

THE EFFECT OF TEMPERATURE AND LOADING RATE ON THE RHEOLOGY OF BUTTER

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Abstract

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Series of the indentation of the cone (60°) by the constant speed into blocks butter has been conducted. The indentation tests were performed at different speeds (1, 6 and 60 mm.min⁻¹), and the corresponding force – displacement responses were fitted with an analytical solution to obtain the time-dependent constants and the instantaneous force–displacement response. Experiments have been performed on 18 different commercially available butters. A puncture test was performed to investigate the rheological properties of the food materials at 4 °C and at 19 °C. The indentation force decreases with the temperature. It increases with the loading rate. The recently proposed method for the indentation of the cone into viscoelastic solids have been used for our data analysis. This procedure which needs the use of the numeric methods enables to obtain stress relaxation modulus which describes the initial viscoelasticity of the tested materials.

butter, cone penetrometry, loading rate, rheology, relaxation modulus

Butter is produced by a mechanical phase inversion of cream, an oil-in-water emulsion, to reach a water-in-oil emulsion. Butter consists of a continuous fat phase in which water droplets; fat globules and a network of fat crystals are dispersed. The fat crystal network is essential, since it determines the spread ability, appearance and mouth feel of the butter and is strongly related to the butter composition and overall structure. The ratio between the solid and liquid fat is of outmost importance for the rheological properties of butter and spreads: without solid fat, butter is fully liquid. Without liquid fat, the butter would appear hard and brittle (Narine and Marangoni, 1999). Even though the solid fat content is the same, fat can have very different physical characteristics (Haighton, 1965; Shama and Sherman, 1970). Since a greater part of the solid fat is inside the fat globules, not all fat crystals are able to form a network outside the globule. Due to the large volume fraction of fat globules in butter, their presence is thus believed to influence the firmness of the product although results are not conclusive as to what extent (Fedotova and Lencki, 2010; Mulder and Walstra, 1974). In addition to this obvious industrial importance,

fat crystal networks form a particular class of soft materials, which demonstrate a yield stress and viscoelastic properties, rendering these materials plastic. From a materials sciences point of view, these materials are also extremely important. Efforts to model the mechanical strength (Kamphuis and Jongschaap, 1985; Kamphuis *et al.*, 1984; Nederveen, 1963; Papenhuijzen, 1971; Papenhuijzen, 1972; Payne, 1964; Van den Tempel, 1961) of these network have met with more failure than success over the past 50 years, mainly due to the lack of a comprehensive model to relate structural network characteristics and solid/liquid ratios of lipid networks to their mechanical strength. The next mason consists in the lack of reliable experimental data.

The most commonly used test to evaluate butter texture has been penetrometry (DeMan and Beers, 1987). Brulle (1893) first applied this technique by placing a steel rod just above a butter sample and loading it with weights until it rapidly penetrated the fat. In penetrometry, the depth to which the penetrating body (a cone, needle, or sphere) falls when released for a specific length of time, or the rate at which it falls, is measured (Sherman, 1976). Cone penetrometry with constant load is still widely

used to evaluate butter texture. It offers a simple and economical method, and the results obtained correlate well with sensory evaluation (Dixon and Parekh, 1980).

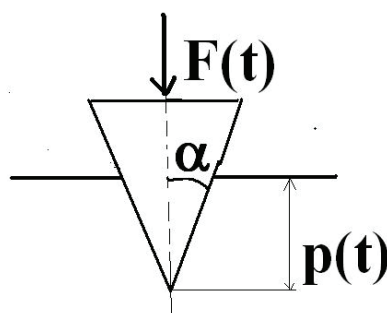
In the given paper the problem of butter texture evaluation using cone penetrometry is solved. In this study the constant speed penetrometry is applied in which the penetrating body is mechanically driven into a sample at a constant speed and the force required to doing so. The influence of the speed is studied. The theory of viscoelasticity is used for the description of the butter response at small deformation.

MATERIAL AND EXPERIMENTAL TECHNIQUE

Seventeen butters from different producers were purchased from market and transferred chilled to the Mendel University in Brno and stored at 4 °C. The main characteristics of these products are given in Tab. I.

Blocks of the butters were removed individually from 4 °C storage and quickly placed on the platform of the TIRAtest 27025 testing machine texture analyzer (TIRA, DE). The puncture test was performed immediately using a cone with angle 60° – see Fig. 1 at a crosshead speed of 1, 6 and 60 mm.min⁻¹.

The test was stopped when about 10mm penetration had been reached. Each test was repeated 10 times using fresh blocks. The whole procedure was repeated for butters after equilibrating blocks at 15 °C for 24 h. The force-displacement measurements were recorded.



1: Schema of the indentation test

RESULTS AND DISCUSSION

In the Fig. 2 the experimental records of force vs. displacement are displayed. The same qualitative features exhibit experimental records for all tested butters, temperatures and penetration velocities. The experimental points force (F) vs. displacement (p) can be fitted by the power function:

$$F(N) = Ap^n \quad [p] = \text{mm.} \quad (1)$$

Parameters A and n are given in the Tab. II and Tab. III. These parameters were obtained for the average values of the force and displacement. It observed that the force F increases with the penetration velocity of the cone.

Its value decreases with the temperature by structure changes of different fat temperature. Effects of the penetration velocity and temperature are illustrated in the Fig. 3 and Fig. 4.

I: Specification of the examined butters

Butter No	Product name (in Czech)	Milk fat content [%]	Dry matter [%]	Water [%]	Acidity number [-]
1	Máslo Milkpol s.r.o – CZ	82.50	85.11	14.88	0.81
3	Výběrové máslo – PL	82.25	85.18	14.81	0.91
4	S-Budget Spar – CZ	88.88	85.65	14.34	0.63
5	Máslo Olma – CZ	88.25	84.81	15.18	0.66
6	Horácké máslo – CZ	82.00	84.38	15.61	0.60
7	Farmářské máslo – CZ	85.50	87.15	12.84	0.51
8	Kerrygold tradiční – IE	83.50	85.89	14.10	1.24
9	Pilos – DE	83.50	85.40	14.59	0.45
10	Dr. Halíř – DE	83.00	85.14	14.85	0.54
11	Máslo – PL	83.75	85.52	14.47	1.27
12	Máslo Kunín – CZ	83.75	84.89	15.10	0.69
13	Máslo Tesco – CZ	82.75	84.63	15.36	0.54
14	die Alpenbutter – DE	83.50	84.64	15.35	0.63
15	Čerstvé máslo Polabské mlékárny – CZ	83.50	84.71	15.28	0.75
16	Máslo Belgie – BE	83.25	85.17	14.82	1.18
17	Čerstvé máslo Mlada – CZ	83.75	85.82	14.17	0.63
18	Tradiční máslo Jaroměřice – CZ	83.50	85.28	14.71	1.12

II: Values of parameters of Eq. (1), temperature 4 °C

BUTTER No	PENETRATION VELOCITY								
	1 mm.min ⁻¹			6 mm.min ⁻¹			60 mm.min ⁻¹		
	A [N]	n[l]	R ²	A [N]	n[l]	R ²	A [N]	n[l]	R ²
1	0.0611	1.9883	0.999	0.1471	1.7825	0.9963	0.2035	1.7394	0.9983
3	0.1090	1.7536	0.998	0.1908	1.6050	0.9982	0.3138	1.6646	0.9994
4	0.0601	1.9936	0.998	0.1795	1.6933	0.9977	0.2472	1.5962	0.9919
5	0.0812	1.9430	0.999	0.1372	1.7952	0.9661	0.2274	1.6461	0.9991
6	0.0881	1.8325	0.996	0.1460	1.6962	0.9979	0.2469	1.6728	0.9996
7	0.1025	1.9546	0.997	0.1652	1.8254	0.9919	0.2428	1.6759	0.9984
8	0.0564	1.9437	0.999	0.1354	1.6969	0.9991	0.1652	1.6402	0.9272
9	0.0740	1.9523	0.999	0.1439	1.8452	0.9996	0.1686	1.7636	0.9953
10	0.0582	1.9610	0.999	0.1238	1.8076	0.9984	0.1725	1.6849	0.9970
11	0.1067	1.8734	0.998	0.1705	1.8589	0.9272	0.2819	1.6654	0.9974
12	0.1170	1.6983	0.998	0.1721	1.7734	0.9953	0.2758	1.6538	0.9574
13	0.0956	1.7661	0.997	0.1653	1.7464	0.9970	0.1976	1.7366	0.9994
14	0.0582	1.9368	0.999	0.0949	1.8966	0.9974	0.1670	1.7423	0.9974
15	0.0960	1.8285	0.998	0.1444	1.8659	0.9574	0.1978	1.8000	0.9827
16	0.0429	1.9728	0.997	0.0778	1.9109	0.9994	0.1376	1.7005	0.9918
17	0.0865	1.8640	0.996	0.1507	1.7135	0.9986	0.1686	1.6926	0.9921
18	0.0752	1.9224	0.999	0.1365	1.8772	0.9996	0.2132	1.7946	0.9962

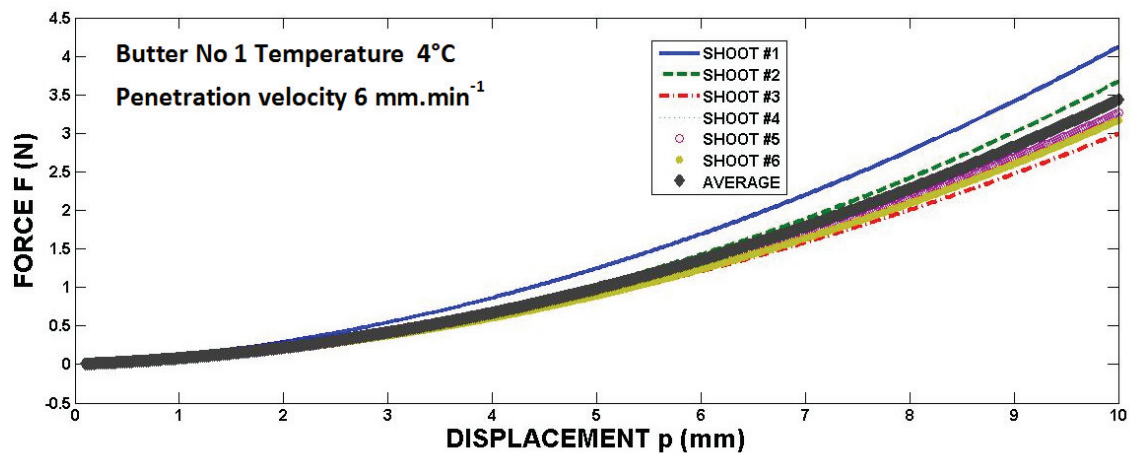
III: Values of parameters of Eq. (1), temperature 15 °C

BUTTER No	PENETRATION VELOCITY								
	1 mm.min ⁻¹			6 mm.min ⁻¹			60 mm.min ⁻¹		
	A [N]	n[l]	R ²	A [N]	n[l]	R ²	A [N]	n[l]	R ²
1	0.0486	1.6439	0.9996	0.0558	1.7857	0.9661	0.0558	1.7857	0.9574
3	0.0476	1.6918	0.9984	0.0733	1.7511	0.9979	0.1290	1.7544	0.9994
4	0.0390	1.7491	0.9272	0.0859	1.7685	0.9919	0.1665	1.7194	0.9974
5	0.0476	1.6609	0.9953	0.0762	1.6897	0.9991	0.1013	1.7412	0.9827
6	0.0804	1.4932	0.9970	0.0561	1.6985	0.9996	0.0828	1.7581	0.9918
7	0.0428	1.7867	0.9974	0.0900	1.7017	0.9984	0.1510	1.7162	0.9989
8	0.0242	1.5012	0.9574	0.0391	1.6643	0.9272	0.0552	1.8000	0.9968
9	0.0216	1.9849	0.9994	0.0521	1.7754	0.9953	0.0675	1.7709	0.9966
10	0.0372	1.9600	0.9974	0.0651	1.7800	0.9970	0.0931	1.7107	0.9997
11	0.0481	1.8058	0.9827	0.0707	1.7882	0.9974	0.1085	1.7024	0.9971
12	0.0587	1.7977	0.9918	0.0789	1.7419	0.9574	0.1092	1.6718	0.9960
13	0.0507	1.8029	0.9989	0.0626	1.7740	0.9994	0.0922	1.6754	0.9986
14	0.0245	1.9265	0.9968	0.0473	1.7508	0.9974	0.0504	1.7572	0.9996
15	0.0391	1.8234	0.9966	0.0608	1.7154	0.9827	0.0844	1.6712	0.9983
16	0.0467	1.5705	0.9997	0.0330	1.7400	0.9918	0.0581	1.7400	0.9994
17	0.0323	1.9799	0.9971	0.0564	1.7580	0.9989	0.0914	1.7624	0.9786
18	0.0350	1.9852	0.9960	0.0733	1.7740	0.9968	0.1122	1.7124	0.9980

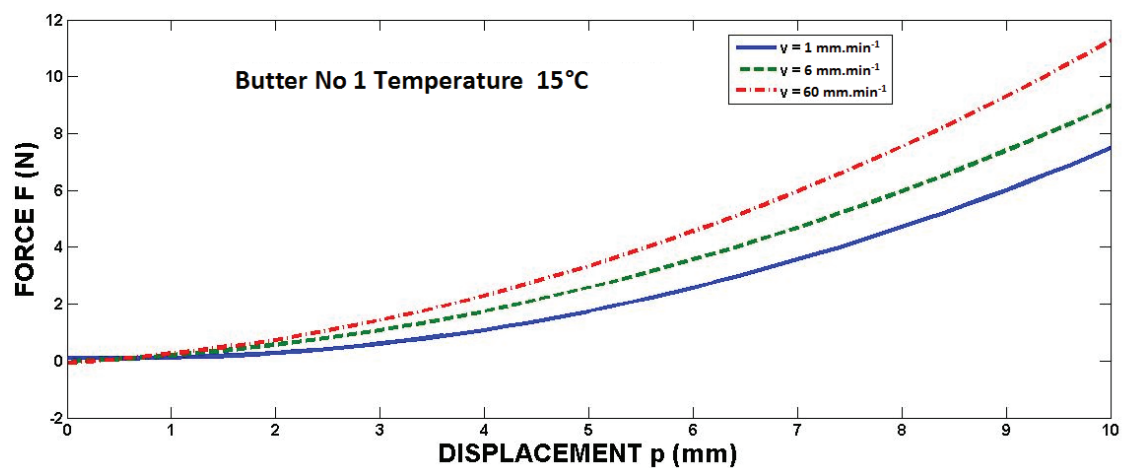
In order to compare different kinds of butter the force F has been evaluated at the cone displacement $p = 10$ mm. Results are displayed in the Fig. 5.

In the Tab. IV the number of butter which exhibits the maximum force are given.

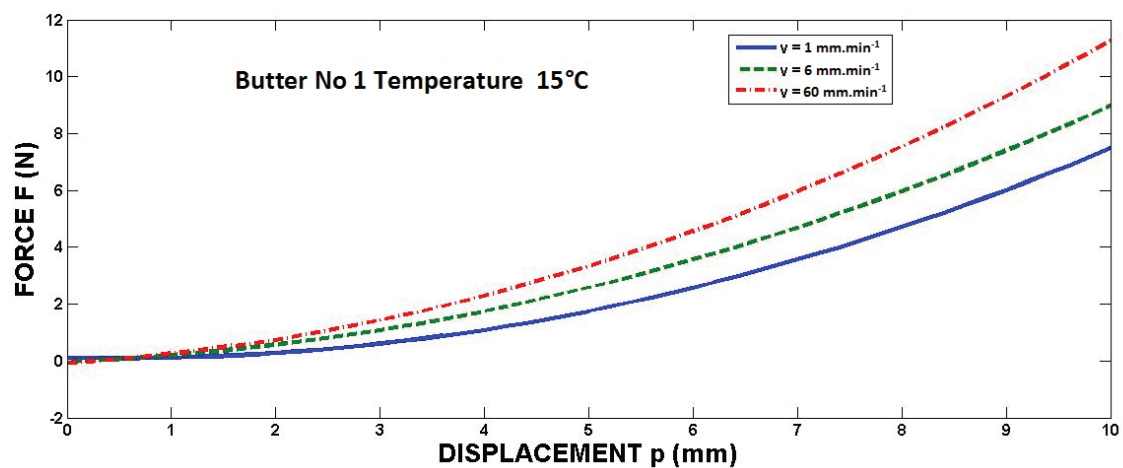
The maximum resistivity against to the cone penetration depends occurs for different butters depending on the temperature and penetration velocity.



2: Experimental records of the force vs. cone penetration depth



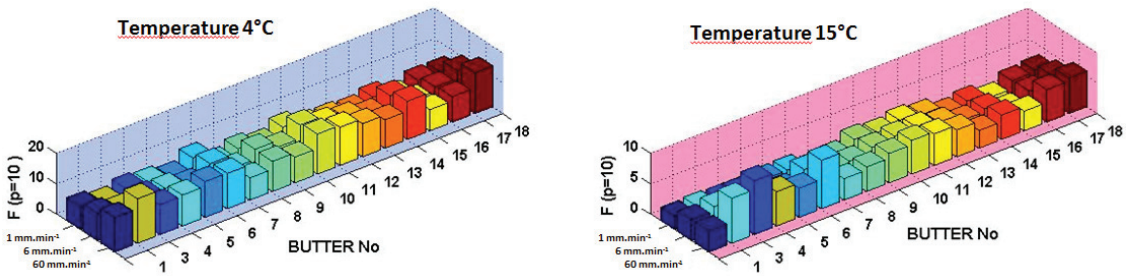
3: The effect of the penetration velocity on the average values of force



4: The effect of the temperature

In order to evaluate butter texture cone penetrometry with constant load is still widely used. The use of this method leads to design one material parameter that is fundamental to the quality of the product. Dolby (1941) defined this as hardness. For

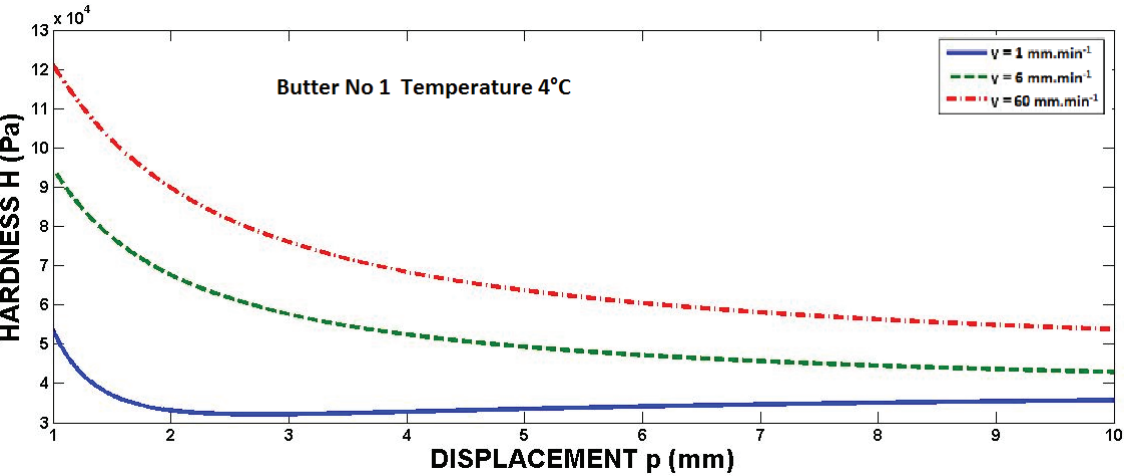
a penetrometer test, hardness has been defined by Vasic and DeMan (1968) as the ratio of load to the area of the impression made by the penetration. The relationship between the applied load (F), the



5: Comparison of the butter resistivity against to cone penetration

IV: Butters which exhibit maximum force

PENETRATION VELOCITY	TEMPERATURE 4°C	TEMPERATURE 15°C
	Butter No	Butter No
1 mm.min ⁻¹	7	12
6 mm.min ⁻¹	10	4
60 mm.min ⁻¹	3	4



6: Examples of the hardness

hardness (H), and penetration impression area (A_{imp}) and depth (p) are given by:

$$H = \frac{F}{A_{imp}} = \frac{F \cos^2(\alpha)}{\pi p^2 \sin(\alpha)}. \quad (2)$$

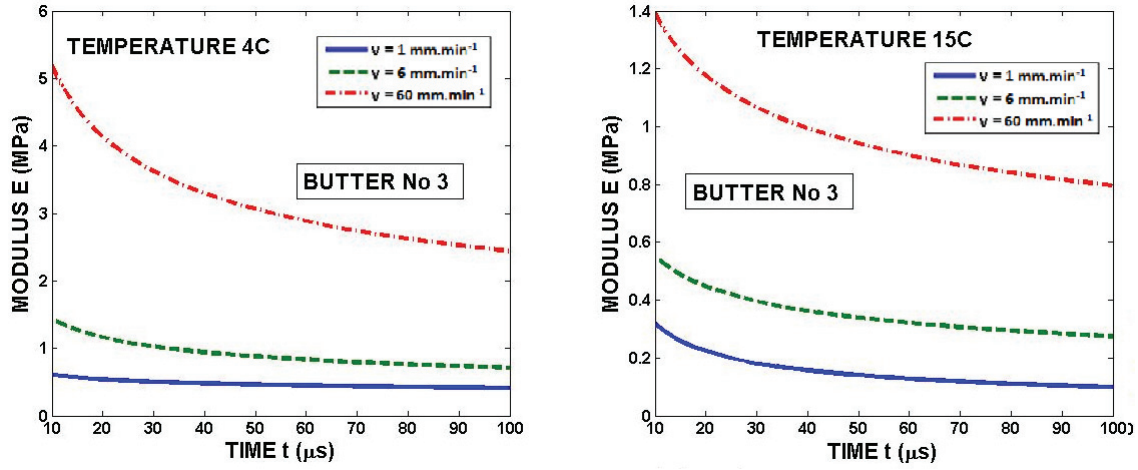
If we use the Eq. (2) to our results we obtain the dependence of hardness on the displacement as it is shown in the Fig. 6. One can see that the hardness decreases with the penetration depth following some interval where the hardness is nearly constant. Its value increases with the penetration velocity.

The obtained results suggest that the cone penetrometry with constant speed of the cone cannot be used for some correlation between instrumental and sensory hardness. This correlation

has been obtained e.g. by DeMan (1976) and Mortensen and Danmark (1981).

The procedure used in this paper can be used for the study of viscoelastic properties. Viscoelasticity of butter at small deformations has been described e.g. by Narine and Marangoni (1999). The viscoelastic descriptions are made of time – dependent indentation load $F(t)$ and the penetration depth $p(t)$ resulting from any prescribed program of penetration and indentation loading, respectively.

The contact stress and strain in indentation problems, even for an elastic contact, are highly concentrated in the contact region, where extremely inhomogeneous deformations are taking place. Such a complex mechanical fields makes difficult to describe the constitutive relations of the applied force F to the internal stress, as well as the penetration depth p to the adjoin strains,



7: Viscoelastic modulus

however. In order to overcome these difficulties Meyer's principle of geometrical similarity can be used (Tabor, 2000). During indentation loading penetration indenter and its contact area both grow with time. The viscoelastic properties are described by the relaxation modulus $E(t)$ instead of the Young modulus E for purely elastic materials. The stress increment is then expressed as:

$$d\sigma(t) = \frac{1}{(1-\nu^2)} E(t-t') d\epsilon(t'), \quad (3)$$

where use has been made of the assumption that Poisson ratio ν of viscoelastic material is independent of time, for simplicity. The theory of indentation of a cone indenter into a block of viscoelastic material has been developed by Sakai (2002).

For arbitrary indentation histories $p(t)$ and $F(t)$ in a linear viscoelastic body at past times t , the resultant load $F(t)$ is expressed in the following equation:

$$F(t) = \frac{\pi t g \alpha}{2} \frac{1}{1-\nu^2} \int_0^t E(t-t') \left[\frac{dp^2(t')}{dt'} \right] dt', \quad (4)$$

where ν is the Poisson's ratio.

The constant rate penetration v_0 simplifies Eq. (2) into:

$$F(t) = \frac{\pi t g \alpha v_0^2}{1-\nu^2} \int_0^t E(t-t') dt'. \quad (5)$$

Differentiating Eq. (2) twice with respect to t explicitly gives the stress relaxation modulus as:

$$E(t) = \frac{1-\nu^2}{\pi t g \alpha} \frac{1}{v_0^2} \frac{d^2 F(t)}{dt^2}. \quad (6)$$

If we use the Eq. (1), where $p = v_0 t$, than Eq. (6) modifies to

$$E(t) = \frac{(1-\nu^2) \cot g \alpha n(n-1) A v_0^{n-2}}{\pi} t^{n-2}. \quad (7)$$

For the evaluation of time history of the relaxation modulus it is necessary to choose a value of the Poisson's ratio. Example of the relaxation modulus is shown in the Fig. 7. The same features exhibit all tested samples of butters. The modulus decreases with the time. Its value is significantly dependent on the temperature. This is evidence of the viscoelastic behaviour. At the same time the modulus is dependent on the penetration velocity. It means the butter exhibits rather nonlinear than linear viscoelastic behaviour. The influence of the penetration velocity on the relaxation modulus is achieved for the $n = 2$. It means the difference $n-2$ can be used as a measure of the nonlinear viscoelastic behaviour. Data presented in the Tab. II and Tab. III suggest that the nonlinear viscoelastic behaviour is significant namely for higher velocities of the penetration velocity.

CONCLUSIONS

The comprehensive study on the cone penetrometry of 17 butters from different producers has been performed. Contrary to up to now used procedure the penetration tests have been performed at constant penetration velocity. The obtained dependencies of the force F on the penetration p can be fitted by a power function with very high reliability. It has been shown that there is a significant dependence of the force on the penetration velocity. The increase of this force with penetration velocity can be interpreted as the rate dependence of the shear stress which describes the resistivity of butter against to a cone penetration. The explanation of this effect must be made on the basis of the butter microstructure. The penetrometry of the butter at constant penetration cannot be used for the butter evaluation. The use of the results of the penetration experiments must

be based on some reliable rheological models of the butter mechanical behaviour. Results of the penetrometry show the influence of the different technologies used different producers on the butter consistency.

The analytical solution of indentation on semi-infinite viscoelastic solid with a conical – tip

indenter has been performed. Application of this theory to our experimental results shows that all tested butters exhibit nonlinear viscoelastic behaviour. The extent of the nonlinearity increases with the penetration velocity.

SUMMARY

The rheological behaviour of 18 samples of butters from different producers has been studied at two temperatures: 4 °C and 15 °C. The cone penetrometry has been used. This procedure is widely used in the fats and oils industry for the measurement of the consistency of plastic fats. Time dependent loading force $F(t)$ and the penetration depth have been measured at constant penetration velocity. Three velocities: 1, 6 and 60 mm.min⁻¹ have been applied. All results can be fitted by a power function with very good correlation:

The indentation function increases with the penetration velocity and it decreases with the temperature. Results show that the indentation force is also significantly different for butters from different producers.

The most up to now used indentation techniques is based on the monitoring the penetration depth reached by the cone at a constant load given by its mass. This procedure is then used for the evaluation of the hardness which is related to the shear stress resistivity against to cone penetration. The analysis of the results presented in the given paper shows that the indentation experiments based on the constant penetration velocity cannot lead to some single parameter describing the butter rheological behaviour. On the other side this technique gives clear evidence of the influence of the loading rate on the deformation behaviour of butter.

An analytical solution of indentation on semi-infinite viscoelastic solid with a conical – tip indenter has been performed. The obtained theoretical results show that all tested butters exhibit nonlinear viscoelastic behaviour. A measure of the extent of nonlinearity is the quantity $n-2$ – see equation connecting F and p above.

Generally, the indentation test at constant penetration rate provides valuable information on the deformation behaviour of the butter. The interpolation of the exact meaning of the obtained quantities (indentation force *vs.* penetration depth) needs some more or less detail rheological model.

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