Surface Modification of an Organic Photoconductor in an Electrophotographic Charging Environment

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Abstract

Prolonged exposure of a commercial organic photoconductor in the plasma environment corresponding to an industrial electrophotographic process caused formation of a parasitic surface layer with the properties different from the original photoconductor. The parasitic film consists of a heavily oxidized surface and oxygen-free subsurface layer with the chemical composition similar to the original photoconductor but a significantly different bonding arrangement. Formation of these two regions has been correlated with damage induced by the energetic radicals and the UV photons originating from the electrophotographic plasma discharge. In-depth understanding of the formation and the properties of this parasitic layer could provide effective means to overcome its detrimental impact on the printing cost and quality.

Introduction

Advances in the commercial electrophotographic printing yielded development of complex organic photoconductors frequently used in conjunction with the charge roller. However, employment of these components in the applications requiring long runs and high speed printing demonstrated potential problems related to not well defined, so-called photoconductor "wear-out", manifesting itself in form of undesirable changes in the physical and chemical properties of the photoconductor and the corresponding print quality degradation [1]. Goal of this work was to investigate the nature of the structural and compositional changes occurring within the surface region of a commercial organic photoconductor occurring during a prolonged exposure of the photoconductor to the plasma within an electrophotographic environment, and to provide path towards elimination of these undesirable photoconductor's modifications in the future electrophotographic applications.

Experimental

An experimental set-up analogous to a common electrophotographic print engine was used. It consisted of an organic photoconductor covering the surface a large diameter drum and a small diameter charge roller in contact with the photoconductor. In several cases a scorotron was used instead of the charge roller. A bank of light emitting diodes in vicinity of the photoconductor was used to neutralize the electrical charges on the surface of photoconductor. All components of the experimental set-up are commercially available. The organic photoconductor consisted of a polycarbonate layer deposited on the metallized Mylar substrate. The bottom part of the polycarbonate film was doped with organic molecules providing holes when illuminated, while the top part contained small amount of the molecules enabling hole transport (arylamine-substituted hydrazone-based species).

Following the common electrophotographic process negative charging of the photoconductor's surface was achieved by applying the negative bias between the charge roller and the metallized base of the polycarbonate layer within the photoconductor under room ambient conditions. Charging of the photoconductor's surface occurred when the bias exceeded the threshold of Paschen discharge. It took place only in the region in direct vicinity of the charge roller (approximately 1/250 of the total photoconductor' surface). In order to imitate the effect of the prolonged plasma exposure on the photoconductor's surface the photoconductor was rotated with charge roller in contact and bias applied. This process corresponded to printing multiple pages.

Current flowing between the charge roller and the photoconductor as a function of the applied bias was monitored throughout the entire experiment. In addition, surface potential of the photoconductor was continuously measured using a non-contact electrostatic probe placed in the vicinity of the photoconductor. Light emission related to Paschen discharge was detected with an optical fiber (UV transparent at wavelengths above 270 nm) pointed at the center of the plasma cloud and analyzed with the help of spectrometer equipped with a photomultiplier detector having resolution of about 0.25 nm and calibrated with an external reference spectrum. This resolution could not resolve all the fine details of the emitted light but allowed for identification of the major emission features.

The X-Ray Photoelectron Spectroscopy (XPS) and the Attenuated Total Reflectance Fourier Transform Infrared Spectroscopy (ATR-FTIR) were used to evaluate chemical modifications introduced by prolonged plasma exposure of the photoconductor corresponding to continuous printing of multiple pages. XPS can measure the chemical composition of the photoconductor's surface, while ATR-FTIR can provide information about the nature of chemical bonding within a thin region below the surface. This technique can detect specific molecular vibrations and it is particularly well suited to monitor modification of the chemical bonding arrangement introduced by the prolonged interactions with plasma. In addition, the wetting angle measurement was used to monitor changes of the photoconductor's surface energy caused by the plasma exposure.

Particle bombardment and UV illumination are the two major mechanisms of interactions between the Paschen discharge and organic photoconductor. In order to elucidate their relative impact on the photoconductor material, samples of the photoconductor were exposed to particle bombardment in a parallel-plate Ar-O_2 plasma etcher operating at pressure of few hundred mTorr and bias of 300V. Its operating conditions were selected to vary the UV generation and maximize the effect of particle bombardment. Although, this experiment did not reproduce exact conditions of the particle bombardment present in the electrophotographic environment, it provided some information regarding the nature of photoconductor modification introduced by the bombardment processes. In a corresponding experiment, photoconductor was illuminated with a UV source providing the emission wavelength and the energy dose corresponding to the UV exposure in our experimental electrophographic set-up. Two UV sources were used: a medium power broadband UV lamp with peak emission of about 365 nm and a defocused 325 nm HeCd laser beam. The UV wavelengths were selected to be strongly absorbed by the polycarbonate. In both cases the energy density of UV illumination was equal several µW/cm2, so it corresponded to the UV energy density emitted by the Paschen discharge in an electrophotographic environment, while the total UV dose corresponded to the dose delivered by an extended plasma exposure in our test system. Plasma UV energy density was evaluated with the help of the aforementioned optical fiber – calibrated spectrometer system.

Results and Discussion

The XPS analysis demonstrated that prolonged exposure of a photoconductor to the charge roller generated plasma significantly increased the oxygen concentration at the surface (Table 1). Even when assuming that some of the surface oxygen is related to post-experiment surface contamination, as presence of Si may suggest, majority of the added oxygen is due to surface oxidation caused primarily by the oxygen radicals and to a lesser degree by the oxygen ions. Nitrogen atoms observed in the XPS spectrum originate from dopant molecules uniformly distributed within the polycarbonate matrix. Figure 1 shows that this oxidation phenomenon is limited to the photoconductor's surface; the oxygen increase does not extend beyond the top several tens of nm.

Table 1. Chemical composition of the organic photoconductor (XPS). Only elements detectable by XPS are included.

Concentration (at.%)	C	O	N	Si[1)]
Unused photoconductor	83	15	2	0
Used photoconductor (after 6hrs)	61	34.5	2	2.5
Used photoconductor after prolonged soaking that removed the modified surface layer	81	17	2	0

[1)] due to extraneous contamination

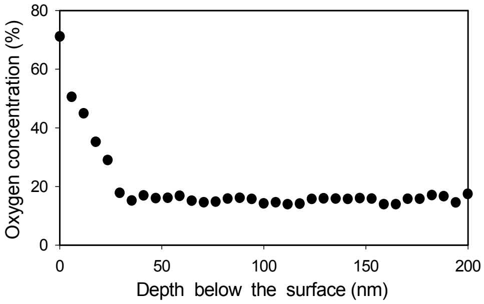

Figure 1. *XPS measured photoconductor's oxygen depth profile after 6 hrs plasma exposure.*

Deeper region of the photoconductor has been tested with the help of ATR-FTIR. IR spectrum of an unused photoconductor is virtually identical with the spectra of an undoped reference polycarbonate (Figure 2). The majority of the observed features can be associated with the specific vibrations of a Bisphenol-A molecule (polycarbonate monomer) or polycarbonate network [2]. Prolonged plasma exposure in our experimental set-up doesn't change the IR spectrum, except for the region of 3000 cm^{-1} - 2700 cm^{-1}, where stretching C-H vibrations of the aliphatic methyl (CH_3) and methylene (CH_2) groups occur (Figure 3). Methylene groups, though not present in a model Bisphenol-A molecule, can be frequently observed in polycarbonate as part of the end- and side-groups of the polycarbonate macromolecules (Figure 3).

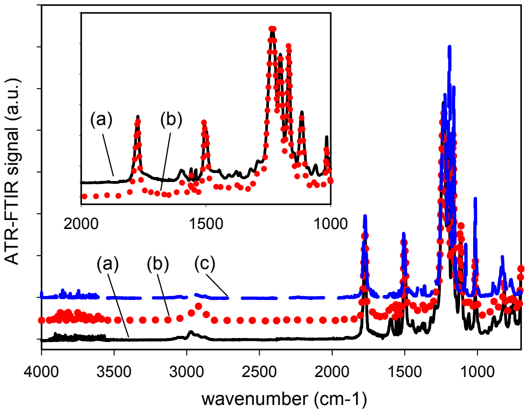

Figure 2. *ATR-FTIR spectra of: (a.) new photoconductor, (b) photoconductor after an extensive use, (c) reference polycarbonate .Insert shows region of intense absorption associated with carbonyl groups.*

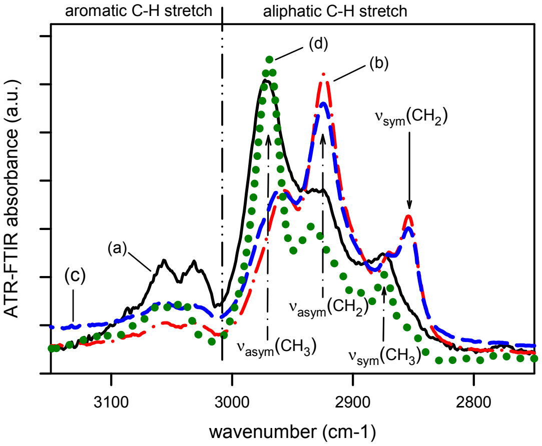

Figure 3. *C-H stretching region (ATR-FTIR): (a.) new photoconductor, (b) used photoconductor (charge roller), (c) used photoconductor (scorotron), (d) reference polycarbonate. Components of the aliphatic C-H stretching have been identified. "used": photoconductor has been exposed to plasma for 6 hrs.*

ATR-FTIR spectra shown in Figure 3 and in the subsequent figures have been normalized with respect to the highest absorption peak in this spectral region. The typical ratio of the CH_3/CH_2 peak heights, hereafter called Ψ, is about 1.55 for both asymmetric and symmetric stretching. The Ψ value gradually decreases as the photoconductor is exposed to the plasma indicating changes of the chemical bond arrangement within the subsurface layer probed by the ATR-FTIR (Figure 4). Eventually, after a prolonged plasma exposure, the Ψ reaches steady state indicating that plasma-induced bond modification within the subsurface region is a self-limiting process. This evolution of the

Ψ is accompanied by the well understood [3] change of the photoconductor's surface energy manifested by decreasing H_2O wetting angle (Figure 4). These changes have always been observed during the prolonged plasma exposure of the photoconductor and, due to simplicity of the ATR-FTIR measurement, the Ψ value has been used as a routine indicator of the photoconductor modifications.

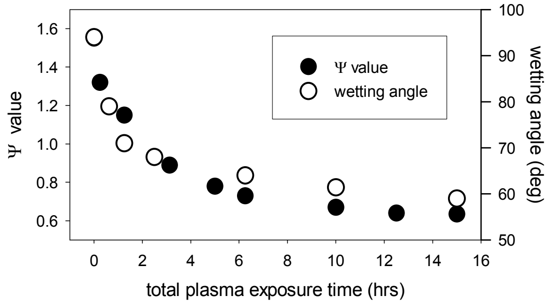

Figure 4. *Ψ parameter and photoconductor's wetting angle as a function of plasma exposure time. Ψ reaches the steady-state after approximately 4 hours.*

Large Ψ change caused by the plasma exposure suggests that the surface region may have completely different properties than the underlying, undamaged photoconductor, and that it could be removed with a proper solvent. This observation was tested by either wiping the photoconductor with a cloth wetted with a solvent or by soaking the photoconductor in a solvent for up to 15 minutes. The seconds approach was preferred because it avoided accidental scratching of the relatively "soft" photoconductor's surface. Only the solvents that did not attack the polycarbonate were used. Many of the typical organic solvents removed the modified surface region and even wiping with a cloth soaked with water provided its partial removal, as demonstrated by the Ψ value (Figure 5). The corresponding depth profiling (Dektak) of the selectively removed modified region provided an estimate of its thickness, equal approximately 150 nm - 200 nm.

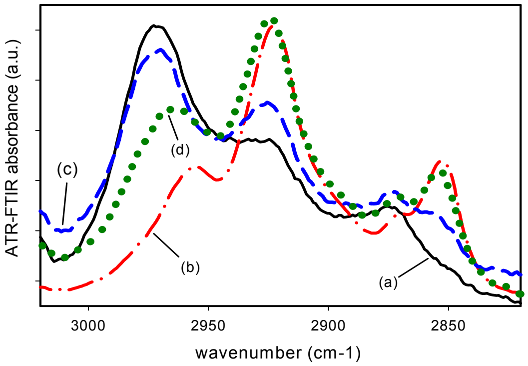

Figure 5. *Evolution of the C-H stretching signal during the plasma exposure and subsequent removal of the modified surface layer: (a) new photoconductor, (b) used photoconductor (4 hrs exposure), (c) used photoconductor after soaking in isopropyl alcohol, (d) used photoconductor after wiping with H_2O.*

The aforementioned experiment involving prolonged UV illumination resulted in photoconductor's modification similar to the changes caused by the prolonged plasma exposure in our experimental set-up (Figure 6). Interestingly, the corresponding experiment, where photoconductor was subjected to particle bombardment in a Ar-O_2 plasma etcher, provided a similar changes of Ψ only within a narrow Ar/O_2 range (Figure 7).

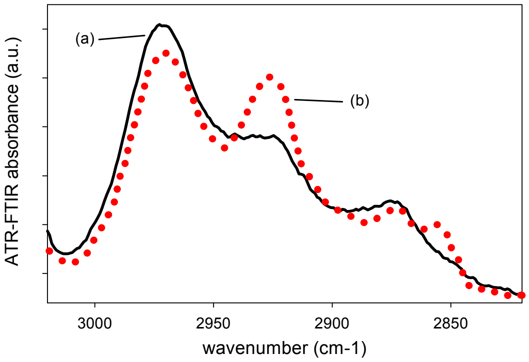

Figure 6. *Evolution of the C-H stretching signal caused by the long term UV irradiation (continuous illumination for 3 hrs using 325 nm monochromatic source with energy density of approximately 5 μW/cm^2): (a) new photoconductor, (b) photoconductor after UV exposure. Similar result was obtained when a broad spectrum UV source with emission centered at 365 nm and corresponding energy density was used.*

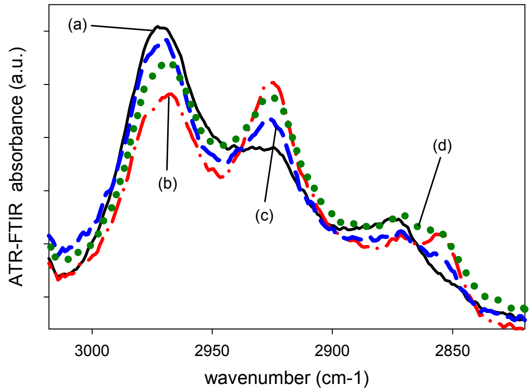

Figure 7. *Modification of the photoconductor's surface region under the Ar/O_2 plasma exposure, as demonstrated by the changes of the aliphatic C-H stretching signal: (a) new photoconductor; (b), (c) and (d) represent photoconductor exposed to the plasma with the respective Ar/O_2 ratio equal 50:50, 20:80 and 80:20. Plasma exposure time was equal up to 10 minutes.*

These results suggest two major processes occurring within the photoconductor when exposed to Paschen discharge plasma in an electrophotographic environment. Neutral and charged energetic particles and UV photons from the plasma discharge region impinge upon the photoconductor's surface breaking chemical bonds and forming unstable, reactive molecular species undergoing further reactions in search of the respective energy minimum. These reactions occur at depths corresponding to the respective penetration ranges. Radicals, electrons and ions are primarily limited to a shallow surface region, while UV photons can penetrate at least several hundred nm below the surface. According to previous reports [4,5] cracking of the benzene rings within polycarbonate may be the main source of the newly formed aliphatic species. This reaction is more energetically favorable than breaking of the O-(C=O)-O carbonate groups in polycarbonate [6,7]. Unstable molecular species rapidly evolve into aliphatic CH_2 groups that are then likely associated with the polycarbonate macromolecules. ATR-FTIR measurements show that vibrations associated with the carbonate groups, observed in the range 1800 cm^{-1} - 1700 cm^{-1} and 1250 cm^{-1} - 1200 cm^{-1}, remains relatively constant throughout the plasma exposure (Figure 1). At the same time a signal from the aromatic C-H stretching becomes weaker while the aliphatic C-H stretching absorption increases demonstrating that the ratio of aromatic to aliphatic carbon decreases within the volume probed by the ATR-FTIR (Figure 3). This reaction slows down after long enough plasma exposure, as the majority of benzene rings within the region reachable by the UV photons have been broken and the ratio of aromatic to aliphatic C-H groups reaches an equilibrium steady-state. Therefore, the thickness of the photoconductor's layer with altered properties (approximately 200 nm) corresponds to the UV penetration depth (150nm - 300 nm). This conclusion is further supported by the observation that aromatic C-H stretching is still visible (it originates mainly from the region further below the surface than the UV penetration depth, as the ATR-FTIR probing depth is approximately 400 nm) and that the decrease of Ψ value ceases after a very long plasma exposure.

Reactive molecular species formed at the surface of photoconductor undergo reactions with readily available oxygen radicals forming a variety of compounds containing C-O groups, as indicated by the XPS results. However, due to continuous surface bombardment with energetic particles, these compounds are likely sputtered away from the surface. Therefore, only a very thin oxygen-rich layer (Table 1 and Figure 1) can survive on the surface of photoconductor.

In addition to the present work primarily focused on the charge roller- based electrophotographic system, preliminary evaluation has also been made for the case when scorotron was used instead of the charge roller. Although the scorotron plasma generation mechanism is quite different from the charge roller, the photoconductor exhibits similar degradation manifested by the Ψ decrease after an extended exposure. It appears that even though the energy of scorotron-generated particles impinging upon the photoconductor may be lower than in the case of a charge roller, scorotron likely produces copious amounts of the UV photons degrading the surface region of an organic photoconductor.

Conclusions

Goal of this work was to elucidate degradation mechanism of a commercial organic photoconductor within a modern electrophotographic environment aimed at the high-speed, high-throughput applications. It was observed that the prolonged exposure of the photoconductor to energetic particles and UV photons originating from the discharge region caused significant structural and compositional changes within the region up to several hundred nm below the surface of the photoconductor, corresponding to the UV penetration depth. The cracking of the aromatic carbon rings appears to be the major mechanism driving these changes. Broken bonds rearrange themselves into most stable configurations leading to increase of the aliphatic CH_2 species within the bulk of the modified region, while the surface reactions with oxygen radicals result in formation of multiple C-O bonds near the surface. Similar degradation mechanism occurs regardless of whether charge roller or scorotron are used for charging of the photoconductor.

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Seongsik Chang joined HP Labs in 2003 as a electro-photographic physicist and has been working on liquid electro-photographic processes in Commercial Printing Engine Laboratory. He received his B.S. from Seoul National University in 1990 and his Ph.D. from Yale University in 1998, all in Physics. In his earlier career, his research focus was on micro-cavity physics, optical chaos, and integrated photonics.

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