Abstract

The elastic modulus and viscosity of gum candy are linearly depended on the applied mechanical stress presumably in consequence of the structure changes in gelatine gel changed under mechanical stress. The electrical impedance spectroscopy can be used for detection such structural changes. The relaxation curves and the electrical impedance spectra of gum candies under various deformations were detected. The measured relaxations were approached with stretched exponential function and the impedance spectra were modelled with a circuit consisting of serial connection of a resistance and a distributed element. The connection of rheological parameters with electrical parameters was determined.

Keywords

candy gums, rheology, electrical impedance, stretched exponential function

1. Introduction

The gum candy is sucrose based, combined semisolid gel, which contains approximately 10% gelatine. The sugar contain (sucrose, glucose syrup, and dextrose in certain proportion) ensures the required texture profile, while the gelatine secures the typical viscoelastic rheological behaviour [1]. The objective texture description can be very important in quality assurance during the manufacturing processes.

In our earlier work the rheological behaviour of gum candies were described with various models – as two, three and four elements (Burgers) models and the best approach was resulted by Burgers model [2]. These models gave good fitting both in creep and recovery curves except of the beginning of curves. Nevertheless the use of stretched exponential function in approaching showed much better fitting in the whole curves [3].

The parameters – elastic moduli and viscosities – of used models were linearly depended on the applied loading stress [2, 3]. The increasing viscosities and elastic moduli can refer to structure changes in gum candies under loading stress.

Really according to Mitchell’s [4] comprehensive study of gel rheology, the majority of food materials gels shows linear viscoelastic behaviour up to strain of 0,1 range. If the strain is higher than 0,1, the creep and the stress relaxation of gels would suggest the move and the brake of non-covalent cross links under stress.

The gelatine is a biopolymer protein, obtained by hydrolytic degradation of collagen. Native conformation of collagen is a triple helix held together by inter-chain hydrogen bonding. Above 37°C in aqueous solutions the gelatine molecules exist as separate, disordered chains (coils). When a solution containing around 1 wt% gelatine is cooled to room temperature, the gelatine molecules form an infinite network cross-linked by hydrogen bonding [5]. The role of the coil-helix transition in this mechanism has been thoroughly investigated. Gelatine gels are quite soft and flexible, and the gel strength is dependent on the gelatine concentration [6].

The changes in structure of gum candies under loading stress can be investigated by several physical methods among others with electrical impedance spectroscopy. The conductivity and the polarizability of materials strongly depend on motility of charges and charged groups in macromolecules [7].

The aim of this study was to measure the relaxation curve of gum candies under various deformations and under these deformations to measure the electrical impedance spectrum, too. The measured relaxation curves were approached with stretched exponential function and the model parameters were determined. The electrical impedance spectra were also fitted with Cole circuit model and model parameters were obtained. In this work we try to answer the question is there any effect of loading stress on electrical impedance spectrum or not, and we try to find connection of rheological parameters with electrical parameters.

2. Materials and Methods

Gum candies purchased from local shop were used for both rheological and electrical measurements. The initial average height of gum candy was 9,5±0,3 mm.

Relaxation curves were determined with a texture analyzer Stable Micro System (Godalming, UK). The diameter of measuring head was 2 mm and the speed of head was 0,1 mm/s. At various constant deformations - 0.5, 1, 1.1, 1.4, 2, 2.7, 3.4, 3.9, 4.5, 5.7, 6.2 and 7.2 mm – the decrease of force was detected during 100 s.
The measured relaxation curves were approached with stretched exponential function

\[ F = F_0 + F_0 e^{-\left(\frac{t}{\eta}\right)^\beta} \]  

(1)

where \( F \) is the decreasing force, \( F_0 \) is the equilibrium force, \( F_0 \) is a constant, \( t \) is the time and \( \eta \) is a relaxation time, \( \eta \) is the viscosity, \( E \) is the elastic modulus and \( \beta \) is the stretching exponent. The stretching exponent can characterize the distribution of relaxation times caused by various structures in macromolecular complex [8]. The \( \beta \) stretching exponent was practically independent on applied stress, but depended on applied creeping time in the 30-120 s range [3]. Average of values at various creeping times showed a decreasing tendency at increasing creeping time. At longer creeping time the longer relaxation times appeared and the distribution of relaxation time became wider causing lower stretching exponent value [8].

The magnitude and phase angle of electrical impedance of gum candies were determined with a HP 4284A and a HP 4285A precision LCR meter in the frequency range from 10 Hz – 1 MHz and from 75 kHZ – 30 MHz, respectively. ECG electrodes (Fiab Spa) were glued on the vice-grips. Between the electrodes was the sample and the deformation was realized with removing the vice-grips towards each other. The impedance spectra were measured under the same deformations used in relaxation curves. The impedance spectra were approached with serial connection of a resistance and a distributed element

\[ R = R_0 + R_1 \left(1 + i \omega \tau\right)^{-\psi} \]  

(2)

where \( R_0 \) is the resistance of investigated object extrapolated for infinite high frequency, \( R_1 \) is also resistance, the length of the secant of Cole-arc, \( i \) is the imaginary unit, \( \omega = 2\pi f \) is the angular frequency, \( f \) is the measuring frequency, \( \tau = R_1 C \) is the relaxation time, \( C \) is the capacity and \( \psi \) is an exponent. \( \psi \), similar to \( \beta \), can characterize the distribution of relaxation times. If the investigated sample is homogeneous then \( \psi \) is near to one, but if the sample is inhomogeneous value of \( \psi \) is near to zero [7].

From the geometrical data of samples the relative dielectric constant and the specific resistances belong to the \( R \) and \( R_1 \) were calculated.

The curve fitting was realized with the Solver function of Excel program. Correlation of the rheological parameters to the electrical parameters was investigated.

3. Results and Discussion

The sum of a stretched exponential function and a constant – equation (1) – is approaching well the whole range of relaxation curves, a typical curve fitting can be seen on Figure 1/A. The expression (2) resulted good approximation of measured impedance spectrum (Figure 1/B). Both the rheological and the electrical parameters were evaluated and represented in the function of applied deformation.

Both \( F_e \) and \( F_0 \) parameters increased as the deformation increased (Figure 2. A and B). At low deformation – strain less then 10 % - the connection of these force parameters with deformation seems linear. At higher deformations the rate of increase becomes quicker. Relaxation time (Figure 2/C) is increasing at low deformations (lower than 2-3 mm), but at higher deformation remains practically constant. Change of \( \beta \) parameter in the function of deformation shows similar tendency according to increasing of relaxation time.

![Figure 1. Typical force relaxation (A) and Argand diagram of impedance spectrum (B) of gum candy](image)

![Figure 2. Rheological parameters – \( F_e \), equilibrium force (A), \( F_0 \), amplitude (B) of exponential function, \( T \), relaxation time ( C ) and \( \beta \), stretched exponent ( D) ](image)
The increasing forces can refer to more compacted structure, to increasing elastic modulus under loading. The increasing relaxation time (\( \tau \)) can be observed because of the increased viscosity. Under the loading the macromolecular chains can be closer to each other. It is interesting, that the practically constant \( T \) at higher deformation (Figure 2/C) can show to the same increasing rate of elastic modulus and viscosity. At higher deformation the practically constant \( \beta \) can reflect the unchanged distribution of relaxation time.

Figure 3. Electrical parameters – \( R_1 \) and \( R \), resistances (A and B), \( \tau \), relaxation time (C) and \( \psi \), exponent (D)

Resistances \( R \) and \( R_1 \) are decreasing at increasing deformations (Figure 3. A and B). Presumably the distances between the various conductive parts of macromolecular complex are reduced under the loading. This structural change can cause the decrease of resistances. Increase of \( \tau \) relaxation time (Figure 3/C) can reflect the increasing viscosity and the decreasing mobility of charged groups. The increase in \( \psi \) parameter (Figure 3/D) can show the more ordered structure under loading.

Figure 4. Electrical parameters – \( C \) capacitance (A), \( \rho_1 \), and \( \rho \), specific resistances (B and C), \( \varepsilon_{rel} \) relative dielectric constants (D)

The capacitance of gum candies increases under increasing deformation (Figure 4/A). The specific resistance of \( R \) is also increasing under increasing load (Figure 4/B) and the specific resistance of \( R_1 \) is decreasing (Figure 4/D). The relative dielectric constant increases (Figure 4/D) at low and at high deformations, but practically constants between these two changing part. The changes of specific resistances and relative dielectric constant prove the structural changes in gum candies.

Good correlation of \( F_e \) and \( F_0 \) parameters with all electrical parameters was found.

4. Conclusion

The electrical model parameters are able to follow the structure changes under increasing deformation. The force parameters are in good correlation with all electrical model parameters.

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