# MONITORING THE ACID COAGULATION PROCESS OF MILK BY DIELECTRIC MEASUREMENT

**<u>Réka Dobozi</u>[1], Zoltán Jákói[2], József Csanádi[1], Sándor Beszédes[2]**

[1]*Department of Food Engineering, Faculty of Engineering, University of Szeged,*
*H-6724 Mars ter 7, Hungary*
[2]*Department of Biosystems Engineering, Faculty of Engineering, University of Szeged,*
*H-6725 Szeged, Moszkvai krt. 9, Hungary*
*e-mail: dobozireka@mk.u-szeged.hu*

**Abstract**
The application of dielectric measurement techniques is becoming increasingly widespread in several fields of science and industry, due to its simple, quick and accurate usability. The dielectric behavior of almost all materials largely depends on – among other factors – their physical structure and chemical composition, and when these properties change even to just a relatively small extent, it can be detected by monitoring appropriate dielectric parameters. In our work, we have investigated the process of acid coagulation of milk to see whether a correlation can be established between the rheological behaviour of milk and two dielectric parameters, namely the dielectric constant, and the dielectric loss factor.

**Introduction**
In food processing technologies, the development of rapid, sufficiently accurate and reliable controlling – monitoring methods is becoming increasingly important to ensure adequate product quality, process controllability and the stability of production capacity.
Dielectric measurements present a promising method for process monitoring and control, and have been frequently used in food industry for quite a long time now, especially for detecting moisture content [1]. Materials behave differently when put into an electric or electromagnetic field, and this behavior is mostly defined by the various physiochemical properties of the material matrix, the strength of the electromagnetic field ($E$), the applied frequency ($\omega$). If an electromagnetic field with a strength of $E$ affects a material, it will cause its charge distribution to change, and this change equals to the electric displacement $D$. The connection between the displacement and the applied electromagnetic field is represented by the absolute permittivity of the media as follows:

$$D = \varepsilon \cdot E \rightarrow \varepsilon = \frac{D}{E} \tag{1}$$

In practice, the permittivity is often represented by a dimensionless quantity called relative permittivity ($\varepsilon_r$), which is the ratio of the absolute and vacuum permittivity ($\varepsilon_0$). As opposed to vacuum, the response of normal materials depends on the frequency of the electromagnetic field, i.e. the polarization of the material does not change in an instant when it is affected by an electromagnetic field, and therefore, the response can be represented by a phase shift. Complex numbers allow the specification of phase and magnitude in the same time, and for this reason, the permittivity of real materials should be treated as a complex function of frequency of the applied field:

$$\varepsilon \rightarrow \varepsilon^*(\omega) \tag{2}$$

where $\varepsilon^*$ denotes the complex permittivity.
Since $\varepsilon^*$ is a complex function, the real and imaginary part can be separated as follows:

$$\varepsilon^*(\omega) = \varepsilon'(\omega) - i\varepsilon''(\omega) \tag{3}$$

In Eq. 3, ε' denotes the real part of the complex permittivity function and often called the dielectric constant, ε'' is the imaginary part, and stands for the dielectric loss factor, and $i = \sqrt[2]{-1}$. In the so-called lossy materials (in which $\frac{\sigma}{i\varepsilon'} \gg 1$), the total dielectric loss usually occurs to two different mechanisms: energy dissipation due to dipole rotation, and effective conductivity loss due to ionic conductivity. These different losses are covered by the dielectric loss factor, and can be given by the following equation:

$$\varepsilon'' = \frac{\sigma}{2\pi\omega \cdot \varepsilon_0} + \varepsilon''_d \qquad (4)$$

This indicates that those materials that contain either charged particles (free ions) or dipolar molecules (or both) in high concentrations tends to "lose" their stored electrical energy, and the extent of this loss can drastically change if the chemical and / or physical structure of the material undergoes a given kind of transformation. Therefore, measuring either the storing capability ($\varepsilon'$), or the lossyness ($\varepsilon''$) of a material during a process which involves the biological, physical and / or chemical transformation of the material (such as coagulation of milk), provides the opportunity to monitor this given process via dielectric measurements.

At the normal pH of milk (6.7), the surface charge of the casein micelles is negative. During acid-type coagulation, the added inoculum bacterial culture begins to metabolize the lactose content of milk, producing nascent lactic acid. The accumulating lactic acid progressively decreases the pH of the milk, and when its value reaches the 4.5-5.0 interval, the surface charge of the casein micelles becomes neutral; this is the isoelectric point of these micelles. When they lose their surface charge, a phenomenon called destabilization begins to take place. During destabilization, the casein micelles, overcoming the potential barrier, begins to bond with each other, producing first larger and larger casein aggregates, and later these aggregates form polymer chains, and in the meantime, free $Ca^{2+}$-ions are released from the amino acids. The secondary molecular bonds between these chains will eventually develop the final gel form; the clot starts to solidify, and the viscosity of the now coagulated milk is significantly increased. The coagulation process involves numerous physical and chemical changes inside the bulk material, and the aim of our research was to see whether a correlation between these changes and the change in dielectric behavior can be established.

Numerous studies investigated the applicability of the measurement of dielectric properties in food-related processes in the past few years. Harindran et al. found that the proportional relationship between $\varepsilon'$ and $\varepsilon''$ (denoted as tanδ, which is called the dielectric loss tangent) has a strong correlation with the change of pH in milk during coagulation [2]. Guo et al. conducted an experiment where the dielectric properties of yogurt were measured during fermentation, and found that the dielectric loss factor positively correlated with fermentation time [3].

The effect of storage time on the dielectric properties of milk and yogurt was also investigated, and results indicate that the dielectric constant of both milk and yogurt decreased with storage time, and the dielectric loss factor was found to be in connection with the changes of pH value [4]. Dihn et al. investigated the formation of yogurt by using contactless dielectric sensors, and they found that this technique is capable of monitoring both the conductivity and permittivity of the yogurt during the formation process [5].

**Experimental**
The acid coagulation experiment was conducted by using ESL milk in 500 ml volume, and a thermophilic yoghurt culture (FD-DVS, YC-X11, Yo-Flex, *Lactobacillus delbrueckii* subsp. *bulgaricus* and *Streptococcus thermophilus*) inoculum bacterial culture was added to the system in a concentration of 3g/100ml. The milk was kept at a constant 45 °C temperature. For the

measurement of apparent viscosity, an *A&D SV-10* vibratory viscometer was used, and the dielectric properties were measured with a *SPEAG DAK 3.5* dielectric sensor connected to a *Rhode&Schwarz ZVL-3* vector network analyzer by an open-ended 50Ω coaxial cable. The rheological and dielectric measuring took place during the process at 15, 35, 55, 75, 85, 90, 95, 100, 105, 115, and 120 minutes.

**Results and discussion**

Observing the results presented on Figure 1 it can be seen that as the coagulation process progressed, the maximum value of the dielectric constant gradually decreased, while the inflexion point of the curves is shifted slightly towards higher frequencies. The slope of the curves is essentially correlated with that of high water content systems, but it is noticeable that the rate of the initial rising stages decreases to a slight extent with time.

The most observable differences occurred in the low-frequency range, around 400 MHz. The rate of decrease of the dielectric constant was highest up to 95 minutes, with the differences gradually reducing in the interval thereafter.

A clear explanation to this is that the solidification of the clot, i.e. the formation of the protein-polymer network, started at about 90-95 min, as supported by the rheological data (see later).
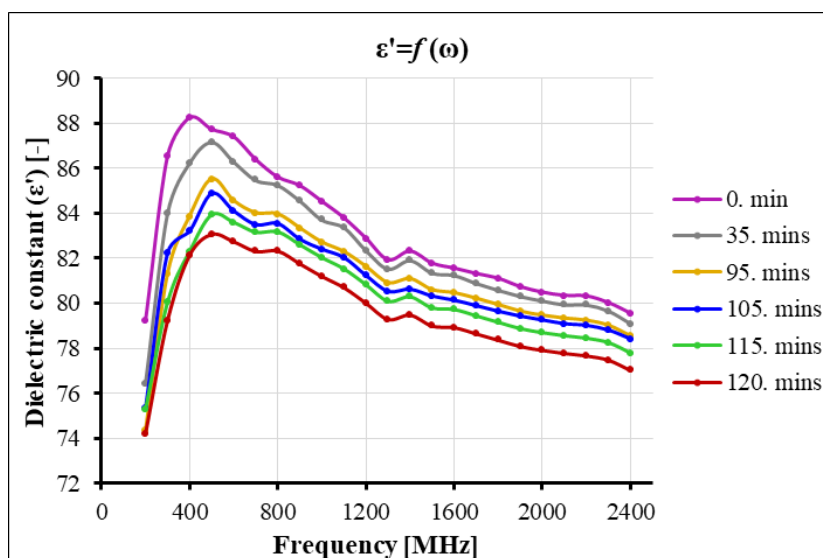


**Figure 1.** The change in dielectric constant in the function of frequency at different times of the coagulation process

The data obtained for the values of the dielectric loss factor indicates that as the coagulation process progressed, a decrease in the dielectric loss was present, especially in the time interval of 35-95 minutes. This strongly correlates with the tendencies experienced during the investigation of the dielectric constant, i.e. when the formation of casein aggregates begun, the dielectric behavior of the material matrix went through a significant change (Figure 2).

The sudden drop of the ε'' can be explained by the destabilization of casein micelles, which altered the average micelle concentration of the medium. High micelle concentration, especially above CMC (critical micelle concentration), has a huge impact on the conductivity of a colloid system, i.e. the conductivity above CMC increases rapidly. The destabilization of the casein micelles caused the micelle concentration to decrease, with which the conductivity of the milk also declined, and based upon Eq. 4, it caused the dielectric loss factor to decrease. Since the most observable differences were occurred in the low-frequency region, we plotted the rheological curve representing the clot formation and the relationship between the two dielectric parameters separately at 400 MHz as well (Figure 3a and 3b).
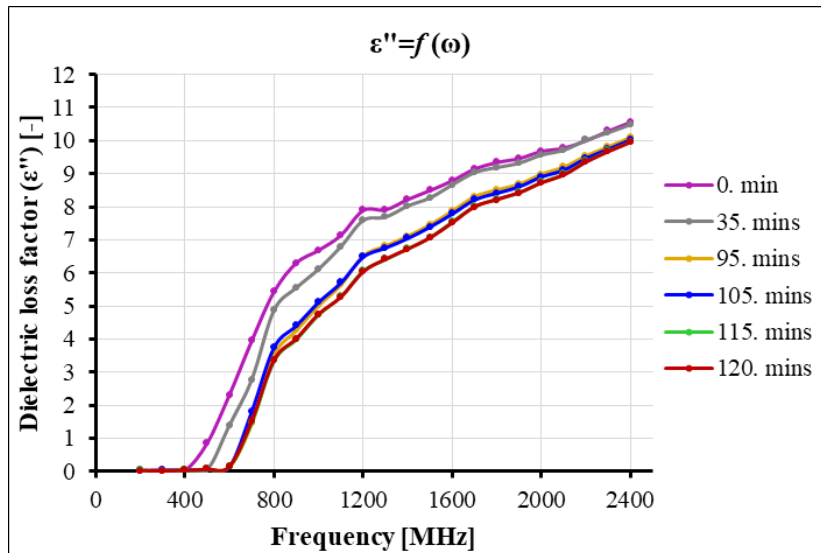
**Figure 2.** The change in dielectric loss factor in the function of frequency at different times of the coagulation process
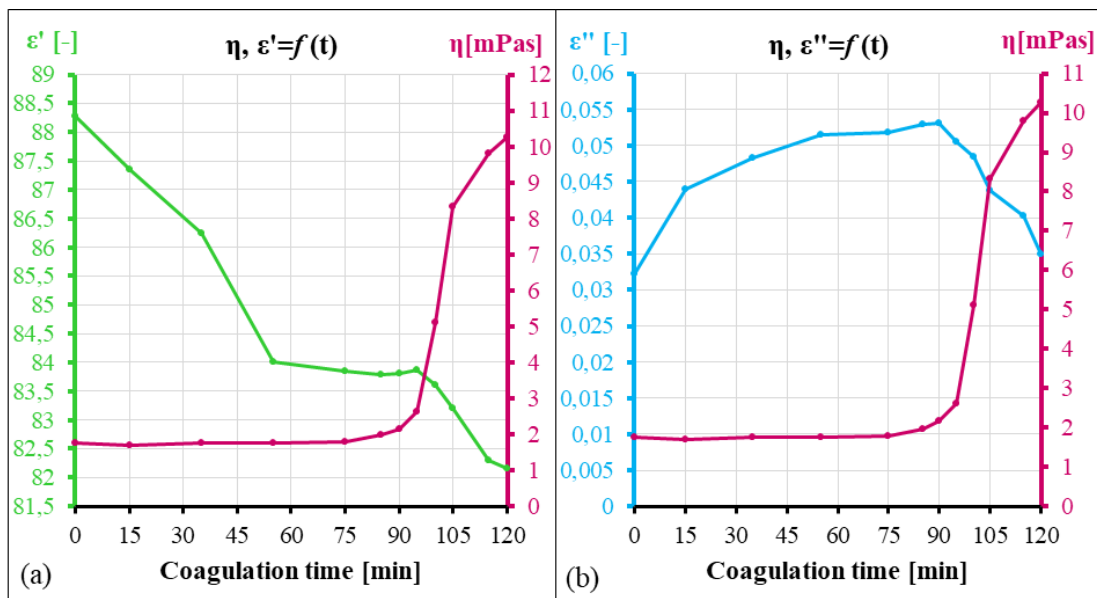


**Figure 3.** The apparent viscosity and dielectric constant (a), and the dielectric loss factor (b) in the function of coagulation time

From the apparent viscosity curves, it is clear to see that solid aggregates starts to form at around 90 minutes, after which the initial viscosity of around 8 mPas increases sharply to 47 mPas. During the process, the dielectric constant first decreases steeply (between 0 and 50 minutes) and then stagnates between 50 and 90 minutes. This change in the dielectric constant can be explained by the fact that the concentration of lactose, which is basically easily polarizable, gradually decreased over the 0-50 min interval due to bacterial decomposition, causing a steep decrease in the values of dielectric constant. During this period, the lactic acid, which was continuously accumulating in the system, gradually reduced the pH to the isoelectric point of the casein micelles, thus initiating the destabilisation phase (50-90 min). At this stage, the physico-chemical structure of the material matrix had not yet changed significantly, and therefore no significant change in the dielectric constants was observed. Subsequently, however, when the casein micelles, which had undergone charge loss, gradually formed the

protein-polymer network by growing into larger aggregates (i.e. the coagulum started to solidify) the dielectric constant started to decrease at a similar rate with a steep increase in apparent viscosity.

In contrast, the dielectric loss factor showed a saturation-curve-like slope over the 0-90 min interval, which could be explained, on the one hand, by the fact that the positively charged $Ca^{2+}$ ions were being gradually released from the amino acids during the process, and especially at this frequency, this increased the conduction loss from ionic conduction, and on the other hand, by the slight increase in the free water content in the system due to the rearrangement of the casein micelles. However, at the clot solidification phase, which started around 90 min, the loss of conductivity due to micelle rearrangement was so large that it could not be compensated by free $Ca^{2+}$ ions, so that the loss factor, similar to the dielectric constant, started to decrease sharply in the last stage of sol-gel transformation.

## Conclusion

Our experimental results revealed that the process of acid coagulation of milk can be monitored by the measurement of the dielectric constant and loss factor, and that these two parameters have a strong correlation with the changes in the apparent viscosity of the milk when it undergoes the coagulation process.

## Acknowledgements

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