is increased, the toner adhesion level is lowered.

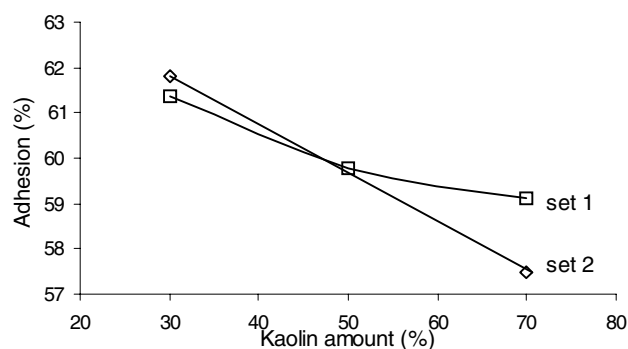


Figure 3. Effect of kaolin amount on toner adhesion.

Table 1. Peak assignments for polyester toner. R equals resin, P pigment. Symbols: ν stretching vibration, δ deformation vibration, ϕ aromatic ring.

Tentative assignment	R	P	Band position (cm ⁻¹)
OH, ν	x		3426.6
NH, ν		x	3344.7
ϕ -H, ν	x		3047.4
CH, CH ₂ , CH ₃ , ν asym.	x		2967.0
CH, CH ₂ , CH ₃ , ν sym	x		2873.3
CN, ν		x	2212.7
C=O, ν	x		1725.3
C=C ϕ , ν	x		1608.3
C=C ϕ , ν	x		1581.8
C=C ϕ , ν	x		1511.3
CH, CH ₂ , CH ₃ , δ asym.	x		1460.4
CH, CH ₂ , CH ₃ , δ sym.	x		1380.9
C-O + C-C, ν	x		1273.4
ϕ -O, ν	x		1246.7
ϕ -H, δ in plane	x		1184.3
ϕ -O-C, ν	x		1047.0
ϕ -H, δ out of plane	x		931.4
ϕ -H, δ out of plane	x		832.1
ϕ -H, wag	x		731.5

Toner Layer Structure

The yellow toner used in this experiment consists of polyester resin and acetamide pigment. The polyester toner resin in question has five different components: two bisphenol A derivatives, an aromatic acid and two different polycarboxylic acid anhydrides. There is great complexity in the spectra obtained from the toner due to the existence of overlapped bands, changes in their shapes and displacements along the frequency axis. The assignments of significant peaks of the toner powder measured with FTIR rapid-scan PAS are shown in Table 1.

FTIR spectra were measured from the yellow prints with SS-PAS and two ATR crystals. This means that spectral data were obtained from seven different depths in the print sample (from the surface: ATR g (germanium), ATR d (diamond), PAS 900-100Hz). There were specific regions in the spectra where differences between the depths were found. In general, peaks from the papers were clearly seen deeper in the sample (at 100 Hz) but not visible in the surface. ATR spectra contain only peaks from the toner resin.

Relevant regions in the spectra were the carbonyl stretching region around 1725 cm^{-1} and C-O-C region of the ester around $1280\text{-}1240\text{ cm}^{-1}$. Figure 4 shows an example of the carbonyl peak position on one of the calendered samples.

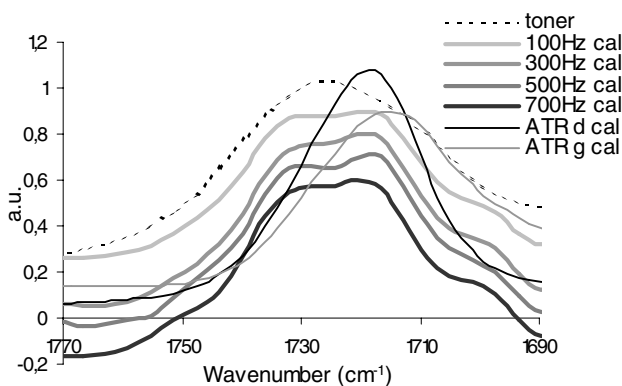


Figure 4. Shifts of C=O peak position on a calendered sample.

When the carbonyl band (1725 cm^{-1}) measured from the toner powder is compared with the spectra measured from the prints at different depths, a peak splitting is detected. It is noted that as the focusing depth decreases, the intensity of the carbonyl band at 1719 cm^{-1} increases in relation to the band at 1730 cm^{-1} . This increase may indicate an increase in concentration of a distinct component of the polyester towards the surface of the toner layer. It has been previously found by Urban¹³ that on polymer films one of the factors that may significantly influence the surface composition of a substrate in the direction normal to surface are the stratification processes of individual components. This kind of stratification is also possible in polyester toners.

When spectral data from the ATR measurements are compared with those of the SS-PAS, it can be seen that the peak around 1730 cm^{-1} disappears. Also, a shift from 1719 to 1715 cm^{-1} is noted when diamond and germanium crystal data are compared, respectively. Because the ATR measurement is made at the very surface of the sample, the peak in 1715 cm^{-1} could originate from the yellow acetamide pigment, which also contains carbonyl groups. However, this is not the case, because other pigments do not contain carbonyl and the same peak is detected from cyan, magenta and black prints.

One explanation of the peak splitting is hydrogen bonding. The formation of hydrogen bonds requires proton-donating groups, such as hydroxyl or carboxyl groups, and proton-accepting groups like carbonyl, ether etc. Hydrogen bonding is manifested by frequency shifts, band broadening and intensity changes in the carbonyl and hydroxyl bands of ester and alcohol groups of the polymers. It is also known that the carbonyl band shifts to lower frequency with band broadening due to intermolecular hydrogen bonding.¹⁴ It has been shown that the peak around $1730\text{-}1730\text{ cm}^{-1}$ can be assigned to the free carbonyl group present in the soft segment (or amorphous) of the polyester and the peak around 1725 cm^{-1} to the hard segment (or crystalline).^{15,16} He¹⁷ et al. claim that in addition to the aforementioned peaks, the peak at 1713 cm^{-1} can be assigned to hydrogen bonded carbonyl vibration. This, together with the results shown earlier, would indicate that there is inter- or intramolecular hydrogen bonding involved also in the toner resin layer in question. Since the ATR measurements show only the peak at 1719 cm^{-1} , it can be reasonably assumed that direct contact with the hot roller fuser induces stronger hydrogen bonding.

The phenomena of Fig. 4 are evident with every calendered paper sample. The separation of hydrogen bonded and a free carbonyl peak is nonetheless more pronounced for some samples. Figure 5 illustrates a comparison between the samples containing 70% kaolin and samples containing 30% kaolin. The spectra have been offset for clarity.

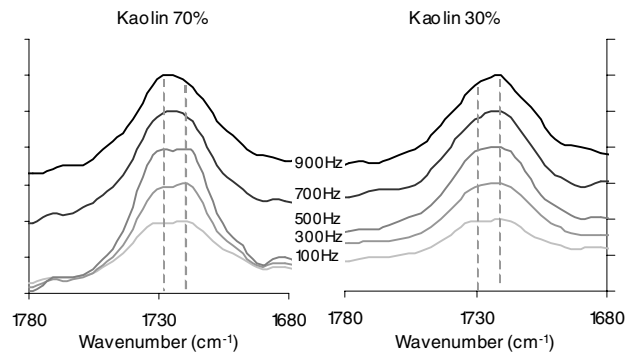


Figure 5. Effect of kaolin on splitting of the carbonyl peak.

It can be seen from Fig. 5 that splitting is strongest when the kaolin amount is largest. It is also noticed that in the spectrum measured nearest to the surface (900Hz), the maximum peak intensity is achieved at 1730 cm^{-1} for 70% kaolin samples and at 1719 cm^{-1} for 30% samples. It seems that the hydrogen bonded region is at a different spatial depth for these samples and thus the toner layer structure is different. The effect of the kaolin amount on peak splitting is of the same kind as the effect on toner adhesion. It can therefore be concluded that the changes in the carbonyl peak position can be linked to the toner adhesion levels. Chemical changes in the toner layer are induced by the paper surface properties, influencing the acquired toner adhesion level. It is worth noting that the peak splitting is not so clear on uncalendered samples, which have lower adhesion levels.

A 2D correlation spectrum of a collection of spectra at different depths gives information on the locations of the peaks in the spatial axis in relation to each other. Figure 6 illustrates a synchronous 2D correlation spectrum of the region of $1850\text{-}1450\text{ cm}^{-1}$ of the same calendered sample as in Fig. 4.

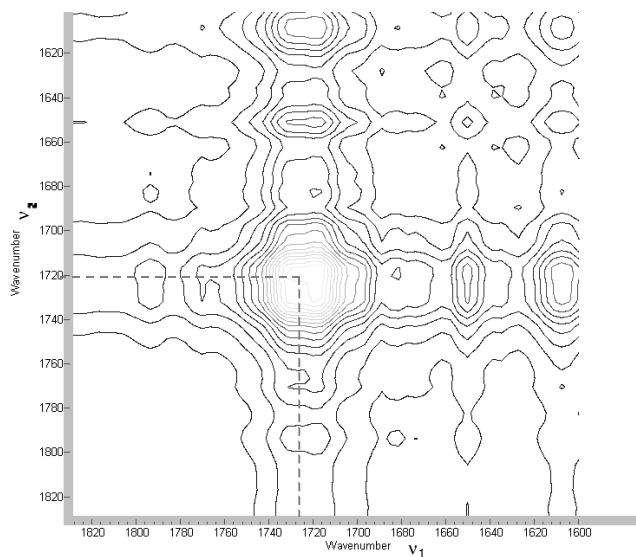


Figure 6. 2D-correlation spectrum of a calendered sample.

In 2D correlation spectra, a positive (v_1/v_2) means that the peak in v_1 (x-axis) is located deeper in the sample than the peak in v_2 (y-axis). Correspondingly, a negative contour means that v_1 is shallower than v_2 .¹⁸ Positive contours are indicated in Fig. 6 with light areas and negative ones with dark areas. It can be seen that there is a positive contour at $1730/1719\text{ cm}^{-1}$, indicating that the origin of band 1730 is deeper than that of 1719 cm^{-1} . This verifies the results shown earlier. There is a similar effect in the C-O-C region of ester.

Confocal Raman measurements of the prints confirm that the toner layer structure of calendered and uncalendered samples is different. Figure 7 shows an example of the

Raman measurements of the same sample as in Figs. 4 and 6.

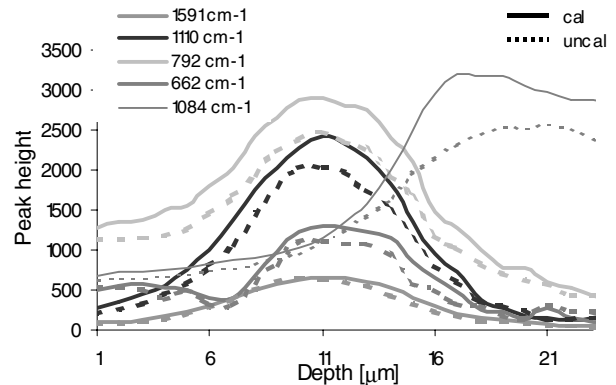


Figure 7. Confocal Raman spectrum of a calendered sample.

On calendered samples the characteristic peak of the paper arises before that of the uncalendered samples. This means that the interfacial region between the toner and paper is thinner in the calendered samples.

Conclusion

This study showed that in addition to process and toner parameters also paper properties influence the formation of the toner adhesion and toner layer structure on coated papers. Physical surface properties have a more meaningful impact on uncalendered samples and the other chemical properties have more influence on calendered samples. It is well known that on uncoated papers paper roughness has a significant effect on adhesion, in agreement with the results of this study.

When polyester toners are used on coated papers, stratification will occur. This layering is to some extent induced by paper surface properties. Detailed examination of the splitting of the carbonyl peak of the print samples reveals that hydrogen bonding is involved. The contact of the hot roller seems to induce more intramolecular hydrogen bonding in the surface of the toner layer. The amount and strength of the hydrogen bonding is affected by the paper structure.

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Biography

Ph.D. student Katja Sipi works as a research scientist in the Laboratory of Media Technology of the Helsinki University of Technology (HUT) in Finland. Ms. Sipi received her M. Sc. degree in Graphic Arts Technology from HUT in 1998 and her current work involves analytical studies of the interaction between toner surface and paper structure. She is a member of the IS&T. E-mail: katja.sipi@hut.fi.