Electrical Conductivity Measurements in Toners with Conductive Surface Additives

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Abstract

The objective of this study is to establish correlation between toner conductivity measured in a pressed pellet, and conductive properties of an individual toner particle. Electrical conductivity of toners with conductive surface additives was measured as a function of applied voltage, pellet pressure and additive surface area coverage. Conductivity of toner pellets increases with additive surface area coverage in a percolation manner, and depends on additive-to-toner size ratio, and applied pressure. Possible sources of errors of pellet measurements include enhancement of inter-particle contacts and migration of the additives under high pressure.

Introduction

Electrical properties of toner particles influence the processes of accumulation and relaxation of electrostatic charge, as well as toner particle transport in external electric fields. For example, in dual-component development, increase in toner conductivity often results in a reduction in average triboelectric charge and increase in the rate of charge exchange between the aged and fresh toner particles.[1,2] Toner conductivity also affects single component development.[3] gap transfer, and traveling-wave toner transport.[4] Therefore, design of xerographic toners or developers for particular applications requires a reliable method to assess toner conductivity. Typically, toner conductivity is measured by compacting toner into pellets with plane-parallel electrodes, and then applying standard current-voltage methods for solid specimens (such as the 2-probe current-voltage method). However, because xerographic printing processes involve toner as a free or loose powder, the relevance of toner pellet measurements to toner performance in a xerographic machine is not obvious.

The relationship between conductivity of individual particles and particle compacts is determined to a great extent by the quality of inter-particle contacts. The area and conductance of inter-particle contacts are controlled by inter-particle mechanical forces, such as the Van der Waals force or the external compacting pressure.[5] Since in the course of the printing process toners are exposed to high electric fields, high-voltage conductivity measurements can be of particular interest. At high voltage, the relationship between electrical conduction in individual particles and powder compacts is further complicated by the non-linear conduction components. Conductivity of compacted granulated materials typically changes with applied voltage as $\sigma=\sigma_0 exp(BV^{1/2})$.[6]

The type of inter-particle contact can vary between insulative (blocking) and conductive (ohmic) in the same powder, simply by changing the compacting pressure. The shape of the low-voltage part of the conductivity-voltage curve changes depending on the type of inter-particle contacts. The characteristic abrupt drop of conductivity at low-voltage typically indicates that the inter-particle contact is non-ohmic.[7]

Electrical conductivity of toners can be modified using conductive fillers or surface additives. A theoretical study based on an equivalent circuit model[8] showed that electrical conductance of an individual toner particle containing conductive surface additives changes with additive surface area coverage (SAC) in a percolation manner. Particle conductance decreases exponentially with a decrease in additive SAC until it reaches the percolation threshold where particle conductance decreases very rapidly. The SAC corresponding to the percolation threshold can vary with the additive-to-particle size ratio from approximately 0.45 at a size ratio of 0.2, to 0.7 at a size ratio of 0.005.

While measurements on a toner pellet can provide valuable information about toner conductivity, it is important to understand the relevance between conductivity measured in a pellet and conductance of an individual toner particle, and to account for possible measurement errors and artifacts associated with pellet pressing. The purpose of this study is to establish a correlation between conductivity measurements in a toner pellet and SAC, compaction pressure and applied voltage, and to determine the optimum conditions for electrical conductivity measurements in toners.

Experimental

Conductive toner samples were prepared from polyester toner particles with an average size of 8 μm cold-blended with nano-sized conductive additives. Two conductive nano-powders were used in this study, tin oxide powder with an average particle size of 20 nm and specific gravity of 6.6 g/cm3, and tin-doped conductive titanium dioxide with an average particle size of 45 nm and specific gravity of 5 g/cm3. Preliminary SEM analysis showed that the additives were uniformly distributed on the surface of the experimental toners. Table 1 lists the types, amounts and SAC of the surface additives in the toner samples used in this study. The SAC was determined in an assumption that the additives form a hexagonal close-packed surface layer.

Table 1. Surface Additive Compositions of the Experimental Toner Samples

Surface additive	wt%	Size (nm)	Density (g/cm3)	Surface area coverage
SnO	4	20	6.6	0.74
SnO	6	20	6.6	1.10
SnO	8	20	6.6	1.47
SnO	10	20	6.6	1.84
Sn-TiO	4	45	5	0.43
Sn-TiO	6	45	5	0.65
Sn-TiO	8	45	5	0.86
Sn-TiO	10	45	5	1.08

The resulting composite powders were compacted into circular pellets with a diameter of 10 mm and a thickness of 1 mm in a die with steel plungers and an insulative inner wall. Compacting pressure was monitored with a pressure gauge. Current-voltage curves were measured *in-situ* by sweeping DC voltage V applied to the plungers up to 1600 V, and measuring the series current I with a Keithley electrometer. Conductivity was calculated conductance (I/V) multiplied by the ratio of pellet thickness to pellet area.

Results and Discussions

Effect of Pellet Pressure

The effect of pellet pressure on the current-voltage response was studied in two toner samples containing 8 wt. % of conductive surface additives with two different sizes. The sample with 20 nm tin oxide had a SAC of 1.47, i.e., more than one full monolayer of conductive additives. The sample with 45 nm tin-doped titanium oxide contained only a fraction of a monolayer at a SAC of 0.8.

Figure 1 shows a semi-logarithmic plot of conductivity with the voltage square root in the sample at SAC=1.47 under different compacting pressures. This type of plot format has been found to be helpful for interpreting current-voltage data in compacted particulate materials.[7] The shape of the conductivity-voltage curve in this format can help distinguish between various conduction mechanisms including ohmic (constant conductivity), $V^{1/2}$ dependence (straight line), and the characteristic conductivity droop associated with blocking inter-particle contacts.

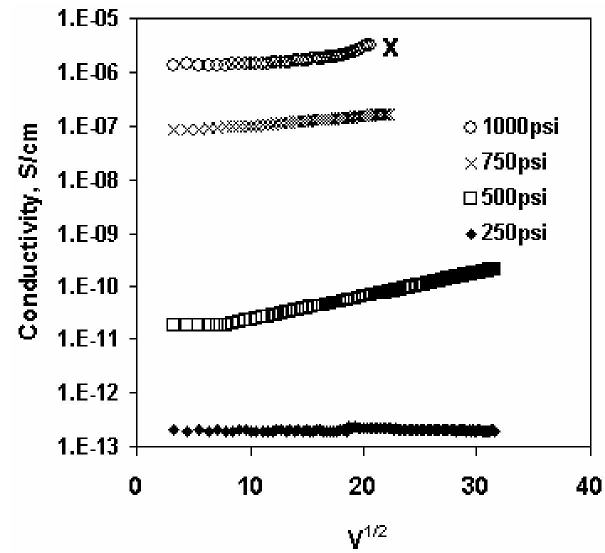

Figure 1. Change of conductivity with voltage in toner samples containing 8 wt. % of 20 nm conductive surface additive at SAC=1.47 compressed into pellets at 250, 500, 750 and 1000 psi.

As can be seen from Figure 1, conductivity varies with applied voltage and pressure in a broad range between 10^{-13} and 10^{-5} S/cm. At 250 psi, very low conductivity is registered indicating that this pressure is too low to establish effective electrical contacts between toner particles. At 500 psi, pellet conductivity does not change with voltage at voltages below 100 V indicating the presence of stable ohmic contacts between the additive particles. At voltages greater than 100 V, the plot of conductivity logarithm with voltage square root is a straight line indicating that the $V^{1/2}$ mechanisms dominates the conduction process.

Further increase in pressure to 750 psi and to 1000 psi results in an increase in pellet conductivity. The slope of the current-voltage curve flattens as the conduction process becomes "more ohmic" at the higher pressure, probably due to the redistribution of the force between additive particles and enhancement of the inter-particle contacts. The rapid increase in conductivity at 1000 psi at voltages greater than 350 V (see the "X" mark in Figure 1) was associated with the overheating and melting of the pellet under high electric current.

Similarly, Figure 2 shows the change of conductivity with voltage in the pellets compressed at different pressures from the toner with a sub-monolayer of conductive particles at a SAC of 0.8. As expected, this toner is generally less conductive compared to the above high-SAC toner (Figure 1). At 750 psi this sample shows very low conductivity. At 1000 psi, the high-voltage part of the conductivity-voltage plot is a straight line indicating the domination of the $V^{1/2}$ conduction mechanism. However the low-voltage portion of the curve differs from that observed in the high-SAC toner. In the low-SAC toner, the low-voltage behavior is clearly non-ohmic which is indicated by the rapid drop of conductivity with a decrease in voltage. This indicates that the contacts between the surface additives are not sufficient to provide stable ohmic conduction at the toner surface. In other words, the sub-monolayer SAC of this toner is below the percolation threshold. Similar sub-percolation behavior was observed at 1250 psi.

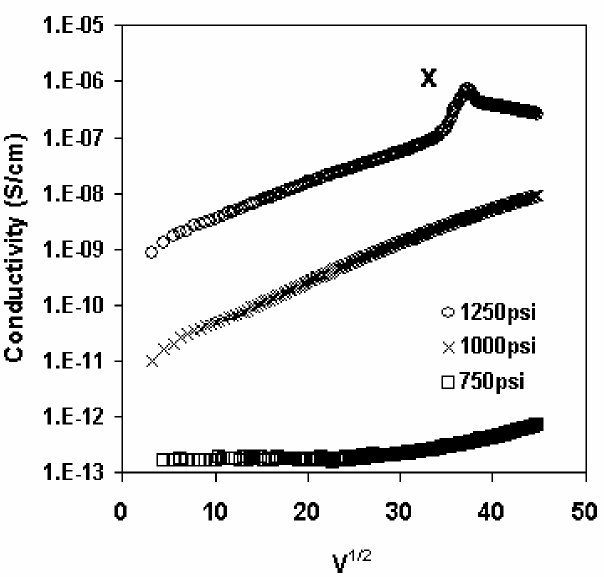

Figure 2. Change of conductivity with voltage in toner samples containing 8 wt. % of 45 nm conductive surface additive at SAC=0.86 compressed into pellets at 750, 1000 and 1250 psi.

At 1000 V, the pellet melted causing the peculiar peak on the conductivity-voltage curve (see the "X" mark in Figure 2). This rapid change in conductivity occurred probably due to the migration of the additives. In both cases, the melting of the toner sample was monitored as a rapid pressure drop as the pellet yielded.

Figure 3 shows the overall effect of pellet pressure on the conductivity measured at a constant voltage of 100 V. It is seen that conductivity of the toner pellets increases exponentially with the applied pressure.

Effect of Surface Area Coverage

A prior theoretical study[8] has showed that conductance of an individual toner particle with a surface layer of conductive additives decreases exponentially with a decrease in SAC until the percolation threshold is reached. At SAC below percolation threshold, conductivity drops abruptly and the toner becomes effectively insulative. The percolation threshold increases and approaches a full monolayer (SAC=1) with a decrease in additive-to-particle size ratio. Generally, the model[8] predicted that SAC can be used to control conductivity of toner particles only when the particle-to-additive size ratio is sufficiently large.

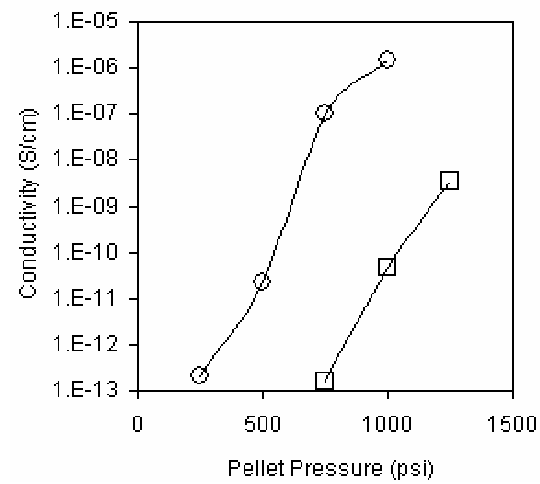

Figure 3. Change of pellet conductivity with compaction pressure in toners at SAC=0.8 (squares) and SAC=1.47 (circles).

Figure 4 shows the change of toner pellet conductivity with SAC of the 20 nm conductive additives. Conductivity in this experiment was evaluated at a constant voltage of 200 V and at two different pellet pressures, 1000 and 2000 psi. The pellet pressures were chosen relatively high to enable current-voltage measurements in a broad range of SAC, including that near and just below the percolation threshold. The dashed line indicates the position of percolation threshold according to the model in Ref. [8]. It is seen that the experimental percolation threshold (i.e., SAC at which toner pellet conductivity drops to very small values) shifts slightly towards lower SAC with increase in pressure. It is possible that the applied pressure changes the distribution of the conductive nano-particles on the toner surface and enhances the inter-particle contacts between the additive particles. Thus, excessively high pellet pressures can result in measurement errors by exaggerating conductivity values and inducing percolation in sub-percolation toners.

Similarly, Figure 5 shows the change of conductivity with SAC for toners with the 45 nm conductive additive. Note that in this case the ratio of additive to particle size is greater than with the 20 nm additive, and the percolation threshold is shifted towards the lower SAC as predicted by the model.[8]

In both Figures 4 and 5, note the relative agreement between the experimental and predicted percolation thresholds.

Conclusions

Electrical conductivity of toners with conductive surface additives was measured in toner pellets as a function of applied voltage, pellet pressure and additive surface area coverage. The conductivity logarithm increases proportionally to $V^{1/2}$ at voltages > 100 V.

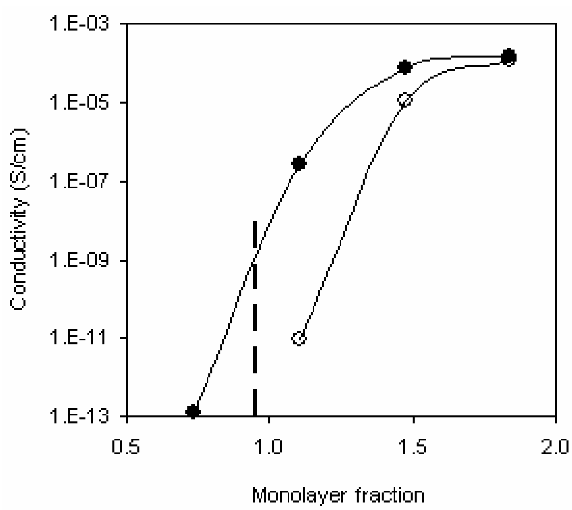

Figure 4. Change of conductivity with SAC in toners with 20 nm conductive additives compressed into pellets at 1000 psi (open symbols) and 2000 psi (filled symbols). The dashed line shows the position of the calculated percolation threshold.[8]

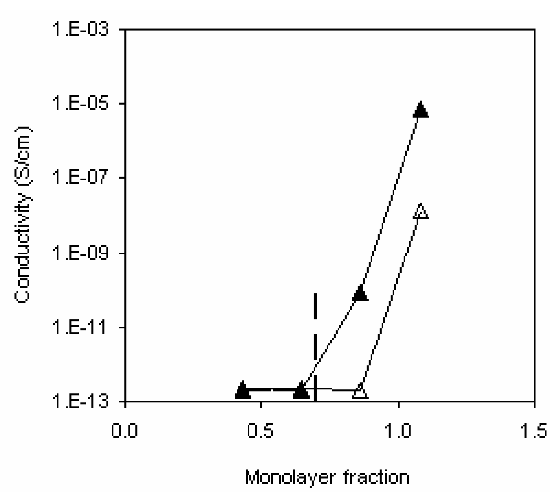

Figure 5. Change of conductivity with SAC in toners with 45 nm conductive additives compressed into pellets at 1000 psi (open symbols) and 2000 psi (filled symbols). The dashed line shows the position of the calculated percolation threshold.[8]

The shape of the low-voltage portion of the conductivity-voltage dependence can be used as an indicator of whether the additive SAC is below or above the percolation threshold. For sub-percolation SAC, conductivity decreases abruptly with a decrease in voltage. At SAC above the percolation threshold, low-voltage conductivity is constant (i.e., ohmic).

Conductivity of toner pellets increases exponentially with compacting pressure. Generally, the ohmic component of electrical conduction in a pellet becomes more significant with increase in pellet pressure. It is possible to induce percolation by applying high pellet pressure to a sub-percolation toner pellet. This effect can be responsible for a serious measurement error, as an intrinsically insulative toner will appear as conductive.

At extremely high pellet pressures and under high applied voltages, toner pellets can melt causing incorrect conductivity readings due to the migration and irreversible re-distribution of the conductive surface additives.

For very small additive-to-toner size ratios of < 0.01 typical for most toners, the percolation threshold approaches one full monolayer, as predicted in a previous theoretical study.[8]

Therefore, in order to ensure that the conductivity measurement in a toner pellet is most relevant to the conductance of individual toner particles, it is important that an optimum measurement condition be chosen at the possibly lowest pressure and relatively low voltage such that the measurements are conducted within the ohmic region, and no artifacts are introduced by an excessive compaction.

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Biography

Vladislav Skorokhod received a Ph.D. in Materials Engineering from Queen's University (Canada) in 1998. His work at the Xerox Research Centre of Canada is focused on the integration of chemical toners into xerographic printing systems, and physical and electrophysical properties of particulate, granulated and nanostructured materials.