# Modeling Dielectric Constant Variability in Aggregate Polymers from CV Measurements

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***Abstract*—Recently a new technique based on capacitive sensing has been developed and used to estimate the amount of moisture in polymers by means of the deviation of the dielectric constant. This technique is expected to be used for in-line monitoring of aggregate polymers. Despite its interest for industry, only a few papers have been published on modeling these systems in which the material has a granularity in the mm range. In this paper the problem of variability of the dielectric constant extracted in aggregate polymers was addressed. It was demonstrated that, while keeping the same average density of the material, the orientation of the elementary rod may be critical. In particular, assuming that rods can have two orientations, below a given population, the variance of the dielectric constant induced by random arrangement of rods could exceed the change in the dielectric constant arising from the content of water. In addition, guidelines were proposed to estimate the confidence interval for these CV-based humidity sensors.**

***Index: polymer, capacitance, dielectric constant, variability, aggregate.***

## I. Introduction

During polymer processing, the presence of moisture may degrade considerably their mechanical properties, which requires an in-line control of the moisture content during fabrication [1-5]. Ideally, this content should be maintained below 200ppm. As discussed by Barrettino et al. [1, 6], the variation of the dielectric constant in polymers is an effective method to measure the moisture in polymers since water is a highly polarizable with a high dielectric constant ($\varepsilon_r \sim 80$), i.e. even small concentrations can modify the effective capacitance [1, 7-9]. Dedicated capacitors architectures have been developed and analyzed to measure such a dielectric constant, see [10] for discussion. A high precision cylindrical shape capacitor device was used in [1, 6] to sense the dielectric constant of polymers in forms of mm scale pellets, see Figure (1) and Figure (2) respectively. Following the analysis developed in [1], the relative variation of the inner fringe capacitance $\Delta C_{inner}/C_{inner}$ was shown to be equal to the relative variation of dielectric constant $\Delta\varepsilon/\varepsilon$ of the aggregate polymer inside the capacitor system:

$$\frac{\Delta C_{inner}}{C_{inner}} = \frac{\Delta\varepsilon}{\varepsilon} \quad (1)$$

When polymer rods are poured into the capacitor, they are assumed to be randomly distributed.

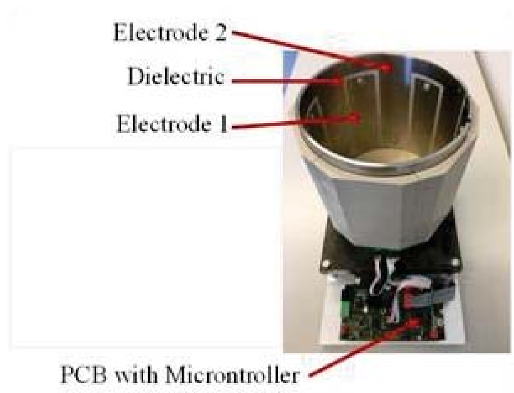


Figure 1. Picture of a comb-like capacitive sensor system for moisture for polymer pellets.

In a given volume, one can wonder if only the amount of matter (i.e. moles) is important for the capacitance or if the local orientation of the rods also plays a role in the apparent dielectric constant obtained from CV measurements.

Figure 2. Photo of polymer pellets used in the capacitor sensor. Squares are 5 mm side.

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## II. Electrostatic Analysis of a single Polymer rod

Assuming an ideal planar capacitor, the orientation of a single polymer rod was analyzed. The dimensions of the capacitor were large enough to neglect the fringing fields. To investigate the influence of rods orientations, rods of equal diameter and length, namely *2R*, were considered in order occupy the same volume in both configuration and to guarantee the same averaged density. For simplicity two orientations were used: the cylinder aligned and perpendicular to the electric field between the capacitor plates, see Figure (3).


Figure 3. Parallel (a) and perpendicular (b) representations of the polymer rod between planar capacitor plates as used in 3D numerical simulations.

This hypothesis, which is not very restrictive for the aim of this work, implies that the molar volume remains constant upon flipping the pellets, a necessary condition for the analysis. Since there is no charge density in the polymer as in free space, the electric field displacement vector D between the capacitor plates satisfies divD = 0. A simple analysis can be done assuming that D is independent of x, with or without polymer. In addition, D reverts to the local charge density Q (absolute value) per unit surface on each electrodes at points a and d (see figure 4). Such an uniform displacement vector justifies that each pellet can be modeled as an equivalent capacitor as shown in the subsections below.

### A. *Rod Normal to the electric field*

Figure 4 represents the case where the cylindrical axis of the rod is aligned normal to the electric field. This conformation is modeled as a capacitor $C_N$ as detailed hereafter.

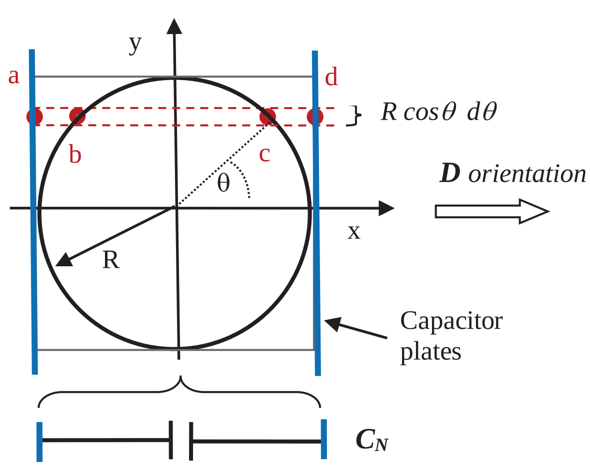


Figure 4. Cross section of the polymer rod oriented perpendicular to the electric field (D : displacement vector)

For modeling purposes, the rod is subdivided in elementary sections [a,b], [b,c] and [c,d], see figure 4. Each section can be seen as an infinitesimal capacitor of width $2R$, cross section $2R(R\cos\theta\, d\theta)$ and length $2R\cos\theta$. Considering $\varepsilon_p$ and $\varepsilon_0$ as the dielectric constant of the polymer and vacuum, respectively, the expressions can be written as the following:

$$dC_{bc}(\theta) = 2R\,\frac{\varepsilon_p}{2R\cos\theta}\,R\cos\theta\, d\theta \qquad (2)$$

$$dC_{ab+cd}(\theta) = 2R\,\frac{\varepsilon_0}{2R-2R\cos\theta}\,R\cos\theta\, d\theta \qquad (3)$$

Combining these elements in series, the elementary capacitance between *a* and *d* becomes:

$$dC(\theta) = \frac{1}{(dC_{ab+cd}(\theta)^{-1}+dC_{bc}(\theta)^{-1})} \qquad (4)$$

Integrating from $\theta = -\pi/2$ to $\theta = \pi/2$ gives the total capacitance of the elementary rod in the *normal* configuration:

$$C_N = \int_{-\pi/2}^{\pi/2} dC(\theta) = 2R\int_0^{\pi/2}\frac{\varepsilon_0\varepsilon_p\cos\theta}{\varepsilon_p+(\varepsilon_0-\varepsilon_p)\cos\theta}\,d\theta \qquad (5)$$

### B. *Rod aligned with the electric field*

A similar analysis is done for the rod where the cylinder is parallel to the electric field, see Figure 5.

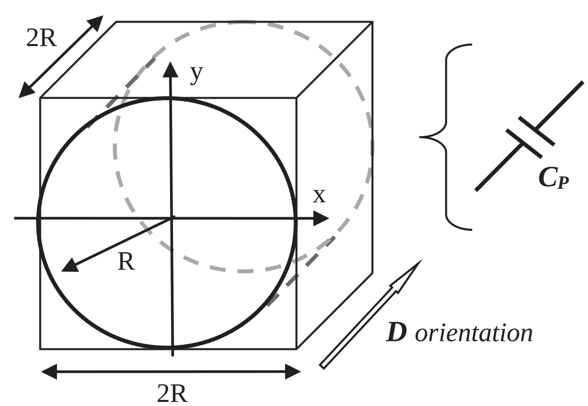


Figure 5. Cross section of the polymer rod oriented parallel to the electric field (D: displacement vector)

In this case, two contributions can be easily identified for the total capacitance, namely one from the polymer itself $\pi R^2\varepsilon_p/2R$ and one from the empty space between the polymer and the virtual square box enclosing it, $\varepsilon_0/2R\,(4R^2-\pi R^2)$. The sum of both contributions gives the equivalent capacitance of the rod for the parallel configuration:

$$C_P = \frac{\varepsilon_p}{2R}\pi R^2 + \frac{\varepsilon_0}{2R}(4R^2-\pi R^2) = \frac{\varepsilon_p-\varepsilon_0}{2}\pi R + \varepsilon_0 2R \qquad (6)$$

Comparing relations (5) with (6), it can be noticed that the equivalent capacitance is different for each configuration. For instance, imposing $\varepsilon_p = 2\varepsilon_0$, the normal capacitance is approximately given by $C_N = 3.39\,\varepsilon_0 R$, while the capacitance when the rod is aligned with the electric field is $C_P = 3.57\ \varepsilon_0 R$. The relative change between these two situations is about 5%, is agreement with the value extracted from full 3D numerical simulations [11], i.e. 3.7%. This difference suggests that capacitance measurements in aggregate polymers are subjected to intrinsic fluctuations rooting in random rods orientations, while the average density of the material remains the same. Therefore, this effect should be carefully evaluated before proceeding further in the analysis of CV measurements.

## III. Equivalent capacitive network of random rods placement.

Noting that the difference in the capacitance between the normal and parallel configurations is small, we derive a general property for capacitors that are connected in series. This will greatly simplify the statistical analysis detailed in the next section.

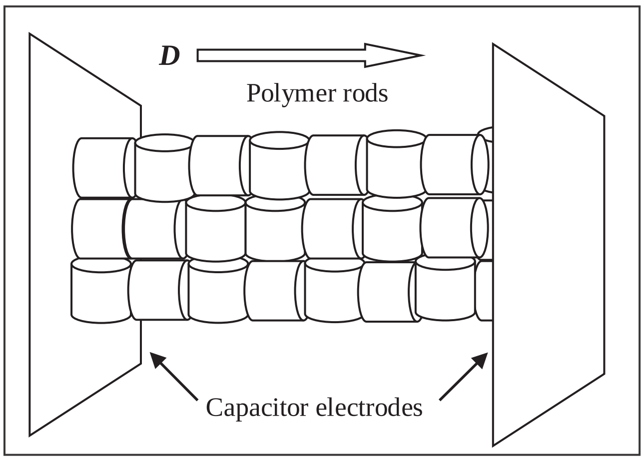


Figure 6. Sketch of random polymer rods distribution across the capacitor electrodes.

Considering $n$ capacitors $C_i$ distributed in series, each rod capacitance can be written as:

$$C_i = C_0(1 + \delta_i) \qquad (7)$$

Where $C_0 = C_N$ is the capacitance when the rod axis is perpendicular to the electric field, and $\delta_i$<<1 since $\delta_i$ is about 5% when the rod is aligned with the electric field (otherwise $\delta_i = 0$). Then, the equivalent capacitance of a row (labeled *k)* $C_{row-k}$ is:

$$C_{row-k} = \left(\sum_{i=1}^{n} C_{i_k}^{-1}\right)^{-1} = C_0\left(\sum_{i=1}^{n}\frac{1}{1+\delta_{i_k}}\right)^{-1} \cong C_0\left(\sum_{i=1}^{n}(1-\delta_{i_k})\right)^{-1} = C_0\left(n - \sum_{i=1}^{n}\delta_{i_k}\right)^{-1} \cong \frac{C_0}{n}\left(1+\frac{1}{n}\sum_{i=1}^{n}\delta_{i_k}\right) \qquad (8)$$

For a capacitor with $p$ rows, the total number of polymer rods $N$ is equal to $p$ rows times the pellets per row $n$ (i. e, $N = pn$). Thus the total capacitance $C_T$ is:

$$C_T = \sum_{k=1}^{p} C_{row-k} = \frac{C_0}{n}\left(p + \frac{1}{n}\sum_{k=1}^{p}\sum_{i=1}^{n}\delta_{i\_k}\right) \qquad (9a)$$

$$C_T = \frac{pC_0}{n}\left(1 + \frac{1}{pn}\sum_{k=1}^{p}\sum_{i=1}^{n}\delta_{i_k}\right) \qquad (9b)$$

This analysis allows to consider that only the sum of the correction terms are necessary to calculate the total capacitance, i.e. there is no need to know the position of individual rods upon their orientation, only the orientation matters.

Note that the term $pC_0/n$ is the capacitance of the aggregate polymer rods system when each rod is perpendicular to the electric field. Then, the quantity

$$\frac{1}{pn}\sum_{k=1}^{p}\sum_{i=1}^{n}\delta_{ik} = \frac{1}{N}\sum_{k=1}^{p}\sum_{i=1}^{n}\delta_{ik} \qquad (10)$$

reverts to the *relative variation* of the total capacitance arising from rods *configuration* only, $\Delta C_{conf}/C_T$, where $\Delta C_{conf}$ holds for the change in total capacitance due to the rods misorientations.

The relation 10 can also be understood as the mean value of the relative deviation in the capacitance of the rods population. In addition, the capacitance variation due to the moisture is given from relation 1, where $C_{inner}$ is $C_T$ (because the system is a simple planar capacitor there is no external fringing field). As such, it must be added to the relative variation $\Delta C_{moist}/C_T$ arising from the change in the moisture content of the polymer.

The total variation of the capacitance is then:

$$\Delta C/C_T = \Delta C_{moist}/C_T + \Delta C_{conf}/C_T \qquad (11)$$

## IV. Statistical analysis in rod polymer populations

Since rods are distributed randomly, the variance of $\Delta C_{conf}/C_T$ will set an intrinsic upper limit to the capacitor sensitivity regarding moisture estimation.

The aim of this section is to calculate this variance while assuming that only three configurations are possible, one for the rod aligned along the displacement vector, and two where the rod is normal to the displacement vector ('up' and 'down'). We assume that for any rod *(i,k)* aligned with the electric field we have $\delta_{ik} = \delta$ (the configuration mismatch is the same for all rods).

Next, we note $P$ as the probability to have the rod parallel to the electric field, and *(1-P)* the probability to have it perpendicular. In addition, we assume independent arrangement processes.

Under these hypothesis, the statistic to be used is the binomial distribution where the variance satisfies $\sigma^2 = NP(1-P)$. This quantity (its square root) represents the variance in the *number of rods oriented* parallel to the electric field. Next, the *variance in the relative capacitance change* follows from relation 10:

$$\sigma_{\Delta C_{conf}/C_T} = \frac{\sigma\delta}{N} = \frac{\sqrt{P(1-P)}}{\sqrt{N}}\delta \qquad (12)$$

If we assume that each rod has an equal probability to be set along the x, y or z axis we have *P=1/3*. This conformal induced variance should be smaller than the relative change in the sensor capacitance induced by moisture (see relation (1)):

$$\frac{\sqrt{2}}{3}\frac{1}{\sqrt{N}}\delta < \frac{\Delta C_{moisture}}{C} = \frac{\Delta\varepsilon}{\varepsilon} \qquad (13)$$

Relation (13) gives the condition on the minimum set of population that satisfies this critical condition:

$$N > \frac{2}{9}\left(\delta\frac{\varepsilon}{\Delta\varepsilon}\right)^2 \qquad (14)$$

According to [1, 6], $\Delta\varepsilon/\varepsilon$ is about $10^{-3}$ when the polymer contains 100ppm of water. From the analysis done in section II, it can be written $\delta \cong 0.05$. Thus, the minimum number of polymer rods N ensuring that the capacitance change induced by their random configuration remains below the water induced capacitance variation is found to be around 500 elements.

## V. CONCLUSION

Assuming a simple model, we discussed the influence of random distribution of polymers pellets in capacitive sensors and revealed that the apparent dielectric constant of the aggregate compound could exhibit significant deviation upon rods arrangements. A general rule is discussed further to optimize water detection in polymers based on dielectric constant measurement.

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