Detecting and Evaluating Toner Property Changes after Exposure to Coating Materials

Heather Gulley-Stahl, Whitney Burress, Jeremy Daum, Jim Doeltz, Connie Haberman, David MacMillan, Dale Massie, James Semler and Robert Glenn Smith; Lexmark International; Lexington, KY/USA

Abstract

This presentation highlights a specific case of toner plasticization that occurred during a storage situation. Three aspects of the investigation are discussed: determination of the root cause, analytical results with a correlation to functional testing, and the development of an offline materials compatibility screening test. Once the contaminant causing a change in toner properties was identified, functional testing and materials analysis confirmed a strong correlation. After the realization that coating materials from any location within the EP system could potentially interact with toner in an undesirable way, an offline materials compatibility test was developed. It is anticipated that this test method could provide a screening tool for low risk materials for use in EP subsystems.

Introduction

There are six basic steps in the electrophotography (EP) process: charging, exposure, development, transfer, fusing, and cleaning.[1] During these six steps, toner can be exposed to multiple environments and various types of materials. Toner is designed to maintain specific properties and is intended to flow only during the fusing step. However, because toner has the potential to interact with a wide range of materials, even in a static situation, changes in properties such as glass transition temperature (Tg) can occur. One example of such a change is Tg suppression caused by plasticization. After the toner has been plasticized, the end result can be an unrecoverable print quality defect. Detrimental toner plasticization has been reported and can create storage problems, especially at elevated temperatures.[2,3] Because storage conditions are not always predictable or controllable, defects may take weeks or even months to manifest. Long test times are usually required to discover these types of defects and they may not be observed at all before a product is released.

Toner Tg suppression can occur after exposure to high heat and humidity conditions alone. However, when toner plasticization occurs during storage due to a combination of environmental conditions and a materials interaction, determining the identification of the problem material is essential. The quick identification of unknown debris can be approached using a variety of analytical techniques. One of the most popular techniques for identifying an unknown material is infrared spectroscopy (FTIR).[4] In particular, when analyzing small particles (~20 µm) microspectroscopic approaches prove most beneficial.[5] Infrared microspectroscopy has been around since the 1980s and the technology has grown over the last few years to include such techniques as attenuated total internal reflection (ATR) imaging. ATR imaging allows one to achieve a spatial resolution on the order of the wavelength of light allowing the analysis of particles down to ~3 µm.[6,7] This spatial resolution is ideal for analyzing small particles such as toner which can be on the order of ~6 µm.

When considering interactions between the various types of materials used in EP subsystem components, polymeric coating materials seem most relevant due to their high likelihood of coming in contact with toner. Like toner, coating materials should maintain their desired properties. For example, if a low molecular weight polymer migrates to the surface of a roller, this polymer could potentially interact with other EP materials such as toner. Identifying these extractable materials and quantifying their contribution is important to determine the potential risk they may have in creating a problem. One way that extractable materials can be quantified is by using accelerated solvent extraction (ASE). ASE allows one to expose a solid material, such as a roller coating, to a solvent of choice at a specific temperature and pressure for a certain amount of time. The extractable material can then be collected and weighed to quantitatively determine the amount of non-volatile residue (%NVR) available in the material. Once the extractable materials are collected, a spectroscopic method such as nuclear magnetic resonance spectroscopy (NMR) can be used to identify the components present and determine their relative amounts.

Identifying a contaminant material is only the first step in correcting a potentially large and detrimental storage issue. Once the contaminant responsible for altering toner properties has been identified, a method to eliminate or reduce the component must be successfully developed. Sometimes, the necessary changes to a component may take months to qualify. Ideally, one would prefer to have the proper protocols in place to predict and determine any potential risks during development and avoid making major changes after production has begun. Procedures such as offline materials compatibility tests and analytical tests can provide a critical understanding of the materials used in EP subsystem components and their potential interactions.

Experimental

Materials and Methods

An accelerated ship/store test was developed to more quickly assess the failure rate of developer rollers placed in storage conditions. This faster test was designed to yield results that correlate to traditional ship/store testing that required three weeks of test time. The accelerated ship/store test was carried out by first toning the developer roller surface. Then, the rollers were placed into a fixture and a metal bar was pressed against each roll with varying force across the bar/developer roller interface. This fixture was exposed to specific environmental conditions for 72 hours. After 72 hours, the developer rollers were removed from the

fixture and allowed to reach thermal/humidity equilibrium with the ambient environment. The rollers were then print tested to determine if a print defect could be observed. The print defect was assigned a score from 0 to 5, with 0 being no failure observed, 3 being a thin horizontal line across the page and 5 being the worst failure typically showing wide bands across the page.

An offline materials compatibility test was developed to screen raw materials and determine the risk they may have on the performance of toner within an EP system. A clean, flat substrate such as a glass slide was cleaned by UV-ozone and weighed. The suspect raw materials were dissolved in an appropriate solvent (such as xylene or toluene) and applied to the substrate in a uniform fashion via spin coating. This application can be performed using any method capable of producing a relatively uniform thickness such as spraying, dipping, draw down bars, etc. The total mass of polymer and substrate were measured. A relatively uniform layer of toner was then applied to the polymer material with any excess toner blown off. The mass of the toner, polymer and slide was then measured. The sample was then conditioned at a specified temperature. The toner was then imaged by scanning electron microscopy (SEM) to observe any plasticization; signified by a fused appearance. Finally, the toner was sampled by differential scanning calorimetry (DSC) to determine the change in Tg.

Instrumentation

Scanning electron microscope (SEM) images were collected on a JEOL JSM-6460LV SEM. Samples were prepared on carbon tape and mounted on aluminum stubs, followed by gold sputtering. Sample images were collected at 5,000x magnification.

ATR-FTIR images were collected with a Perkin Elmer Spectrum Spotlight 400 infrared imaging microscope equipped with a liquid nitrogen cooled HgCdTe (MCT) 16x1 linear array detector. The ATR imaging accessory employs a germanium hemisphere which has a refractive index of 4.0. As a result, the pixel resolution is 1.56 µm. For the IR images in this investigation, spectra were collected at 8 cm^{-1} resolution and 16 scans were averaged per pixel.

Accelerated solvent extraction (ASE) was performed using a Dionex ASE200 Unit. The system was run with chloroform as the extraction solvent. The parameters for the accelerated extraction were 100ºC and 1500 psi, with three 5 minute static cycles totaling 15 minutes.

NMR spectra were collected on a Bruker Ascend 400 operating at a 1H frequency of 400.1 MHz and equipped with a 5mm PABBO BB probe. Samples were dissolved in $CDCl_3$ for analysis and spectra were collected with 64 scans, a 2 sec acquisition time and 1 sec delay time.

DSC measurements were collected on a TA Instruments Q1000 with a refrigerated cooling accessory. Measurement parameters included a 20°C/min ramp rate from -90ºC to 100ºC.

Results and Discussion

The realization of a storage issue occurred during print testing, when an unrecoverable print quality defect presented itself as horizontal bands or sharp lines across the entire width of a printed page. After close inspection of the developer unit parts, a visible line of toner debris was observed along the length of the developer roller. The line of toner debris remained adhered to the roller surface even after the surface of the roller was vacuumed. The environmental storage conditions alone were not such that plasticization of the toner should occur. Therefore, a contaminant on the roller surface was implicated in toner Tg suppression resulting in an unrecoverable print quality defect.

The toner defect line on the surface of the developer roller was first imaged by SEM as shown in Figure 1. The toner defect sample was not removed from the developer roller surface; a small section of the coating was cut away from the roller and prepared for imaging. The SEM image illustrates that the toner particles in the defect line are fused, or plasticized together. The toner particles have lost their rounded shape and have become unrecognizable. To determine if the detrimental toner plasticization shown in Figure 1 was the result of a contaminant, further investigation was required.

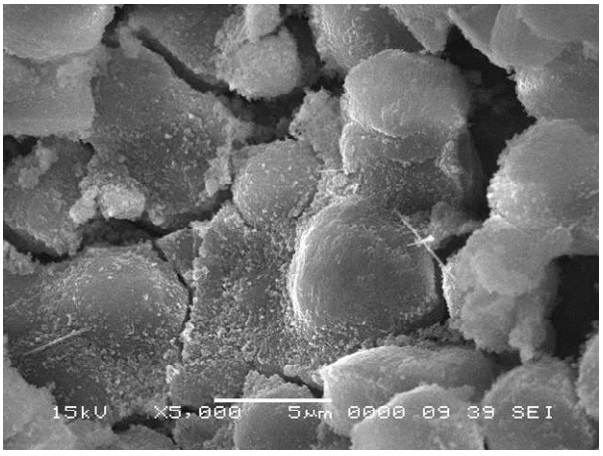

Figure 1*. SEM image of plasticized toner collected from the toner defect line. Sample was exposed to ship store conditions.*

After SEM revealed that the defect area consisted of fused or plasticized toner, a neighboring defect area was analyzed by ATR-FTIR imaging. ATR-FTIR imaging can provide chemical information on particles as small as ~3 µm - the critical spatial resolution needed for analyzing materials on the toner particle size scale. The ATR-FTIR image of the defect area is shown in Figure 2. A 200 x 50 µm area was imaged with a 1.56 µm pixel resolution. Each pixel in the image represents an infrared spectrum. After the data collection, a principal component analysis was conducted on the image to determine the number of unique chemical components present in the field of view. The image showed three distinct colors (black, gray and white) representing the detection of three different chemical components. The infrared spectra from the black areas show these areas are consistent with toner material. The infrared spectra from the gray areas are consistent with the developer roller surface. Finally, the infrared spectra from the white areas surrounding the fused toner material are consistent with a contaminant suspected to be the material responsible for toner Tg suppression.

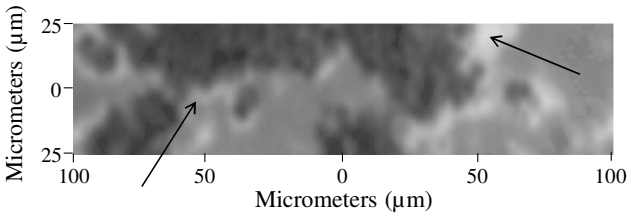

Figure 2. *ATR-FTIR image of the defect where all the white areas (examples marked by arrows) indicate the presence of a contaminant. Black areas are consistent with toner material and the gray areas are the roller surface.*

An infrared spectrum from a white area of the ATR image along with the spectral match is shown in Figure 3. From the match, the spectrum from the white area was identified as a glycol material, which was recognized as a low molecular weight polymer that was potentially migrating from the developer roller coating. Ideally, this glycol material should not be present on the developer roller surface. However, because this particular glycol is used as a starting material for the coating synthesis, residual material could still be present in the coating. It was realized that even after the coating was assumed cured, residual glycol material could potentially migrate to the surface of the roll, especially under storage conditions. From the ATR image, a low molecular weight glycol was identified as a contaminant and was further investigated as the potential cause for toner Tg suppression.

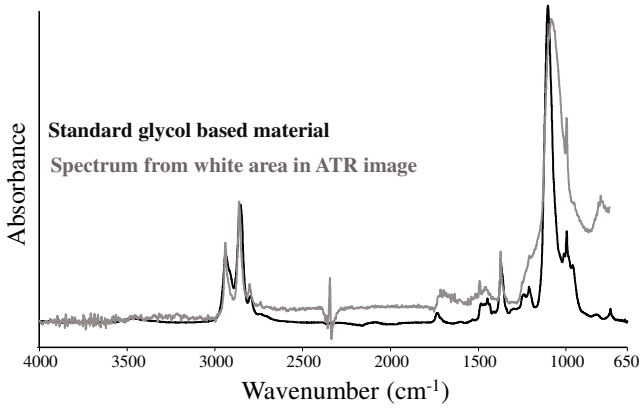

Figure 3. *IR spectrum from a white area of the ATR image matched to a standard glycol based material.*

Once the component of interest was identified, ASE and NMR analyses were employed to determine the amounts and types of extractable materials that could migrate from the developer roller coating. The ASE was first conducted on a set of rolls from various lots to determine the amount of extractable material (%NVR) present. Figure 4 is a plot that correlates the rating from the offline accelerated ship/store test with the ASE results (mass of extractable material) per roller. Failures from the offline test were assessed on a scale of 0-5. For example, a rating of 0 was given for no print quality defect observed. A print sample was assessed with a rating of 5 if the defect showed wide bands across the page. As the plot in Figure 4 shows, a strong positive correlation was observed between the amount of extractable material and the print quality defect rating.

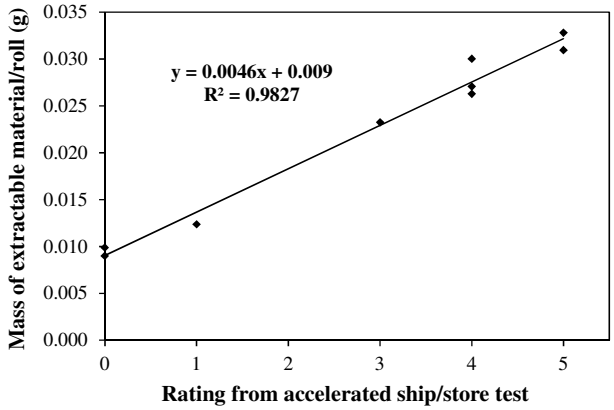

Figure 4. *Correlation plot showing a linear increase in the ship/store test failure rating as the mass of extractable material in a roller increases.*

After the roller extractables were collected, NMR was used to determine the composition of the different components and their relative concentrations. The NMR analysis confirmed that as the total amount of extractable material increased per roller, the amount of this specific glycol material increased much more than any other component. This further supported the hypothesis that the low molecular weight glycol material was to blame for the observed toner property changes. The NMR spectra shown in Figure 5 are examples from low and high total extractable rolls. As can be seen in the spectra, the roller with high percent extractables shows large contributions from glycol indicated by the two peaks at ~1.6 and 3.4 ppm. Close observation of the spectrum from the roller with low percent extractables shows the contribution of the low molecular weight glycol decreases significantly compared to the other components in the spectrum.

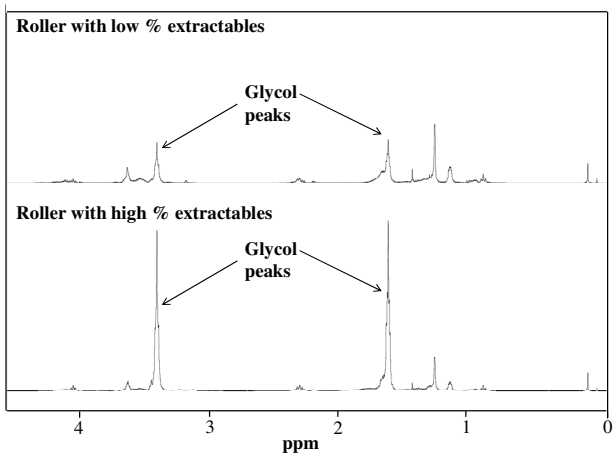

Figure 5. *NMR spectra of the extractables from rollers that showed a high level of extractables (%NVR) and a low level of extractables.*

Under storage conditions, failures may take weeks or months to manifest. Therefore, a quick, offline screening method was designed to determine if toner could have an unfavorable interaction with a coating material. The method involved spin-coating thin layers of polymer material onto a substrate followed by the placement of a relatively uniform layer of toner. The polymer/toner sample was exposed to an elevated temperature, and analyzed by DSC to determine if Tg suppression had occurred. Table 1 lists several samples and their recorded Tg after exposure to both ambient and 43ºC for 24 hours. The measured Tg for control toner at both ambient (25ºC/24 hours) and 43ºC/24 hr was 56ºC. Sample 1A represents a sample consisting of toner sitting on top of a glycol material which had a thickness of 0.7 µm. Even at ambient conditions (25ºC/24 hours), the Tg of the toner was suppressed 18ºC. For sample 1B, increasing the test temperature to 43ºC decreased the toner Tg down to 19ºC, which was now below room temperature. The most extreme case of toner Tg suppression using this approach was shown with samples 2A and 2B. The glycol layer thickness was increased to 7.0 µm and with both ambient and increased heat, the toner Tg is suppressed 45ºC.

Table 1. Measured toner Tg shifts after exposure to various conditions

Sample ID	Glycol Thickness	Treatment Conditions	Tg (ºC)	ΔTg (ºC)
Control Toner	-----	25C/24hr	56	0
Control Toner	-----	43C/24hr	56	0
1A	0.7 µm	25C/24hr	38	-18
1B	0.7 µm	43C/24hr	19	-37
2A	7.0 µm	25C/24hr	11	-45
2B	7.0 µm	43C/24hr	11	-45

The initial test results in Table 1 suggest that the toner-to-glycol ratio is an important factor. However, this information is only for a single point measurement. To allow this offline materials compatibility test to serve as a metric for determining high and low risk materials, it is required that multiple measurements be conducted over a range of glycol or "polymer"-to-toner mass ratios. Two polymers were chosen for testing, Resin X and Resin Y. Figure 6 shows that as the polymer-to-toner ratio increases for Resin Y, the risk for toner Tg suppression increases. However, as the polymer-to-toner ratio increases for Resin X, the Tg stays above the acceptability threshold making it a low risk material. This quick, quantitative, offline test can be used to assess the compatibility of toner with various polymeric materials it may interact with throughout the EP process. It is anticipated that this method will provide a screening tool for discovering low risk materials for use in EP subsystem components.

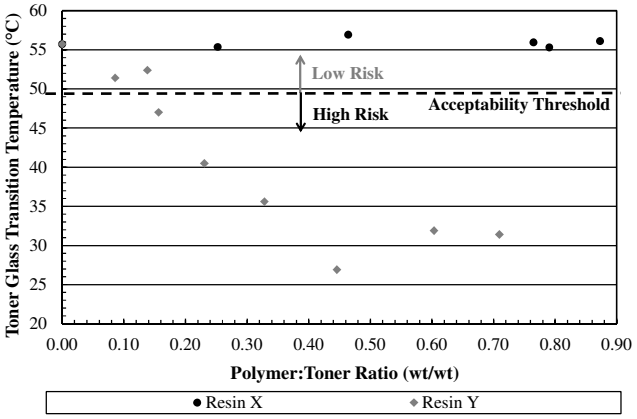

Figure 6. *Threshold plot showing that as the polymer-to-toner ratio increases for Resin Y, the toner Tg shifts to lower temperatures. This type of plot can be used to determine if a potential material is of high or low risk for toner Tg suppression.*

Conclusions

Toner has the potential to interact with various types of materials throughout the EP process. Coating materials in particular can pose the risk of facilitating toner Tg suppression. Utilizing analytical techniques such as SEM, ATR imaging, ASE and NMR, contaminants can be identified and quantified to ensure an effective solution to the problem. The combination of materials analysis and functional testing was shown to be a powerful approach to identifying the plasticizing material and working toward a solution. Toner compatibility can further be assessed by performing an offline test and monitoring Tg suppression. This type of method can provide a screening tool to discover low risk materials for use in EP subsystem components.

References

[1] Julien, P.C. and Gruber, R.J. "Dry Toner Technology", in Handbook of Imaging Materials (Marcel Dekker, New York, 2002) pg. 173-208.

[2] Mang et al., Methods for Reducing Plasticization and Blocking in Polyester Toner Compositions; United States Patent, Patent Number: 7,833,688 (2010).

[3] Mang et al., Methods for Reducing Plasticization and Blocking in Toner Compositions; United States Patent Application Publication, Pub. No.: US 2011/0020744 A1 (2011).

[4] P. R. Griffiths and J. A. De Haseth; Fourier Transform Infrared Spectrometry (Wiley-Interscience, 2007), 2nd ed.

[5] Sommer, A.J.; "Mid-Infrared Transmission Microspectroscopy" in Handbook of Vibrational Spectroscopy (Wiley, UK, 2002) pg. 1369.

[6] Gulley-Stahl, H.J.; Bledsoe, S.; Evan, A.P.; Sommer, A.J. Applied Spectroscopy (2010), 64(1), 15-22.

[7] Gulley-Stahl, H.J.; Evan, A.P.; Sommer, A.J. "Evanescent Wave Imaging", in Vibrational Spectroscopic Imaging for Biomedical Applications (McGraw-Hill, New York, 2010) pg. 99-124.

Author Biography

Heather Gulley-Stahl received a B.S. in chemistry from Northern Kentucky University in 2006 and a Ph.D. in chemistry from Miami University in 2010. Heather has been an analytical chemist at Lexmark International since 2010.