The Expanding Role of Semi-Conductive Polyurethane in Electro-Photographic Systems

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Abstract

This paper explores the increasing use of semi-conductive polyurethane materials in dry toner Developer, Charging, Cleaning, Intermediate Transfer and Transfer functions, and Developer, Intermediate Transfer and Squeegee functions in liquid toner systems. If you design or specify semiconductive polymer materials for these functions, this paper will provide information on the important design characteristics to communicate to the polyurethane manufacturer. Also discussed is a common language for those specifications and for identifying testing and measurement methods for those characteristics. Testing and measuring methods of Volume Resistivity and Electrical characteristics are explored in detail. A common formula for specifying resistivity is explained and the effect of time, temperature and humidity on this measurement are discussed. Basic molding and machining processes used are reviewed briefly at the beginning of this paper, as are application descriptions. The major functional and quality characteristics to be determined and considered for these applications are:

- a) Electrical Properties; Volume Resistivity, Change in Volume Resistivity over time (and/or over total energy transmitted), Change in Volume Resistivity under differing temperature and humidity conditions, Other electrical properties such as R/C charge-decay time and Refresh rate and relation to nip residence time.
- b) Physical Properties: Compression Modulus and Durometer [JIS or Shore] (relation to nip width), Tensile, Tear, Shear and Cut Strength, Resilience, Compression Set, Wear and Abrasion Resistance, Surface Energy and release characteristics and COF. Chemical and ozone resistance, Surface roughness, Load and Dynamic properties ($tan-\delta$, Hysteresis and balancing issues)
- c) Base Chemistry: Material class or base polymer group (i.e. Polyester or Polyether Polyurethane and how this relates to Chemical Resistance and Hydrolytic Stability.), and the use of differing conductive agents in these systems.
- d) Attribute Defect Criteria and Dimensional tolerance issues.

Introduction

Basic Molding and Machining Processes

Polyurethane can be formed by combining a Pre-Polymer resin, containing NCO functional groups, with a curative agent, (polyol or amine), containing OH functional groups. The ratio (molar) of active NCO sites to active OH sites is called the "Stoichiometric Ratio" or "Percent Theory" [inversely the "Index"]. This Ratio is the primary manufacturing control for the molding operation. The Index can be changed and used to adjust product physical (and sometimes electrical) properties given the same base chemistry. Other methods of adjusting physical properties include altering base polymer backbone, curative type, use of chain extenders and hardness modifiers and adjusting catalyst, curing cycles and temperatures.



Figure 1. Basic "Liquid Cast" Molding Process Used to manufacture Polyurethane Rollers for EP Systems

From here the product is "cured" in the mold until sufficient cross-linking and green-strength is achieved. At that point, the product may be de-molded, and further cured (post-cured) if required to complete the cross linking process and optimize physical properties.



Figure 2. Pre and Post-Cure Processing

After curing, the product may be either trimmed only (for as-cast "glass-like" surfaces), or trimmed and ground (for matte or smooth machined surface with tight dimensional tolerances). For ultra-smooth machined surfaces special grinding wheels and additional "micropolishing" can be employed. Rollers are typically ground on cylindrical grinding machines with centers or tooling for the datum journals. A new variety of CNC Ultra High Precision "Roll Grinders" specially designed for these types of rollers are readily available. "Centerless Grinding" is very rare for this purpose.

Dimensional and Attribute Tolerances

Normal "as-cast" dimensional tolerances for low cost (feed, transfer or charge) rolls are cylindricity of around 0.140 mm with smooth surface finishes Ra 0.3 um, Rz 3.0 um. Current best "state-of-the-art" (higher cost – direct image applications) dimensional tolerances for "as-cast" rollers are on the order of 0.065 mm cylindricity, with surface finishes in the Ra 0.25 um, Rz 1.5 um range. For normal (medium cost) applications grinding can achieve cylindricity of 0.050 mm with surface finishes in the Ra 1.0 um, Rz 7.5 um range, and for Ultra-High precision grinding (also higher cost), cylindricity of 0.025 mm with polished surface finishes of Ra 0.25 um and Rz 2.0 um can be achieved.

Product yield (presence/absence of attribute surface defects) is greatly enhanced by grinding. Employing "As-

Cast" process for use in imaging surfaces (Developer & Intermediate Transfer) usually results in higher cost and decreased yields. This is due to the mold surface needing to be perfectly smooth (honed and polished I.D. of mold tube) and can be very dependent upon mold lube (release agent) application method and materials chosen. For this reason, a ground a polished surface for most Developer and I.T. functions is recommended. However, many OEM's are using "as-cast" rollers for liquid toner developer roller function.

Of all the items requiring specification early in the development phase, acceptance and rejection criteria for Surface Attribute Defects is the most crucial. This, unfortunately, is the most often over-looked or "save it for later" item to be worked on. Typically, only the OEM has the breadboard print testing equipment required to determine what can cause an "imaging" defect and what does not. This should be among the first of the quality characteristics to be defined. Doing this up-front will prevent the roll manufacturer from choosing the wrong process, molds, or facilities, or in some instances, even the wrong material.

Ionic Doped Polyurethane Electrical Properties, Physical Properties, Chemistry and EP System Applications

Among recent advances in urethane chemistry is the ability to create an inherently "semi-conductive" urethane. This can now be achieved through the use of Ionic conductive agents instead of electrically conductive fillers (such as carbon black). The types of ionic conductive agents (ionicsalts and metal oxide salts) now in use for doping polyurethane are increasing daily. Keeping up with the choices is becoming increasingly difficult.

From an electrical property standpoint however, using Ionic conductive agents has many advantages over the use of fillers such as carbon black. The major advantage is in the preparation of raw materials, mixing, and molding. These agents can be made soluble in polymer resins, liquid chain extenders, or cure systems. As such, the conductive agent is homogenously dispersed within the urethane chemistry. This is in contrast to carbon black in rubber, or foam, which has dispersion issues leading to "hot spots" or "cold spots" of electrical conductivity. This can result in uneven charging, development, or transfer of toner and ultimately in image quality degradation.

Current urethane technology allows the creation of materials with volume resistivity ranging from 10^{5076} to 10^{11} ohm-cm and hardness of Shore-A 20 to Shore D70. However, volume resistivity is limited to a minimum of 10^{8079} in systems above hardness of Shore A 80. The general relationship is the higher the hardness, the higher the resistance. This is due mainly to the mobility of the ionic charge carriers within the cross-linking system of the urethane. A conductive FDA approved formulation is also currently being researched for use in food packaging media printing applications.

EP Applications for Conductive Urethane Elastomers

Inherently Semi-Conductive, Ionic doped, Polyurethane elastomer rollers and blades are currently being used in EP systems in the following functions:



Figure 3. Current EP Applications using Semi-Conductive Ionic Doped Polyurethane Elastomers

Charge, Donor and Developer, and Squeegee Functions

Starting in EP Process sequence, Ionic doped conductive Polyurethane is being employed for Bias or Primary Charge Roller (BCR, PCR) function. Typical volume resistivity for this purpose is 10⁶ to 10⁸ ohm-cm and hardness of Shore-A 25-50. Hardness and conductivity are the most critical parameters for charging rollers. Surface roughness is not as critical for this function, as it is not directly involved in creating or transferring the image. Conformity of the nip, and nip residence time becomes critical in higher speed copier or digital laser printing applications. Abrasion, cut and tear resistance, run-out and bond to the shaft are not as critical due to the low (spring loaded) idling drive against the smooth surface of the OPC in the absence of toner.

Developer rollers typically have a very smooth surface. The "as-cast" molding process is often used for liquid toner developer rollers, and a fine, matte, ground and polished surface is used for dry toner developer rollers. Surface finish, electrical characteristics, freedom from attribute surface defect, chemical resistance (for liquid systems) and dimensional tolerances and stability are all critical parameters. The developer roller is by far the most difficult application to specify requirements for within the EP System.

Abrasion resistance can be critical in applications where the developer roller surface speed is different than the OPC surface speed (wiping action) employed often in dry toner applications to impart tribo-charging to the toner particles. For this same reason, surface finish and electrical characteristics (including Resistive-Capacitive charge and decay) are critical. For dry toner systems, a "polished" Developer surface of Ra 0.5, Rz 2.5 – 5.0 often is specified. There exists a relationship between toner particle size and optimal Rz surface finish. Rz is more discriminating than Ra because it takes into account the valley distances and other types of defects such as relatively more widely spaced grind patterns than Ra will show. This is due to the way in which Ra and Rz are calculated. For most EP applications, Rz is better employed than Ra, but current EP industry practice is slow to switch to Rz ONLY. Some companies specify both, but this is sometimes a conflict, especially when urethane is specified instead of conventional rubber. The relationship between Ra and Rz is not constant and is a function of material and machining or casting process.

Developer roller surface finishes for liquid toner systems must be on the order of Ra 0.3 um and Rz 2.0 um. Chemical resistance (esp. to Isopar) is required for liquid toner systems. For this reason, a TDI or MDI Poly-*ESTER* based backbone is typically chosen. Where water based systems are used, Poly-*ETHER* systems are usually chosen. New opportunities exist for water based high-speed conventional printing systems for the use of Polyurethane instead of convention rubber or NBR. New urethane technology also allows Polyester-Polyether blends to address instances where water is a component in a solvent based system.

The donor roller in dry systems is usually inexpensive open cell urethane foam, low tolerance, very conformal, used to "brush" a uniform layer of toner onto the OPC. This layer, in turn, is leveled down to a mono-layer (one to three toner particles high) by an elastomer "doctoring" blade. In liquid systems, donor rollers can be solid urethane elastomer, and would have similar characteristics to the developer roller.

This takes us to the Squeegee roller. In liquid systems, the squeegee roller is employed to squeeze down the toner particles, laid out by the developer roller, into more intimate contact with the OPC surface and to squeeze out the residual Isopar or toner suspension media in the pre-nip region. This minimizes the amount of liquid solvent transferred to the paper or print media and subsequently out to the fuser system. While the squeegee does not directly hold or transfer the image, it's function is nearly as critical in that it has the opportunity to distort the image as it is squeezing. Dimensional stability, tight tolerances, and surface finishes are required. uniform Electrical characteristics are not as critical and volume resistivity for this function is usually held between 5×10^{7} and 8×10^{9} ohm-cm. Hardness' from Shore A 40 to Shore A 65 are typically called out, and Polyester based backbones or Ester-Ether blends are utilized for solvent resistance.

Intermediate Transfer and Transfer

The next application is increasingly being utilized, and that is the Intermediate Transfer roller or "drum". This function exists to allow the IT drum to be the "sacrificial" surface and extend the life of the OPC. It also allows for conformance of the image-carrying surface to differing media surface textures and thickness. Conventional OPC drums are hard, non-conforming, low abrasion resistant Polycarbonates. This is increasingly important as the world of digital imaging moves into markets previously dominated by high-speed offset lithography.

By utilizing conductive polyurethane in the IT function, the OEM also decreases the "Total Cost Of Ownership" of the EP printer by making a less expensive part sacrificial, and in a location which is easier to service and replace.

The IT drum is typically the same diameter as the OPC, and is a medium durometer (50-70 Shore A), conductive $(10^6 \text{ to } 10^{80^9})$ medium wall thickness (5-20 mm) drum. Very tight dimensional and surface finish tolerances are required and precision grinding and polishing are often employed to manufacture these drums. Straightness and cylindrical runout are critical as is diameter and surface (both roughness and energy related to transfer and toner retention after transfer). The IT Drum is sometimes coated with a low surface energy, very thin, smooth conformal coating to aid in image transfer and toner release. The surface, being a direct image carrying function, must also be free from attribute defects. As such, very clean environments are required during final finishing operations and coating (similar to OPC manufacture).

Due to the IT drum sometimes being employed as "Idling" (driven by the paper and OPC), a condition known as "Overdrive", which results from excessive torsional stress and rebound post-nip, exists. Print registration can then be negatively affected by poor nip conformance and overdrive in the OPC to IT transfer and again in the IT to Media transfer. Because of this, material properties of hardness, compression set, and resilience can be as critical as the dimensional characteristics, and should be carefully specified.

The Transfer Roller (or sometimes referred to as the Paper Transfer Roller) can function simply to provide transfer bias to the media, or can also feed the media. The surface finish of this roller is not as critical as the others, but must have some grip to it for proper feeding. Dimensional tolerances are typically tight (0.05 mm cylindricity), but not ultra-precision. Volume resistivity is normally in the range of 5×108 to 3×109 ohm-cm with a hardness of around 50-65 Shore A.

A Word on Optimization

Each of the functions described above has many characteristics to be considered on a system level. The interactions between them are often difficult to describe or model. The best method of approach is through designed experimentation. Among the capabilities of liquid cast polyurethane for this purpose is the ability to custom formulate. It is possible then to create say two (or three) levels of conductivity within the same formulation backbone, or change backbones and keep the same resistivity, or change dimensions and surface finish independent of each other. This allows the EP Development engineer the opportunity to evaluate these characteristics against functional parameters of the system. Too often, the dimensional, durometer, and resistivity requirements are specified very "tightly" in a design strategy which divides a total system tolerance among the individual components,

leaving the key rollers with very little room. This results in sub-optimized system performance, and higher than necessary unit purchase cost for the OEM. It is best, up front, to use methods such as fractional factorial experiments {Taguchi, Central Composite Designs, or other classical methods} to optimize the system, determine interactions, and perform true tests of tolerances based on functional performance. In choosing urethane roll vendors, it would be wise to choose those who can speak this language and be able to work closely with the design development team in a concurrent engineering fashion.

Volume Resistivity – A Detailed Discussion

The measurement and specification of volume resistivity can be a complex issue. As such, it deserves discussion in detail. Volume resistivity is simply resistance standardized to a given thickness and surface area [thus the preface "volume"]. Volume resistivity is measured in units of ohm-cm and defined as below in equation 1.

$$\rho_{\Omega^* \text{cm}} = \frac{V \times \text{cm}^2_{\text{(contact area)}}}{I \times \text{cm}_{\text{(thickness)}}}$$

Equation 1. Volume Resistivity, General Formula

The unit "ohm-cm" is derived from voltage over current being ohms and square cm contact area over cm thickness becoming simply cm as below.



Equation 1a. Volume Resistivity Ohm-cm unit derivation

Volume resistivity is measured by applying a known voltage "V", across a known contact area (in a roller this is the nip width x length) and a known thickness (wall thickness of the roller. We then measure current flow "I" and use equation 1 to calculate ohm-cm. This can be done in a variety of ways, some of them more accurate than others, and can be measured on slabs of material, or on rollers and drums directly.

Standard Volume Resistivity Testing of Slab Material

Volume resistivity can be measured on slab stock of materials for comparative, quality assurance, or developmental purposes. When measured in this fashion, a slab of material, typically around 0.250" thick, is placed between two conformal, low resistance, contact plates. Voltage can be supplied by an independent power supply, or by one with a built-in pico-ammeter and digital output. This allows the user to utilize software control via IEEE-488 or RS-232 and gain automated data capture through programs which can be written in Lab-ViewTM, or an equivalent data capture and device control program. Since Volume Resistivity changes over time, it is important to specify at what time this measurement is to be taken. The software employed allows a table and graph to be built. Industry standard times used by many EP OEM's would include 1, 3, 5, 10, 30 and 60 seconds. If no specification of time is made, the 3-second time is typically accepted. This depends on the history of the particular OEM and the relationship with their urethane roller suppliers. If information is required in the less than 1 second time slice, it becomes necessary to capture this information on an Oscilloscope as defined in the next section.



Figure 4. Volume Resistivity Testing, Slab Stock

High Speed Volume Resistivity and RC Charge-Decay

Due to the nature of Ionic conductive agents, and their behavior within the cross-linking structure of polyurethane, the urethane acts like a capacitor and a resistor in parallel. There exists an RC charge up and decay during the initial first millisecond(s) of current flow. This charge acts to inhibit actual current flow to the nip and prevent charging as the ions are rushing to "fill holes" similar to electron buildup on a plate of a capacitor. Once the holes are filled, the current can begin to flow at a level equal to the volume resistivity. This RC charge-decay can be captured using a high speed switching device and a digital capture Oscilloscope of sufficient frequency to gather information in the time slice of importance. In systems where nip residence time is less than 5 milliseconds, this can be critical to understanding charge and resistivity requirements. A good rule of thumb is to work backwards through the equation for volume resistivity (equation 1) using the nip width x length of roller contact as the contact area, and use the cross sectional thickness as the thickness.

From here it is possible to "backwards" calculate the desired volume resistivity if you know the bias in the system and the desired current flow in order to obtain the correct charge on the next surface (OP surface in case of charge roller, nip or paper in case of transfer). From here, one would need to calculate the nip residence time. This would be the nip width in mm divided by the surface speed in mm/second. A good rule of thumb is that the roller

should reach it's desired volume resistivity in roughly ¹/₂ the nip residence time or less. This allows for the R/C charge decay cycle to complete and for current to flow prior to being halfway through the nip. This same method can be used in a roller test fixture.



Figure 5. High Speed R/C Capture Setup

Stationary Roller Volume Resistivity Testing

Among the most often used VR test methods (but least representative of actual functional use) is the "Stationary Roll" Volume Resistivity test. This method employs a flat, or inside radius, contact plate pressed against the roller to either a known force or known nip width. The surface contact area is either limited by the contact size, and therefore known, or it is calculated by the nip width x length. The method is similar to slab testing, only done on a roller. The obvious faults with this system are that contact area is not always known, and the roller is not moving. The contact area for the shaft is all the way around the shaft, and the contact area for the surface is limited by the shape and size of the contact and pressure involved. Also, due to the pressure involved, the cross sectional thickness can vary with differing durometer hardness or with differing compression modulus materials (i.e. foam vs. solid elastomer).



Figure 6. Stationary Roller Volume Resistivity Testing

Dynamic Roller Volume Resistivity Testing

The most functionally reliable test method would be the method that comes closest to the measuring the "in-use" state of the roller. A number of commercially available analog test devices exist for this. One of these is the Anekenisis machine. A better way to grab information about current flow is to employ the method described in Figure 7, utilizing dynamic, moving roller contact. Some of the same problems associated with stationary roll testing (i.e. identifying nip width and cross sectional thickness) will occur with this method, however, it does capture the "inuse" current flow picture. In this method, a rotating contact roll (preferably one of the same diameter as the surface against which the roller will function) is employed as the bottom contact. Volume resistivity is calculated in the same way, and can be captured and graphed over time. With some programming, one could set up a "Volume Resistivity Life Cycle" testing protocol. This would allow measurement and optimization of the life of the volume resistivity and give an accurate measurement of the volume resistivity while the roller is rotating at the same surface speed as in use in the EP system.



Figure 7. Dynamic Roller Volume Resistivity Testing

The Nature of Ionic Conduction in Polyurethane

Little is known about the exact manner in which current flows in Ionic doped polyurethane systems. Most of this information is not gathered in one place, and opinions vary far in excess of the facts that are known. It is theorized that the charge carriers (cat-ions) are exchanged for an-ions at the nip. In this instance, the an-ions flow inward toward the core of the roller. There are documented instances where breakdown (unzipping) of the urethane cross-linking has occurred at the core of the roller. It is thought that this may be a function of the an-ions modifying the pH of the absorbed water in the roller, causing acidic reaction and subsequent breaking of the cross linking bonds. When this happens, the polyurethane can revert back to a liquid. This can happen at the core (typically in negatively biased core when compared to nip), or can happen at the surface (in positive biased core with respect to nip). In either case, the exact cause is still not completely understood.

The main limiting factor in use of ionic-doped polyurethane is the life of the conductive agent. In high speed, long running, high voltage bias, applications, the volume resistivity can degrade (increase) over time with use. It is hypothesized that this is a function of the total charge carried (or coulombs) of energy transferred. This phenomena is known as "Ionic Depletion". It's exact cause is unknown, but through improvements in testing capabilities, is currently being researched and addressed.

Volume resistivity in these systems can also be influenced by temperature and humidity. In general, the volume resistivity goes down (becomes more conductive) when the temperature and humidity go up. This is due to the nature of Ionic conductive agents, and is true to different extents for different conductive agents. Much work is currently being done to optimize (flatten out) this relationship. For this reason, volume resistivity is often specified at three points – High-High (Typically 35-40 deg. C, 80-90% RH), Normal-Normal (Typically 23 deg. C, 50% RH) and at Low-Low (Typically 5-15 deg. C, 10-20% RH) depending on the OEM and common practice in their specific geographical region.

Conclusions

Ionic Conductive Doped Polyurethane is seeing increased use in EP systems for the functions of charge, develop, squeegee, and transfer. The main advantages of this class of materials are improved abrasion and wear resistance, improved within roll electrical variation, and improved physical properties in general and ability to be utilized in the Intermediate Transfer function to conform to multiple media types. Another advantage is the ability of the polyurethane roller manufacturer to custom-formulate physical properties and volume resistivity independent. Care should be used in assigning tolerances that can be achieved, and where tight tolerances are required, the EP system engineer should utilize designed experimentation to optimize and widen tolerances. This will result in decreased total cost of ownership and in decreased unit cost of production.

The test and measurement of Volume Resistivity is a complicated issue and is time dependent. It also requires standardization as it relates the dynamics of rotational or surface speed, cross sectional thickness and nip width, and temperature and humidity. It would be beneficial to the industry to create an ASTM Sub-committee to work on a standard test method, for EP Process roller volume resistivity, which would capture these dynamics.

With proper designed experimentation, and a vendor who understands EP systems and how these systems interact with the roller material and physical properties; it is possible to decrease development times, improve time to market, and improve the total cost of ownership of the systems in which these materials are specified.

The main limiting factor for this class of materials is change in volume resistivity over time due to Ionic Depletion. With improvements in testing methods and ongoing research this is being successfully addressed.

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Biography

Charles Matteliano is currently Vice President of Product Development and Quality for Winfield Industries, Inc., Buffalo, NY. His responsibilities include directing materials, process and product development activities for polyurethane and silicone engineered components including imaging, film and EP process rollers. Charles holds a Graduate Degree in Applied Math and Statistics from RIT, and a Bachelors Degree in Industrial Technology from SUNY. Past experience includes Quality/Materials Manager with BIC SMD, Clearwater FL; Supervisor for Westinghouse Electrical Controls Division, Oldsmar, FL; Quality/Process Development Engineer with Buffalo China, Inc.; and Quality Manager at Winfield Industries, Inc. Charles and his wife Susan reside in Kenmore, NY with their three children.