The Effect of Temperature and Relative Humidity on Dimension, Volume Resistivity and Ionic Depletion Rate of Semi-Conductive Polyurethane

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Abstract

The effect of temperature and relative humidity on the physical and electrical properties of semi-conductive polyurethane used in EP process bias charge, developer and transfer rollers is investigated. Semi-conductive polyurethane materials are often specified and utilized in these applications due to the relative low cost, high endurance and uniform electrical and dimensional properties of this class of materials. As printing speeds and duty cycles increase, and registration requirements increase, the allowable tolerance to change in dimension and electrical properties of rollers utilized in these functions decreases. This puts added importance to defining and understanding the relative change in these properties across differing end user operating environments, across different environmental conditioning cycles during manufacture, and on the change in the mean expected life of these materials due to ionic depletion under these differing environmental conditions. It is known that polyurethane materials continue to cure and cross-link for as long as 30 to 90 days after initial curing. This continued curing along with absorption of moisture during the manufacturing operation, create a situation where final dimensional and electrical properties are different at each stage of manufacture and continue to change in the field. The magnitude of these changes are often much larger than most EP engineers realize. The time-dependence and relative order of magnitude of these changes is explored, as are predictive process control techniques during manufacture. A basic understanding of this dynamic phenomenon and these predictive techniques is required in order to properly specify both dimensional and electrical properties for these functions.

Basic Review

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. Urethanes can be made electrically semi-conductive by addition of ionic conductive agents. These conductive agents can be liquid or made soluble in urethane cure systems or in the reactive polyol or chain extender components within the urethane chemistry. Since these agents are not “electronic” conductors, flow of current through the urethane material depends upon, and is limited by, the nature of the ion used, the total number of charge carriers, and the mobility of the ions within the cured urethane system.

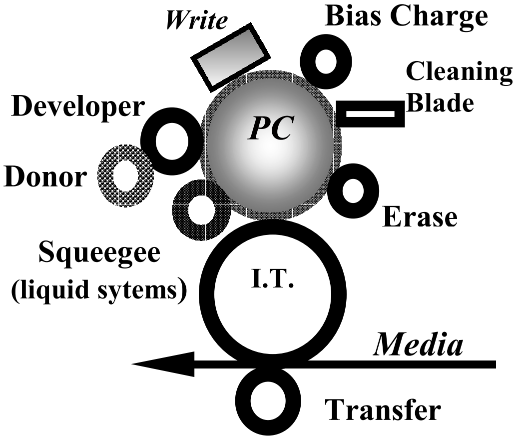

Figure 1. Current EP Applications using Semi-Conductive Polyurethane Elastomers

Effects of Temperature and Humidity on Dimension and Volume Resistivity

One area of interest to EP engineers is how both humidity and temperature affect the dimensions of the typical EP roller. A good general rule of thumb for the coefficient of thermal expansion/contraction of most polyurethane materials is 0.0002 inches per inch (or mm per mm) per degree F. This has been shown to be an acceptable number to use for most applications, however, for extremely tight tolerance requirement applications (less than 25 um) a study of this expansion coefficient is recommended as this number can be as little as half of that stated above, and in some instances as much as twice that stated above.

As we shall see, however, any study of coefficient of thermal expansion must be performed only **after** the part has come to equilibrium at a standardized relative humidity – typically 50% RH. Doing so will allow the coefficient to be calculated free of the confounding effects of humidity growth over time. Methods to calculate and determine thermal expansion are fairly well known and documented elsewhere, and this paper will not cover those methods. The order-of-magnitude of humidity effects, however, are generally much greater than thermal effects, and less widely understood.

The rate of change of volume resistivity is strictly dependent upon the urethane system used and the conductive agent used and there are no rule of thumb estimates of this rate. A discrete study for each given formulation of polymer is required. There is however a good rule of thumb with respect to how long it takes for most ionic conductive urethanes to come to some equilibrium (both for volume resistivity stabilization and for dimensional) when placed in a particular temperature and humidity environment, and that is around five to twelve days. For extremely tight tolerances however, the time period could be much longer. In these situations, it is often necessary to establish a fixed time period at which the dimension and resistivity is to be measured.

The difficult problem for the roller manufacturer is that these effects occur not only after production and shipment of the product, but also during production of the product. In fact, these effects begin the moment the product is removed from the post cure ovens, prior to any machining of the product.

The implication is that during production of tight mechanical tolerance or tight electrical tolerance urethane products, the temperature and humidity effects must be both known, and controlled. Often times this requires predictive feed-forward control. One example is production of an EP roller that has a very tight dimensional tolerance on the order of less than 25 microns. This product has a fairly tight electrical tolerance as well. For production of this product to meet the both the dimensional and electrical requirements, it was necessary to design trials to collect data about how the dimension of the product changed with humidity (independent of temperature). The following is data collected for a particular compound used in a charge roller application. This charge roller had a tight tolerance on diameter because in the particular application, the O.E.M. was trying to maintain a fixed gap between the roller and the image blanket.

In the study, three individual rollers were ground (all to a target of 84.000 mm) at point T= -7 days, then allowed to sit in 70 deg. F/50% RH for 7 days. All three parts grew to a diameter of roughly 84.100 mm (50 um each wall or 0.23% of nominal wall thickness). On the seventh day (T=0 days on the graph), the parts were separated. One part was sent to Low Humidity environment (18% RH, 70 deg. F), one part was sent to High Humidity environment (82% RH, 70 deg. F) and one part remained in the Normal/Normal (50% RH, 70 deg. F) environment. The parts remained in this environment until T=14 days. On the 14th day, the part placed in the high humidity environment had grown to a diameter of 84.600 mm, while the part that was in the low humidity environment had shrunk to a diameter of 83.900 mm.

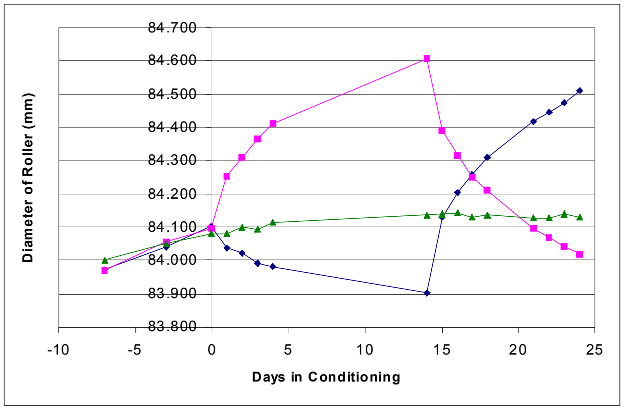

Figure 2. Selected Data, Diameter vs. Days of Conditioning for Winfield D2666e11 NL/NN/NH

The parts in the high and low humidity environment were then switched, and the part in normal/normal remained in its environment. After an additional ten days (at T=24 days), the part that was originally in the low humidity and then transferred to high humidity was now at 84.500 mm. Alternately, the part that was originally in the high humidity and then transferred to low humidity was now at 84.000 mm. Of particular note is that from T=0 to T=14 days, the rate of diameter increase for the initially high humidity conditioned roll exceeded the rate of diameter decrease of the initially low humidity conditioned roll. This being said, one would have assumed that upon switching, this would again be true, but upon close examination of the graph in figure 2, the rate of change of each was now equalized. The part that was at 84.600 mm at T=14 days dropped down to 84.000 mm when T=24 days, or a drop of 600 um for that ten-day period, while the part that was at 83.900 mm grew to 84.500 mm or a growth of 600 um for the same period of time. As a comparison, the part that remained in the 50% humidity environment grew to a nominal of 84.130 mm from its initial ground diameter of 84.000.

Process Control Strategy

For this particular part, with respect to the nominal diameter of the part, a total growth of 130 um can be expected within about 21 days of manufacture when the part is stored at 70 deg. F/50% RH conditions. That being the case, one could set up the grinding process such that parts are ground to a diameter of 130 below the desired true part diameter after growth. This would require the parts to always be ground immediately after post cure, which is not logistically possible at all times. Another approach would be to allow the parts to come to equilibrium first (i.e. allow them to grow as much as they are going to grow), and then grind them. While this would yield a fairly constant size, and allow for the operator to grind parts to the print nominal, it also requires one build 21 days of work-in-process inventory and increases cycle and turn-around time to shipment and product cost. An alternate approach is to use the known rate of growth and predict what the diameter would be after that growth. Typically this is done by creating a "minimum" time for parts to sit in a conditioned environment – say 5 days – then reversing the growth curve (knowing how much more the part has left to grow) to create a "target" grind diameter. This allows full flexibility in scheduling, and achieves correct nominal part diameter upon completion of conditioning at "Normal/Normal".

In order for this to be accomplished, both the urethane manufacturer and the customer must know this growth rate, and in addition, the control strategy and calculations that are to be used up-front. For the manufacturer, this information can then be put into the materials database in the form of growth per unit wall thickness per unit time (given that conditioning is fixed at 50%RH).

Growth and Shrinkage in the Field

For the O.E.M., the data can be expanded to be growth per unit wall thickness per unit humidity. For example, we know in this instance the growth in diameter of the high humidity conditioned part compared to the "normal" humidity part was 84.600 mm – 84.130 mm or 0.470 mm (or 0.235 mm on a wall), wall thickness was 21 mm and RH delta was 82% - 50% or 32% delta. The growth appeared to asymptote around T=15 days. Taking the growth of 0.235 mm divided by 21 mm wall thickness we have 0.0112 mm per mm per 32%RH delta. We can then divide by 32 to put into standardized units per %RH obtaining 0.00035 mm per mm per %RH (from 50% stabilized condition). This can also be done on the shrinkage side when parts are to be used or stored below 50%RH. This then becomes a unit of calculation that can be used to determine ultimate part tolerance required, or used to predict part behavior under different operating environments. It can also be used to either qualify or disqualify a particular compound for a particular application.

What about Volume Resistivity?

The effects of humidity and time on volume resistivity can be measured and predicted in much the same manner as that of diameter. It is normally observed that as ionic conductive urethane is placed in high-humidity environments, the volume resistivity decreases and as it is placed in low humidity the volume resistivity increases. This is true in part because urethanes typically absorb moisture, and this moisture in and of it self is an ionic charge carrier. In some formulations, the moisture modifies certain types of ionic charge carriers and acts synergistically with the charge carrier.

Keep in-mind, the volume resistivity of an ionic conductive urethane is a function of the total number of charge carriers and the mobility of those charge-carriers. Volume resistivity is measured by applying a known voltage across a known contact area (in a roller this is the nip width x length) and a known thickness (wall thickness of the roller). In dynamic testing, a rotating contact roll is employed and current flow data is captured automatically and fed to a database using time and current flow (x,y) pairs.

Results of this testing are then graphed over time. The current flow can be directly transformed into resistance (ohms) using Ohms' law, or to units of volume resistivity (ohm-cm) using contact area and thickness in combination with Ohms.

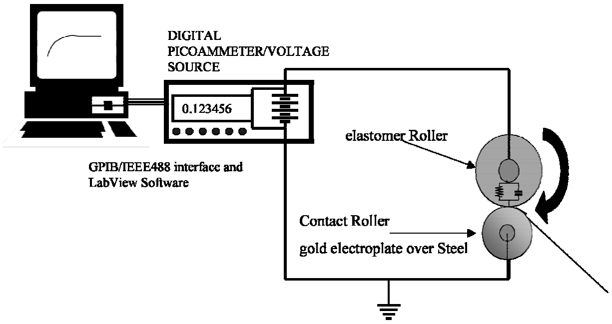

Figure 3. Schematic of Dynamic Roller Volume Resistivity Testing

The same three rollers used in the diameter change study were measured for volume resistivity at the same points in time as their diameters. The data was collected and graphed as follows:

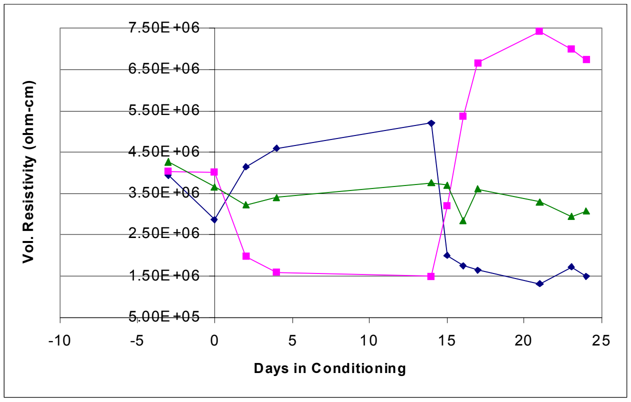

Figure 4. Selected Data, Volume Resistivity vs. Days of Conditioning for Winfield D2666e11 NL/NN/NH

It can be seen in figure 4 that all three rollers started out at nearly identical resistivity of around 3.8 x 10^6 ohm-cm. After seven days in 70 deg. F/50% RH environment, this resistivity changed only slightly down to around 2.9 x 10^6 ohm-cm.* As stated previously, starting at time T=0 on the graph in figure 4, one part was put into high humidity, and another put into low humidity and the third kept in the 50% humidity environment. As expected, at T=14 days, the part put into high humidity decreased in resistivity down to around 1.5 x 10^6 ohm-cm and the part put into low humidity increased in resistivity to around 5.3 x 10^6 ohm-cm. Upon switching environments however, the part that had previously been in high humidity and was now low resistance, increased in resistance up to around 7.1 x 10^6 ohm-cm, yet the part that was previously in low humidity and was now in high humidity dropped to 1.5 x 10^6 ohm-cm, the same as the other roller. The reasons for this occurring are not yet known, but may have something to do with the initially high rate of de-humidification of the part due to the dry environment of the chamber, compared to the initial part having followed the chamber down in humidity over a longer period of time.

So what about standardized units? Putting these data into standardized units requires again a "normalized" roller (the roller in 70 deg. F/50% RH) be used as a base line. From this base line of around 3.4 x 10^6 ohm-cm, we can subtract the high-humidity volume resistivity obtaining 2.4 x 10^6 ohm-cm delta over a difference of 32% RH and obtain standardized base units of 0.0625 x 10^6 ohm-cm per %RH (from a "nominal" of 50% RH) and use this standardized number to predict how the part will behave electrically at given operating environments. We can also see from the graph in figure 4 that this effect took around 14 days to come to near equilibrium.

A Word About Ionic Depletion

The depletion of ionic charge carriers within the polyurethane structure appears to be a function of total charge carried over time. As ion charge carriers flow out of the material, carrying the charge with them, cat-ions or an-ions (depending on polarity of bias to shaft relative to nip) flow inward and are forced to accumulate at the interface between the urethane material and the metal shaft or core of the typical roller. Eventually the flow of charge carriers out of the material leads to increased electrical resistance and lower current flow or charge flow. If this ability to carry charge falls below the flow required for the function of the product, then function is inhibited and the product has reached end of life (resistance is too high).

There is an upper limit to the amount of charge carrier that can be added to most urethane structures without either bringing the initial resistance of the product too low (causing too high of a current flow and system functional failure) or causing some other problem affecting the cross-linking of the urethane chemistry leading to decreased physical properties or to incomplete cure.

In some instances, the accumulation of opposite charge ions at the shaft core can lead to un-zipping of the urethane structure at the bond line of the urethane to shaft and physical - mechanical failure of the product.

There is simply not enough space or time to cover this topic in detail for this paper and the associated presentation, but results measured at Winfield and our customers, indicate that in some urethane-conductive agent combinations, the ionic depletion rate is not affected by humidity conditioning during manufacture, while for others it is. The results clearly show that a "rule of thumb" cannot be used for characterizing this depletion rate and must be characterized for each individual formulation, and may also require characterizing for differing bias polarity and for differing biasing methods (i.e. DC, AC, AC over DC and pulse).

Conclusions

A rule-of-thumb of 0.0002 inches per inch per degree F can be used under most circumstances to predict thermal expansion and contraction of most urethane formulas. A rule-of-thumb cannot be used to predict humidity expansion nor can one be used to predict humidity effect on volume resistivity or on ionic depletion rate.

Softer urethanes typically used in charge or developer rollers have been shown to have humidity expansion coefficients as high as 0.00035 mm per mm per %RH, and harder urethanes of the TDI-Ether MBOCA cure 90A variety have been measured at around 0.00011 mm per mm per %RH.

The volume resistivity change per %RH can also be put into standard units of ohm-cm per %RH, and is completely dependent upon both the type (specific formulation) of urethane and the type or types of conductive agent(s) chosen.

Polyurethane rollers in EP applications continue to grow and change in size over time when placed into "standardized" humidity environments of 50% RH. This growth has been measured as high as 0.020 mm per mm from the initial "cast" dimension (or dimension after grinding prior to conditioning). This growth can take up to 40 days to stabilize, with the majority of the growth occurring within the first 5 to 20 days. This growth can be measured and used to predict final part diameter and "reversed" out of the target dimension for grinding as a predictive feed-forward process control parameter.

In all cases, where both dimensional and electrical properties have very tight tolerances, it is suggested that individual studies be performed on the component in the final product configuration.

Tests of volume resistivity in the form of a roller require standardized test fixtures with standardized pressures, known nip-widths, and minimization of mechanical run-out in order to obtain good repeatability and accuracy.

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* The measurement error in measuring on a roll (as opposed to a more controlled slab of material) resulted in greater variation from part-to-part observed. This was due mainly to variances in pressure on the roll and run-out causing larger or smaller nip-width and subsequent current flow and calculated resistivity.

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. www.winfield-inds.com