

A direct-current resistance technique for determining moisture content in native starches and starch-based plasticized materials

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Abstract

This technique allows the accurate determination of the moisture content of native starch and starch-based materials using a direct-current resistance technique that conforms to established protocols. The technique uses currently available technology and can be used to measure the moisture content of homogeneous powders, pellets, or thin sheets. The range of moisture content studied was 1–40% (w/w). A second-order polynomial equation can be easily utilized to determine moisture content from the measured volume resistance. The accuracy of the resistance technique is within acceptable error for a moisture content range of 5–20% depending on starch type.
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1. Introduction

We are currently investigating the structure–function relationships in starch-based ion-conductive materials (Finkenstadt & Willett, 2001). Those materials, composed of starch or starch-poly(vinyl alcohol) blends, use glycerol or other short chain oligomers as plasticizers; however, since starch-based materials are water sensitive and will absorb and desorb moisture from the atmosphere, it is necessary to account for the contribution of water to the conductance of the polymer matrix. The conductance of a material is expressed by

$$\sigma(T) = \sum_i n_i q_i \mu_i,$$

where σ is the conductance of the material at a certain temperature (T), n is the number of charge species (moles), q is the net charge of each species and μ is the ion mobility of each species. The amount of moisture in the system will affect the polymer mobility and ion mobility within the system.

On a different basis, the quality of extruded starch products is affected by the moisture content. Usually, the moisture content of starch products is currently determined by gravimetric means (ISO 1666:1996).

The method usually takes 25 min. In an industrial setting, this time component can be costly when adjustments need to be made in the processing conditions. Recently, Vlachos and Karapantsios (2000) proposed a method to determine the moisture content of drum-dried maize starch by measuring the alternating current (AC) conductance. Earlier, Brzezinski and Palka (1994) introduced the concept of using an AC conductance technique for the in-line control of moisture content in native potato starch. Both techniques use complicated instrumentation and a linear relationship to predict the water content of starch products. The range of moisture for each technique was 0–20% (drum-dried sheets) and 15–25% (powder), respectively.

Starch is a biodegradable, renewable resource and is composed of a mixture of linear and branched polysaccharides. Amylose is a linear polymer of $\alpha(1,4)$ linked anhydroglucose units (AGU). Amylopectin is a highly branched polysaccharide composed of linear $\alpha(1,4)$ AGU chains with branch points being $\alpha(1,6)$ linkages. While starch is packaged into granules in its native state, the properties of starch materials are exhibited when the granular structure is broken down by mechanical and thermal means. We explore the relationship of resistance and moisture content in four native and extruded starches (or starch blends) with different amylose/amylopectin ratios.

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2. Materials and methods¹

2.1. Starches

Commercially available cornstarch (Buffalo 3401, CPC International), high amylose cornstarch (Hylon 7), and high amylopectin starch (Waxy 7350, A. E. Staley) with ambient moisture contents of approximately 10% were used. Normal cornstarch was also blended with poly(vinyl alcohol) (Airvol 523S, Air Products, Inc.). The moisture content of the starch materials was adjusted by oven-drying (1–3%), using ambient conditions (10%), or adding distilled water (20–60%). The materials were vigorously mixed for 15 min then placed in a refrigerator overnight to allow the water to be fully absorbed before extrusion.

2.2. Extrusion

Samples were extruded by a Brabender single screw (3:1 high shear mixing zone) extruder with four heating zones (3 barrel, 1 die). The barrel temperature profile was 130–150–150 °C. Samples were extruded with an adjustable thickness sheet die with a width of 10 cm or a 2.5 mm diameter rod die. The temperature range of the die varied from 90 to 120 °C depending on the water content of the sample. In general, samples containing high water contents needed lower die temperatures to prevent foaming. Samples were conditioned in different relative humidity environments (20, 50 and 95%) and room temperature.

2.3. Resistance technique

This test method conforms to the standards established by ASTM D 257 and ESD S11.11 and involves a direct-current procedure for surface and volume resistance/resistivity of powders, pellets and thin sheets. Resistance is measured using a defined electrode configuration, test voltage and environmental conditions. Other methods convert the measured resistance obtained from AC methods into normalized ohms per square (Brzezinski & Palka, 1994; Vlachos & Karapantsios, 2000).

The electrical resistance of thin sheets and powders/pellets was measured at room temperature using a Keithley constant current source (Model 487 picoammeter, Electro-Tech Systems, Inc.) with a concentric electrode system (ETS Model 803b) or a Delrin cell (ETS Model 808), respectively. Data was recorded by custom software.

2.3.1. Surface/volume resistivity of thin sheets

The ETS Model 803 Resistance/Resistivity Probe is a circular measuring electrode that is based on a concentric

ring electrode design specified by the standards. This electrode configuration restricts the measurement path to an area between two concentric ring electrodes thus eliminating measurement errors attributed to stray current paths such as those experienced with parallel bar electrodes. The model 803B is capable of measuring surface and volume resistivity of relatively smooth flat specimens. For the concentric ring design, the surface resistivity (R_s) in ohms-square is a function of the ratio between outside diameter of the inner ring and the inner diameter of the outer ring (D_i, D_o) by

$$R_s = \frac{(D_o - D_i)}{(D_i - D_o)} \times R_m,$$

where R_m is the measured resistivity. In this case, the ring geometries lead to a simple relationship of

$$R_s = 10R_m.$$

While surface resistivity is a function of the ratio between inner and outer rings of the electrode, the volume resistivity is a function of the area of the inner ring and the thickness of the sample. The volume resistivity is measured between the inner electrode and the flat plane (a voltage electrode) while the outer ring becomes the grounded guard electrode. The volume resistivity (R_v) in ohms-cm is normalized to the thickness of the sample (t) by

$$R_v = \frac{A}{t} \times R_m,$$

where A is the area of the inner electrode (cm²), and R_m is the measured resistivity in ohms. The area of the inner electrode is 7.1 cm² so that

$$R_v = \frac{7.1}{t} \times R_m.$$

For most samples, the Model 803b probe eliminates the need for additional weight as the probe applies a 5 lb pressure over 3.25 in. The resistance of the electrode contact material is less than 1 ohm (Ω) and enables the probe to measure very low resistance ($10^3 \Omega$). The Model 803b probe is calibrated by using surface (Model 809b) and volume (Model 819) standards with 503 and 500 K Ω resistance, respectively.

2.3.2. Volume resistivity powders or pellets

Sample size for the Delrin cell (Model 808) was approximately 30 g. Samples are packed into the cell. The cell was charged with a potential of 0.75 V, and the electrical resistance was measured as a function of time. The low voltage and testing time reduces the dielectric effect so that the sample-filled cell acts as a capacitor. The resistivity of the sample was taken to be the value where the measured resistivity becomes constant with time. Volume resistivity

¹ Mention of trade names or commercial products in this publication is solely for the purpose of providing specific information and does not imply recommendation or endorsement by the USDA.

(R_v) was calculated by

$$R_v = 10R_m,$$

where R_m is the measured resistivity in ohms and the factor, 10, is the volume of the probe.

2.3.3. Conductance

Conductance (σ) in Siemens/cm (S/cm) was calculated by

$$\sigma = \frac{1}{R_v}.$$

For clarity on plots, the logarithm of the conductance is reported.

2.4. Moisture content

An Ohaus Moisture Balance was used to determine the moisture content (MC) of the starch products by gravimetric methods using

$$MC = \frac{M_f - M_i}{M_i} \times 100\%,$$

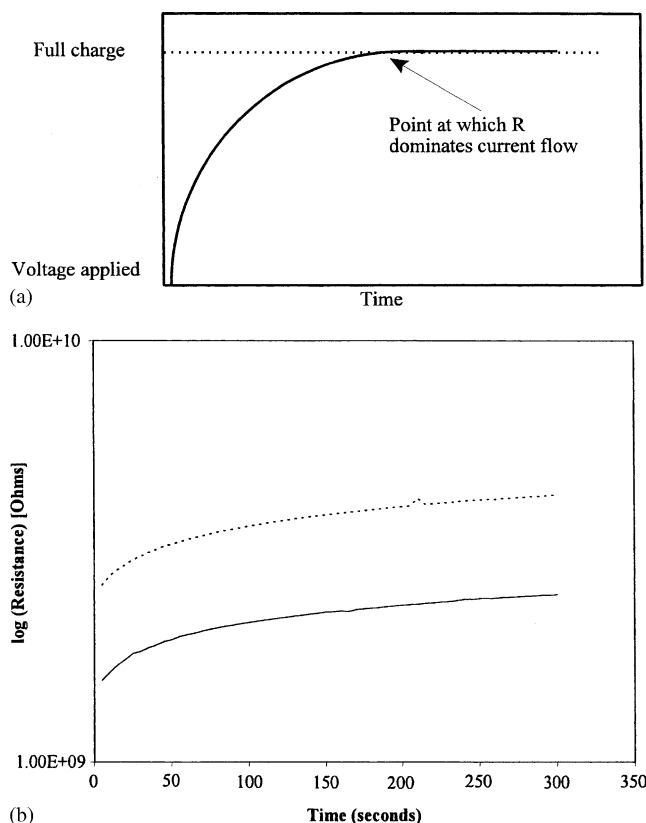


Fig. 1. (a) Diagram showing the time of electrification using the ETS resistance system. (b) Example of raw resistance data indicating time of electrification for two different moisture contents. The final resistance value is taken to be the value where resistance dominates the current flow.

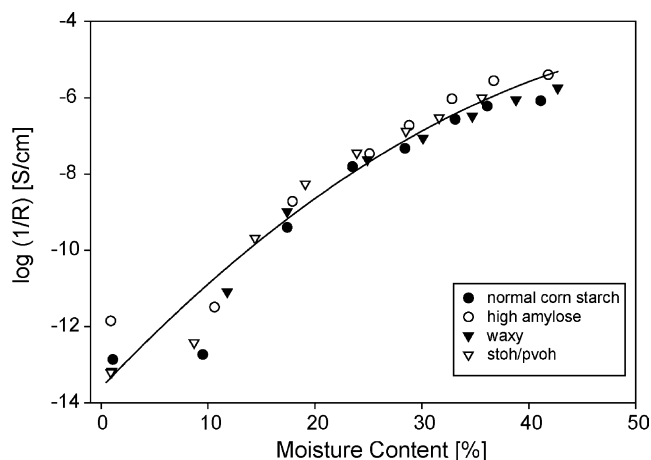


Fig. 2. The relationship of moisture content to conductance of different types of native (powder) starches.

where M_i is the initial weight of the sample and M_f is the final weight after drying. For powder and thin sheet samples, the sample was heated for 25 min at 110 °C. For pellets, the moisture balance was set to an initial temperature of 200 °C for 5 min, cracking the pellets and exposing a larger surface area to the atmosphere. Moisture content was determined after an additional 20 min of heating at 105 °C.

Resistivity and moisture content were measured in duplicate. Statistical analysis was performed using an Excel spreadsheet (Microsoft, Inc.).

3. Results and discussion

3.1. Method development

3.1.1. Material considerations

For most thin films, the Model 803b probe electrode makes total contact with the surface of the material. For more rigid or rough surfaces, additional force may have to

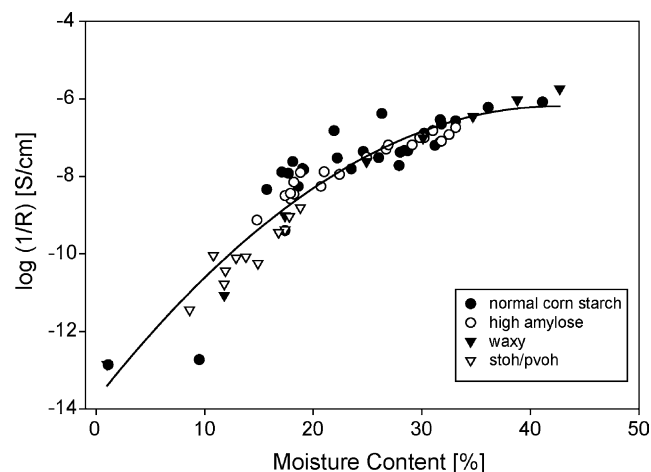


Fig. 3. The relationship of moisture content to conductance of different types of extruded starch and starch blend. Materials were plasticized with water.

be applied. If the material is not homogeneous, then the measurement will fluctuate due to percolation considerations. Thicker material (>1 mm) will require more time for the resistance measurement to stabilize. For powders or pellets, the measurement may also fluctuate before becoming constant. This is noted especially with dry (1–10% MC) samples where the electrostatic forces are high.

3.1.2. Time of electrification and voltage

Once the contact area is sufficient, one must consider the ‘time of electrification.’ Time of electrification (T_e) is

the time it takes for the current to flow between the measuring electrodes. All materials have a capacitance. For materials with low resistance, the capacitance is negligible, and the current flow is only restricted by the resistance of the material. For high resistance materials, the current flow is determined by the capacitance and the resistance of the material. The resistance of the material does not dominate the measurement until the exponential charging of the material capacitance has been completed (Fig. 1a). Fig. 1b shows the raw data for a selected sample. The final resistance value is taken to be the value where resistivity

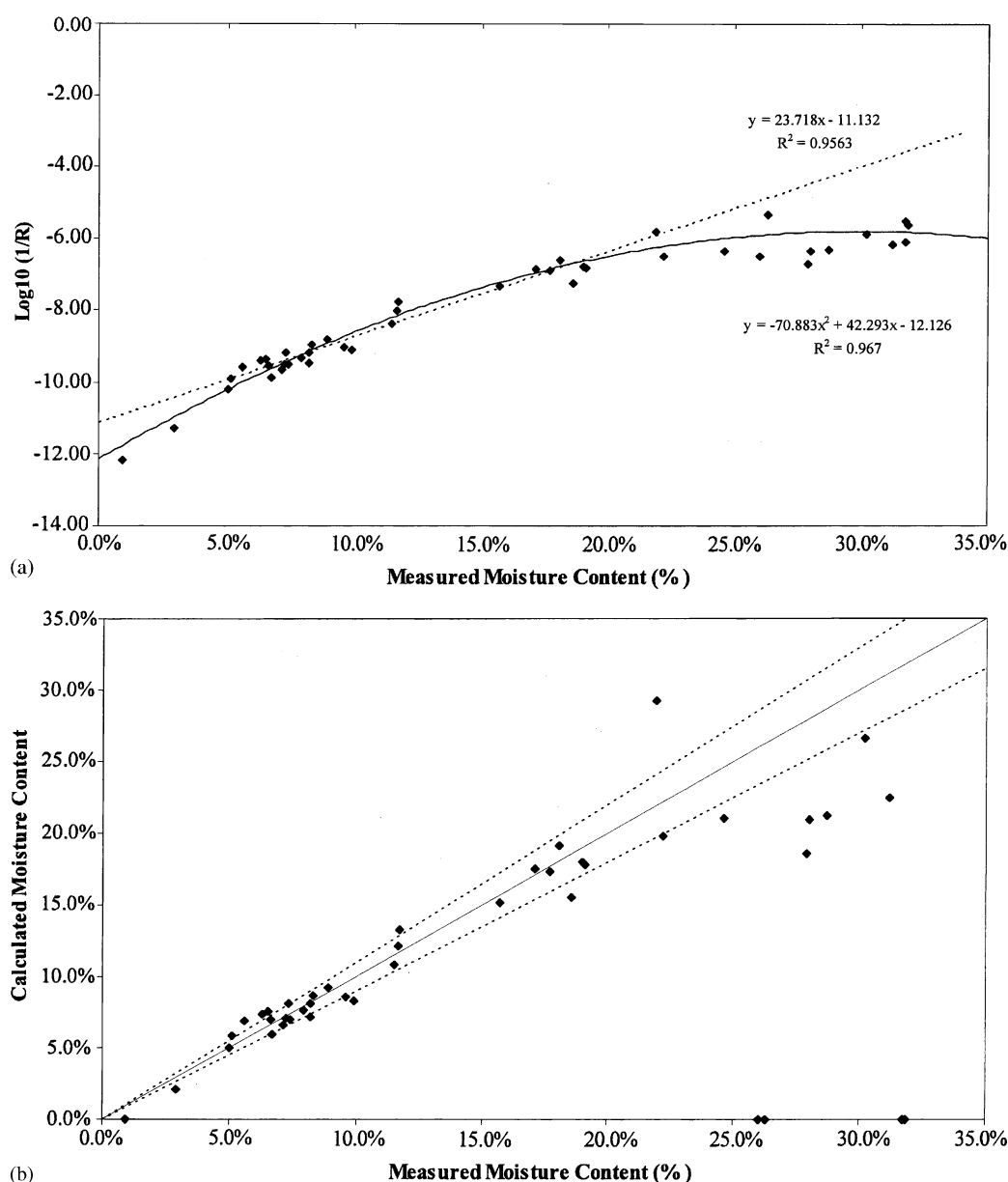


Fig. 4. (a) Relationship of conductance and moisture content of extruded normal cornstarch. The dotted line represents the linear trend for 5–20% MC according to Vlachos and Karapantsios (2000). Each data point represents the average of duplicate readings. (b) Comparison of measured and calculated values for the moisture content of extruded normal cornstarch. Dotted line represents a 10% error. Points located on the X-axis indicate that a moisture content could not be calculated (i.e. y-value indeterminate).

is no longer a function of time. Some materials are voltage dependent; that is, the measured resistance at one voltage will not be the same at another voltage. We determined that, for native starches and extruded starch materials, an excitation voltage of 0.75 V and a time of electrification of 60 s were appropriate for stability and reproducibility.

3.2. Native starches

Normal cornstarch (25% amylose), high amylose cornstarch (70% amylose), waxy cornstarch (0% amylose)

and a blend of normal cornstarch and poly(vinyl alcohol) exhibit the same relationship of conductance versus moisture content (Fig. 2). A second-order polynomial is sufficient to describe the relationship. The model gives good agreement ($R^2 = 95\%$) for moisture contents between 10 and 40%. For native starches with less than 10% moisture, the model does not accurately predict moisture content. During the measurement of dry ($<10\%$) material, there were fluctuations in the resistance during the application of voltage due to the breakdown of the dielectric which resulted in spurious meter readings.

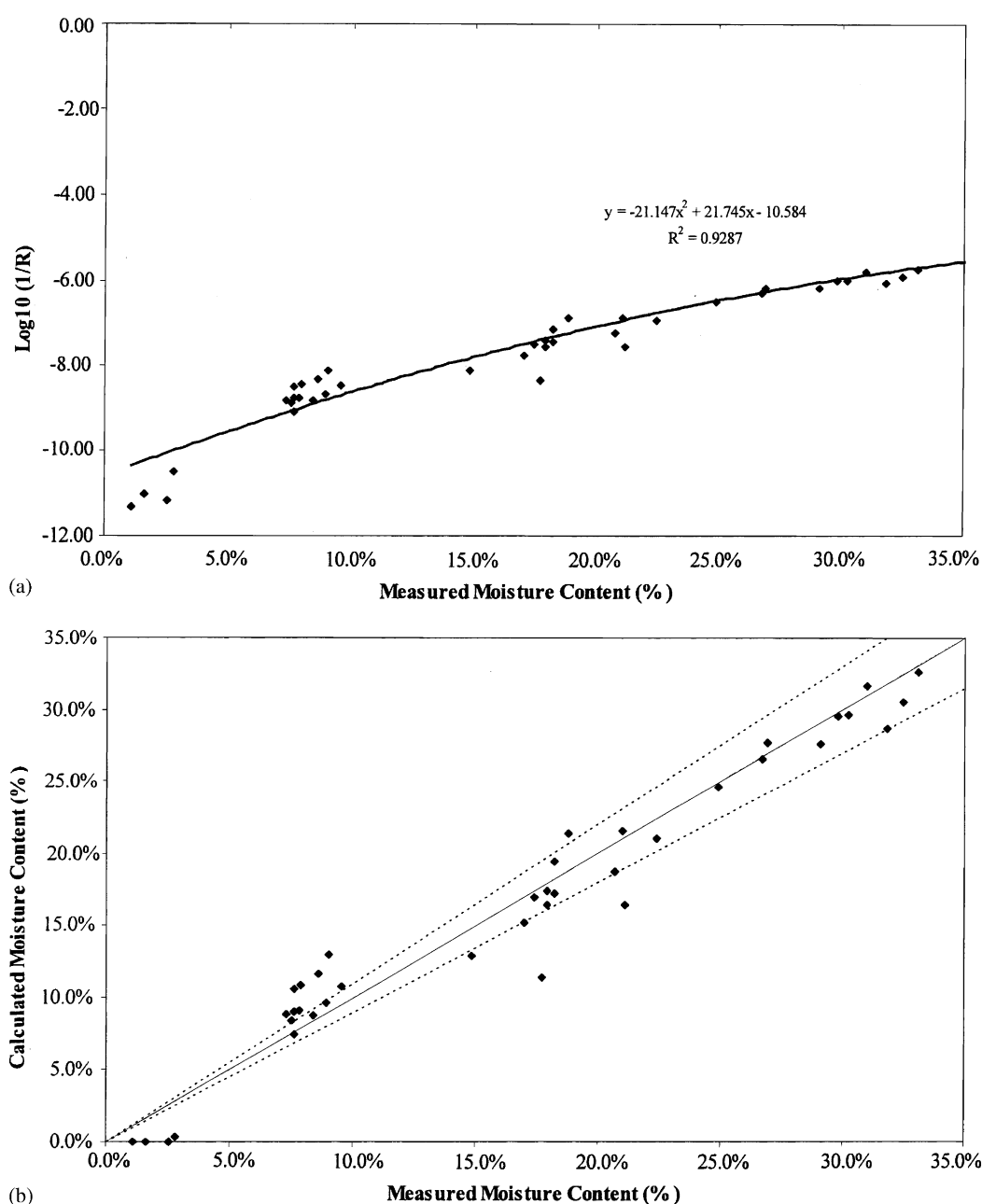


Fig. 5. (a) Relationship of conductance and moisture content of extruded high amylose cornstarch. Each data point represents the average of duplicate readings. (b) Comparison of measured and calculated values for the moisture content of extruded high amylose cornstarch. Dotted line represents a 10% error. Points located on the X-axis indicate that a moisture content could not be calculated (i.e. y-value indeterminate).

3.3. Extruded starch films

Starch is destructured and plasticized during extrusion. Interestingly, a similar relationship between moisture content and conductance applied (Fig. 3). Thin films and pellets showed the similar resistance at a given moisture content from this technique.

We examined the case of extruded normal cornstarch and high amylose cornstarch in depth. A linear model was applied to the data, and the correlation factor was 0.89. Examining Fig. 4a shows that there is a second-order polynomial correlation ($y = -71x^2 + 42x - 12$) between the measured conductance and moisture content of the plasticized starch. The R -factor in this case is 0.97. Increasing the order of the polynomial equation increases the R^2 value of the trend line only slightly; using a fifth-order polynomial equation, the R^2 value is never 0.01 more than that of the second-order polynomial. Plotting the linear model for plasticized starch with a moisture content of 5–20% yields a correlation value of 0.95 which is similar to the results reported by Vlachos and Karapantsios (2000) but fails to account for the plasticized starch samples with moisture contents below 5% and above 20%. Using the second-order polynomial equation and solving with a quadratic formula, it is possible to calculate the moisture content from the conductance of a plasticized starch sample (Fig. 4b). Some points, however, yield no solution since the trend levels out above 25% moisture content. Factoring out the measurements which have an indeterminacy (i.e. yield no solution from the formula), the accuracy of the equation is quite good. The average absolute error was 2.0%.

For high amylose cornstarch, a second-order polynomial ($y = -21x^2 + 21x - 10$) can be fitted (Fig. 5a). The R -factor is 0.93. For this starch type, the moisture content can be determined by measuring the resistance for a moisture range between 5 and 35% (Fig. 5b).

4. Conclusions

The determination of moisture content using a resistance technique was explored for moisture contents between 1 and 40% (w/w) in native and plasticized starches. The water in a sample affects the polymer mobility, but only contributes to the conductance of plasticized starch to a certain degree. In using this resistance technique, unique calibration curves should be constructed for each type of starch. Qualitatively, the relationships between starch types are very similar. Quantitatively, the relationships will have different equations. This technique can be used to determine the moisture content of native and plasticized starch. The actual range of moisture content that can be measured via this resistance technique will depend on the starch type.

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