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Calculated vs. Experimental Values for Volume and Surface Resistivity in Various Polymer Compounds

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Resistant to high stress—such as in the form of extreme temperature and pressure—polymers have many uses in electrical applications, where antistatic or conductive properties are preferred. Examples include conductive seals, oil pipeline spheres, and gaskets. Many factors may affect the electrical resistivity of a given polymer compound, including the type and number of carbons, the type of rubber, its cure time and temperature, and the dispersion. External conditions, such as relative humidity and temperature, also play key roles. This paper will analyze five different rubber compounds by examining the difference between experimental and calculated volume and surface resistivity in both high and low humidity conditions.

Introduction

When electricity is applied to a rubber sample with electrodes on both the top and bottom surfaces, a current flows through the body of the sample. When electrodes are only in contact with one side of the sample, however, the current flows between those two electrodes, across the surface of the sample. The latter case is not as simplistic as it at first appears, however; when a given voltage exists between two electrodes and current is allowed to flow between them, the resulting electric field is not confined to a single plane. This is known as the fringing effect or, as ASTM, the American Society for Testing and Materials, which standardizes and edits, as needed, the procedures for many kinds of properties and materials testing, D257 states, “fringing of the lines of current in the region of the electrode edges may effectively increase the electrode dimensions.”¹



Scheme 1. The Effects of Fringing

Gold rectangles represent electrodes; yellow lines represent current; black rectangle represents rubber sample.

This is due to the presence of an electric field, which is quantified by the formula $E_f = F/q$, where F is the force in Newtons, q is the charge in coulombs, and E_f is the resulting electric field in Newtons per coulomb. These units, Newton per coulomb, are also equivalent to volts per meter

(i.e. $E_f = \Delta V/d$). It, therefore, follows that an increase in voltage supplied results in a larger E_f , which would result in greater fringing effects, or more current passing through the body of the sample, rather than simply the surface². Because the distance between the electrodes, d , remains constant, any increase in voltage necessarily increases the electric field.

A larger path for the current to flow through changes the measured surface resistivity value in accordance with the electronic-hydraulic theory, also referred to as the drainpipe theory³⁻⁴. The theory claims that water pressure in a pipe and voltage through a circuit are analogous, as well as flow rate and electrical current. A larger pipe, thus, allows for a greater volume of water to flow through it at a given pressure. Similarly, a larger path allows for more electrical current to flow through the circuit at a given voltage.

From this, it can be postulated that a rubber sample exposed to high amounts of voltage during a test would experience greater fringing effects. In other words, the electrical field would expand, resulting in a larger path for current flow and ultimately a lower surface resistivity. Even though Ohm's law states that resistance and voltage have a direct relationship, rubber compounds often do not exhibit ohmic behavior⁵. This explanation then fills in where Ohm's law cannot.

This fringing phenomenon begs the question of whether surface resistivity actually exists as a concept separate from volume resistivity in regards to homogenous samples, or as simply a mathematical concept. Some argue that surface resistivity is not a true material property because surfaces do not usually have distinct electrical properties differing from the bulk properties of the sample. The flow of current over a surface *only* cannot realistically be described.⁶

Electrical flow is limited by the length of its path; electricity does not flow as well at the surface alone when compared to the volume of the sample simply because the path size is so much smaller, *not* due to different intrinsic properties of the sample. If a sample were viewed as many small layers, the surface layer would differ only from the interior layers in that the former is in contact with only one other layer, rather than two in the case of the latter.

The fact that the units between surface and volume resistivity differ— Ω/sq vs. $\Omega\cdot\text{m}$, respectively—seems then to be a non-issue when viewed in this light. If these units are used to calculate the volume resistivity in $\Omega\cdot\text{m}$ of the top 0.01% (or any miniscule percentage), then the thickness becomes negligible and the value approaches that of surface resistivity. This paper will, therefore, treat surface and volume resistivity as though they were measured in the same units.

When measuring the volume resistivity experimentally, the surface resistivity can be mathematically calculated as ρ_v/t , where ρ_v is the volume resistivity and t is the thickness of the sample in meters. When measuring the surface resistivity, volume resistivity can be similarly calculated. The only difference between the two measurement methods is the electrode setup.

This study aims to evaluate the effectiveness of measuring volume or surface resistivity. Humidity plays a large role in swaying the electrical resistivity of a sample as well⁷ and thus measurements of both surface and volume resistivity for five different compounds were taken at a 'high' and 'low' level of relative humidity.

Experimental

The equipment used to make the resistivity measurements was the ES125 Volume Resistivity Conductivity Test System manufactured by ESD/EMC (Electrostatic Discharge/Electromagnetic Capability), which is designed specifically to meet the ASTM D991 standard. A humidity and temperature gauge from Cole-Parmer, ISO 17025 Calibrated, provided lab condition measurements. ISO refers to the International Organization for Standardization. The press used to make the slabs was manufactured by Wabash Metal Products, Inc and is Model# 30-1515-2TMB. It runs at 28 tons of force. The slab mold used therein is a single cavity CSCM1 from Benz and adheres to the regulations as per ASTM D3182.

The five samples selected for study have different base rubbers, types and amounts of conductive carbon black, and various fillers, such as antidegradants and plasticizers. The specifics of these ingredients cannot be disclosed here as that compromises confidential company information.

Samples were prepared by curing unvulcanized samples ranging from 57 g to 66 g depending on the specific gravity of the compound. Though all cured at 370°F, each compound requires a different amount of time spent in the press to reach a complete cure. These times ranged from 3-6 minutes, and one compound required a post-cure for 16 hours. All samples were then conditioned at room temperature for >16 hours, as specified in ASTM D991. Each sample was then cut to fit 2.5 x 5 inch dimensions; thickness was also measured and met the D991 standard requirement of uniformity within 5%. The average thickness of all samples was approximately 0.080 inches. For each compound, three samples were made.

Contrary to ASTM D991 standard, samples were not cleaned with Fuller's earth and deionized water, or by any other substitute(s), for the purposes of analyzing the effects of bloom on volume and surface resistivity, both experimentally and mathematically. It was also determined that in most application situations, a rubber piece would not be cleaned thoroughly or regularly. In this manner, this test strives to replicate actual application conditions. Bloom is defined as a "creamy or dusty deposit appearing on the surface of a molded rubber product; caused by the migration of certain compound ingredients to the rubber's surface after molding and storage"⁸.

During volume resistivity testing, samples came in contact with four electrodes across their bottom surface: two potential (voltage) electrodes and two current electrodes. They also came in contact with two current electrodes on their top surface. During surface resistivity testing, these top two current electrodes were removed, leaving only the four on the bottom surface. In both types of testing, 300g of mass in the form of thin metal plates was applied from the opposite side of a highly insulated piece of plastic to provide sufficient pressure to ensure good contact with all electrodes.

Voltage was applied to each sample for 5 seconds, at which time the voltage and current measurements were recorded. The operator then multiplied these values together to determine the power output in watts. ASTM D991 requires an output of 0.1W. Applied voltage can be adjusted during testing to ensure that this requirement is met. Each trial continued until six values resulting in a 0.1W output were attained. The resistivity values at these correct power outputs were then averaged to give the final resistivity result. Between tests, the samples not undergoing electrification were laid on a paper towel. The operator rotated between sample pieces in order to avoid charging the samples and skewing the data. The operator wore gloves at all times while handling the pieces to avoid contamination from skin oils.

Three samples from each of the five compounds were tested in high and low humidity. Here, 'low' is defined as ranging from 41% to 46% relative humidity, and 'high' is defined as ranging from 53% to 66% humidity. According to ASTM D991, electrical testing should not be carried out above 65% relative humidity. However for the 'high' range, it was deemed valuable to test the boundary set by the standard and to exceed it by a small margin (in this case, only 1% over the recommended limit).

The following equation, as specified in ASTM D991, yields the volume resistivity results. Surface resistivity is identical other than the omission of t .

$$\rho = \frac{Vwt}{Il}$$

Where, ρ is volume resistivity, V is voltage, w is width of the sample, t is thickness of the sample, I is the current through the sample, and l is the distance between the potential electrodes.

Results and Discussion

Compounds C07433-1 through -5 were all tested at high and low humidity settings for both surface and volume resistivity. Both values were then used to calculate the other (i.e. volume resistivity used to calculate surface and vice versa). The composite results of these trials are summarized in Table 1. All volume resistivity values are measured in $\Omega\cdot\text{m}$ and all surface resistivity measurements are in Ω/sq .

Table 1. Overall Resistivity Results of C07443 Compound Series

Sample	Temp (F)	Humidity (%)	Surface (exp)	Surface (calc)	Volume (exp)	Volume (calc)
C07433-1	72	45	X	9019.5	18.9	X
C07433-1	72	43	10252.2	X	X	21.5
C07433-1	72	53	X	9336.5	19.6	X
C07433-1	77	62	8117.2	X	X	17.1
C07433-2	72	45	X	5373.7	10.9	X
C07433-2	72	42	6652.0	X	X	13.5
C07433-2	73	61	X	8557.0	17.3	X
C07433-2	75	65	6722.2	X	X	13.6
C07433-3	72	46	X	73.6	0.16	X
C07433-3	73	41	71.4	X	X	0.15
C07433-3	73	64	X	81.7	0.17	X
C07433-3	75	66	78.7	X	X	0.17
C07433-4	72	46	X	45782.7	91.5	X
C07433-4	73	41	49443.1	X	X	98.8
C07433-4	75	64	X	107599.0	215.1	X
C07433-4	75	66	81399.1	X	X	162.7
C07433-5	72	45	X	12404.0	24.4	X
C07433-5	73	41	13162.4	X	X	25.9
C07433-5	75	65	X	19348.2	38.0	X
C07433-5	77	65	14982.4	X	X	29.4

Table 1 gives an overview of the results of the resistivity testing, providing temperature in Fahrenheit, relative humidity (RH) percentage, surface resistivity in Ω/sq and volume resistivity in $\Omega\cdot\text{m}$. The last two columns provide the data for the calculated surface and volume resistivities, which retain the same units as the values experimentally measured. An 'X' denotes a data point that is not applicable. For example, in the first row of the table, both experimental surface resistivity and calculated volume resistivity have an 'X'; this is because that row describes the trial wherein volume resistivity was measured (experimental) and the surface resistivity was calculated. In evaluating the precision of the data regarding the difference between experimental and calculated values, standard deviation between both values were calculated (Table 2).

Table 2. Standard Deviation Between Experimental and Calculated Values

	Low RH Surf. Dev	Low RH Vol. Dev	High RH Surf. Dev	High RH Vol. Dev
C07433-1	871.676	1.838	862.187	1.768
C07433-2	903.909	1.838	1297.421	2.616
C07433-3	1.520	0.007	2.087	0.000
C07433-4	2588.272	5.141	18526.151	37.052
C07433-5	536.207	1.061	4374.067	6.081

Table 2 shows the standard deviation of a given compound's experimental and calculated values at either high or low RH (relative humidity). This seems to imply, however, that surface resistivity varies largely with volume resistivity when examining calculated vs. experimental values. Nonetheless, one must take into account that the volume and surface data differ by two orders of magnitude (or more) for any given compound. This skews the results.

Therefore, it was determined that a more effective way to analyze the data would be to utilize a proportional difference evaluation method, as shown below:

Table 3 shows the results of this evaluation.

Table 3. Proportional Difference Between Experimental and Calculated Values

	Low RH Surf. % diff	Low RH Vol. % diff	High RH Surf % diff	High RH Vol. % diff
C07433-1	12.793	12.871	13.972	13.624
C07433-2	21.260	21.311	24.017	23.948
C07433-3	2.967	6.452	3.679	0.000
C07433-4	7.688	7.639	27.725	27.740
C07433-5	5.932	5.964	25.434	25.519

Table 3 shows the results of a proportional difference method of evaluating the calculated and experimental volume and surface resistivity results as demonstrated in Equation 1.

This method provides a different analysis of the results, showing that volume and surface resistivity measurements methods are comparable in precision. Examining the data in this format also showcases the increase in percent difference between both values with a ~20% humidity swing. The surface percent difference value contains a component of the volume percent difference value, in that the calculated surface value was derived from the experimental volume. The overall difference in precision with an increase in humidity can be noted here, the most marked difference occurring with C07433-4 and -5, both of which experienced a 20% increase (in surface and volume). Therefore, a nearly 1:1 relationship exists between percent RH increase and percent proportional difference increase. This observation is compound dependent, but useful when viewed as a pattern to decipher percent RH values.

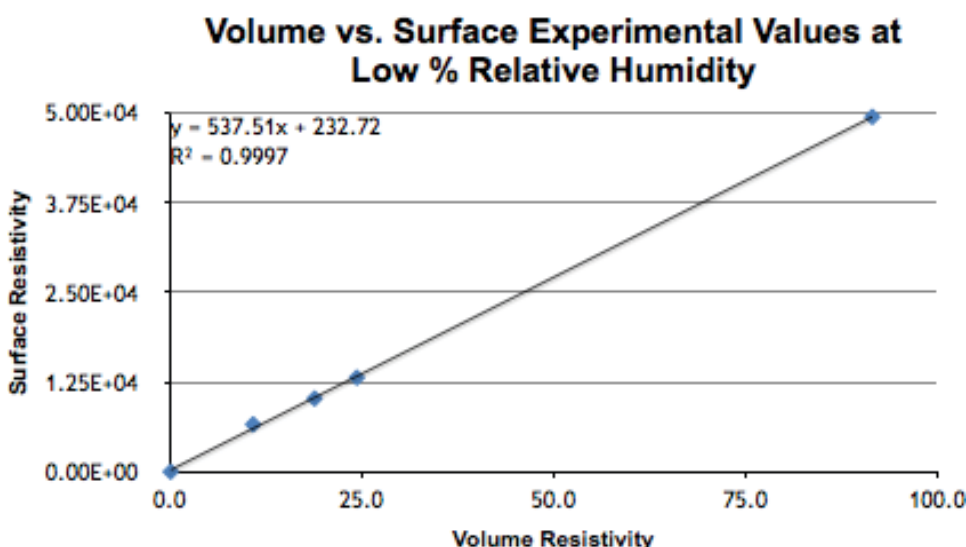
Interestingly, the increase in percent proportional difference with higher humidity may also be indicative of the increase in resistivity across the five different compounds in the higher humidity setting. Both the experimental surface and resistivity increased in the high %RH, with the single exception of C07433-1. At first take, the assumption might be that increased humidity would decrease resistivity due to higher amounts of water droplets in the air, which would assist in electrical conductivity. ASTM D257 even states that "the insulation resistance . . . decreases

with both increasing temperature . . . and with increasing humidity”.⁹ This is not, however, the case with the C07433 series.

One possible explanation is that these are not insulating materials, in contract to those discussed in D257. With the highest volume resistivity value being that of C07433-4 ($215.1\Omega\cdot\text{m}$), these materials fall within the range of conductive materials, or those that have a volume resistivity of $1 \times 10^4 \Omega\cdot\text{cm}$ or less¹⁰. For conductive materials, an increased temperature, alone, is enough to lower conductivity. This is due to addition of kinetic energy to the system and, therefore, more particle collision within the sample. Higher humidity, in this study, appears to indicate higher temperatures; thus, it is likely that the upward shift in resistivity across these fives compounds is due to higher temperatures¹¹⁻¹².

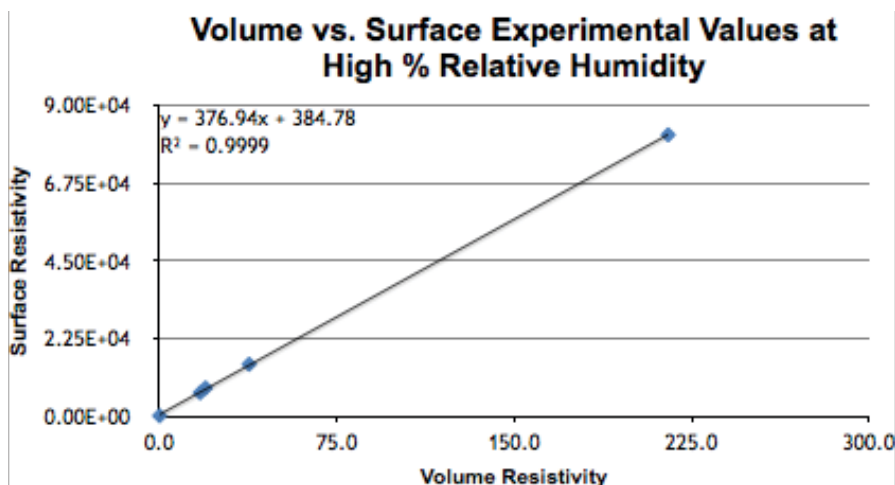
Given the proximity in the shift of percent proportional difference between volume and surface resistivity, it was speculated that a quantifiable relationship existed between the two values. In Graphs 1 and 2 below, experimental volume resistivity values are plotted against experimental surface resistivity values.

Graph 1. Volume vs. Surface Experimental Values at Low %RH



Graph 1 compares the experimentally measured volume and surface resistivities of the five compounds when tested at low % relative humidity. It shows that with increasing volume resistivity, surface resistivity increases also and in a linear fashion. The high R^2 value demonstrates that this is a predictable relationship for this particular compound.

Graph 2. Volume vs. Surface Experimental Values at High %RH



Graph 2 compares the experimentally measured volume and surface resistivities of the five compounds when tested at high % relative humidity. Comparing with Graph 1, it can be seen that at high % relative humidity, surface resistivity does not increase as dramatically with increasing volume resistivity as in low % relative humidity conditions, given the smaller slope of Graph 2.

Experimental, rather than calculated, values were selected in order to avoid propagating any methodological error. These graphs imply that there is a direct, quantifiable relationship between a polymer compound's volume resistivity and its surface resistivity for this set of five compounds. Given the variety in base rubber, antidegradants, carbon blacks, and other additives, however, this data indicates that it is highly likely that this relationship exists for other polymer compounds. Despite the high R^2 value for both of these graphs, it should be noted that the different humidity levels resulted in different equations for the trendline. Based on this data, a stable humidity must be established, in order to formulate an equation from which any conclusions could reasonably be drawn. For this study, it is indicated that volume and surface resistivity have a direct relationship; as one increases, the other increases, as well.

The other method for calculating one value from the other requires only simple mathematical manipulation of equations.

$$\rho = \frac{V w t}{I l} \quad \text{and} \quad \rho_s = \frac{\rho_v}{t}$$

Using these equations, the calculated values of both surface and volume resistivity were calculated when using bottom and bottom/top electrode set ups, respectively.

In calculating surface from experimental volume data, however, the assumption becomes that electricity flow through the sample is uniform at all levels. This is indicated when simply dividing by the thickness, t (Equation 3). This does not account for fringing effects at the surface or for restricted current flow due to a relatively limited pool of mobile electrons at the surface. These two effects do not appear to cancel one another, based on the data in Table 1. At low %RH, the calculated surface resistivity is lower than the experimental (with the exception of C07433-3). From this, it can be postulated then that the lesser amount of mobile electrons at the surface influences experimental surface data more than fringing effects. If fringing effects

had more influence on the data than the limited mobile electrons, one would expect to see that the experimentally measured surface resistivity was *lower* than the calculated resistivity. This would indicate that electrons were flowing through a significant portion of the sample during a surface test and were in a sense ‘overriding’ the limited amount of electrons on the surface alone. However, the data shows that experimentally measured surface resistivity values are *higher* than the calculated values, therefore indicating that the lesser amount of mobile electrons on the surface of the sample—in comparison to the relatively higher amount available in the body of the sample—effects the surface resistivity more than do fringing effects.

At high %RH, however, the calculated surface values were higher than the experimental values. This is likely due to increased temperature affecting the volume resistivity such that even with the thickness of the sample divided out, the resulting calculated surface resistivity became higher than the experimental value. It is also plausible that the increased humidity assisted in surface conductance of the sample, but was not absorbed and, therefore, did not affect the volume resistivity of the sample.

Conversely, calculating volume from experimental surface data implies that the restricted flow experienced across the top of the sample exists throughout the body of the sample. This results in higher calculated volume resistivities than experimental ones at low %RH (with the exception of C07433-3). When measured at high %RH, the calculated volume resistivity values were lower than the experimental ones, which opposes the pattern shown by the surface resistivity. This is likely because at higher humidity levels, surface conductivity tends to improve due to contact with water molecules. This lower resistivity is then propagated throughout the sample when used to calculate volume resistivity.

Conclusion

The volume and surface resistivity of various polymer compounds can be crucial in selecting a particular compound for an application, which may require insulative, dissipative, electrostatic shielding, or conductive behavior. Such applications would include seals, gaskets, parts intended for use in electronics, oil line pipe spheres, and many others.

In determining these values, there are a number of approaches one can take. One may measure separately the surface and the volume resistivity, which, while requiring slightly different electrode setups, does not otherwise require great alteration between testing. This approach is, however, time consuming and therefore more costly, both of which are undesirable from the industrial standpoint.

Before deciding whether to measure volume or surface resistivity and calculating one from the other, it is crucial to consider the environment in which the testing will take place and the eventual application of the compound. In high humidity and higher temperature environments, surface resistivity values drop. This will also reduce the calculated volume resistivity. The opposite is true if volume is measured experimentally in high temperature and/or high humidity; increased kinetic energy within the sample increases electron collision (for conductive samples) and this increase in resistivity is then propagated through to the surface resistivity.

In low humidity and lower temperature environments, the converse of these patterns holds true. Surface resistivity and calculated volume increase, while volume resistivity and surface resistivity decrease.

Regarding accuracy, any type of electrical test is difficult to replicate between and even within laboratories, as demonstrated in ASTM D991’s precision trial and as is mentioned again in D991’s Precision and Bias section.

Table 4. ASTM D991 Precision Evaluation

TABLE 1 Type 1 Precision for Log(ρ)

NOTE 1—Only two laboratories participated in the program for these results.

Material	Mean Level	Within Laboratory ^A			Between Laboratory ^A		
		S_r	r	(r)	S_R	R	(R)
1	3.392 ^B	0.065	0.184	5.4	0.329	0.931	27.4
2	4.855	0.132	0.374	7.7	0.577	1.63	33.6

^A S_r = within laboratory standard deviation.

r = repeatability (in measurement units).

(r) = repeatability (in percent).

S_R = between laboratory standard deviation.

R = reproducibility (in measurement units).

(R) = reproducibility (in percent).

^B Tabulated values (as used for analysis), $\log_{10}(\rho)$.

Table 4 shows the results of the ASTM D991 Precision trial in which two rubber samples (Materials 1 & 2) were tested for volume resistivity at two independent labs. Each lab tested each compound with two operators, separately. The repeatability of measurements within each individual laboratory is reported, as well as the reproducibility of these results between the two labs. Material 2 displayed the best results in terms of reproducibility, but even so only achieved a 33.6%. This demonstrates the difficulty in precisely reproducing volume resistivity measurements.

However, calculating either value from the other can prove to be fairly precise. As demonstrated by Table 3, increased humidity and temperatures can lead to greater differences between calculated and experimental values due to an increased variability in environmental conditions. Still, fringing effects do not appear to cause any great amount of error, likely because they are partially cancelled by limited mobile electrons across the surface of the sample pieces. These two effects do not balance one another out perfectly, but rather seem to limit the overall consequence of the other on the test results. More highly insulating materials, however, require greater voltage outputs to reach the necessary 0.1 W and, therefore, create a larger electric field. This results in higher error due to increased fringing. More work needs to be done in this area to determine this relationship in regards to polymers.

If myriad trials need to be run at the same temperature and humidity conditions, another possibility is to measure both volume and surface resistivity experimentally for several of the compounds. This would ideally be chosen at random, from the large group to be tested. The volume resistivity vs. surface resistivity would subsequently be plotted to determine the presence of a relationship. From this, the remaining compounds would require only surface or volume resistivity testing, and the missing of the two can be calculated from this environment, method, and equipment specific equation. This method, though necessitating further testing in various locations to assure its reliability, holds excellent promise for more efficiently and accurately determining both the surface and volume resistivity values of many compounds.

Ultimately, in arriving at a decision regarding which method to choose, the application of the piece is likely to be the most important factor. Testing conditions should recreate anticipated application conditions to the best ability of the test taker and the laboratory. Cost and any time limits must be taken into account, as well.

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