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COMPARISON BETWEEN APPARENT VISCOSITY RELATED TO IRRADIATION DOSE FOR CORN STARCH AND BLACK PEPPER

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A b s t r a c t. Dose-effect relationship was studied in the rheoviscometric behaviour of geliffied suspensions of irradiated corn starch and black pepper, as the variation of the apparent viscosity and the shear stress related to the dose.

Irradiation has been performed up to 16 kGy. Black pepper was ground and sieved to three particle sizes to analyse also the influence of particle size on the apparent viscosity variation by dose. The rheoviscometric measurements have been carried out by a rotationary viscometer on geliffied suspensions of starch and black pepper, into equivalent starch concentration and alkalinised suspensions for pepper.

For starch, shear stress variation by dose is exponential, where the coefficients depend on the shear rate. For black pepper, the curves of apparent viscosity relation to dose also fit an exponential equation and the influence of particle size is discussed, too.

Viscometric behaviour similar to irradiation of both corn starch and black pepper could be attributed to starch degradation at relatively high doses and should be used to develop an identification and control method for the ionising treatment of starch-based food materials.

K e y w o r d s: irradiation, viscometry, dose-effect, starch, pepper

INTRODUCTION

Nowadays irradiation represents a feasible, reliable and quite usual method of improving quality and reducing spoilage of different dry or dehydrated food items like spices, including black pepper (*Piper nigrum*); crude and modified starches; starch-based materials; other ingredients [4,14,15].

In the last years nutritional behaviour, market and technological requirements led to an increase of demand for spices and starch-based foodstuffs. However, consumer protection and current trends towards improvement of food safety, quality and convenience increase the interest in ensuring hygienic standards for spices and other dehydrated foodstuffs while retaining their technological and organolaeptic qualities [6,9,15,16].

Effectiveness of irradiation of spices and starch-based ingredients is well known. Radio -induced starch damage is also recognised [3,5, 7,10,16]. To promote such a controversial technology as irradiation, it is necessry to check compliance with food regulations and consumer protection rules to set up appropriate methods to investigate all the radio-induced modifications and to control and identify ionising treatments applied to different food materials and foodstuffs [12,16].

Viscosity changes due to starch damage under irradiation is one of the most extensively studied methods for the identification of ionizing treatments [1,5-7,13]. Generally, this method is simple, cheap, and reproducible, however some problems related to its specificity and precision need to be elaborated.

Therefore, this study is focused on clarifying relationships between irradiation dose and viscometric properties of some dehydrated starch-based materials and, to discuss the influences of different experimental parameters on the variation of rheoviscometric properties related to irradiation dose.

MATERIALS AND METHODS

Crude corn starch and black pepper purchased from the market have been used as study materials. Corn starch has a moisture content of approximately 12 %. Black pepper was ground by an electric kitchen grinder for 5 min, divided into three equal parts and then sieved using standard wire mesh sieves with apertures of $\Phi_1 \leq 125$, $\Phi_2 \leq 250$ and $\Phi_3 \leq 500$ µm, respectively. The sieves apertures characterise particle size of ground pepper samples. Moisture content of the ground black pepper was approximately 11 %. The moisture determination was carried out by standard method using a Mettler -Toledo LP 16 moisture analyser. The starch content of ground black pepper was determined spectrophotometrically [17] and the mean value obtained was 40.2 % on d.w. basis. Prior to other treatments or ionisation, both corn starch and black pepper were checked by EPR and TL methods [2,3,8,10,11] to see if they were not irradiated.

From these materials samples of 20-25 g each were packed in sealed foil bags. These samples were irradiated to a ^{60}Co gamma-ray source at different doses, D = 1, 2, 4, 8 16 kGy with a dose rate of approximately 3 kGy/h. Standard chemical dosimetric methods was used to check the doses.

For both corn starch and black pepper non -irradiated (D = 0 kGy) samples, were analysed as well.

Rheoviscometric measurements were performed on geliffied suspensions with a mean starch content of approximately 2.5-4.0 % w/v. For pepper these suspensions were alkalinised by 33 % NaOH solution to adjust pH value to 12.2-12.5 [7,13]. After preparation, the suspensions were homogenised with an electrical stirrer for 8 min, then they were heated in boiling water bath for 30 min, which was followed by cooling at room temperature (20-22°C) for 3 h to reach sample temperature of about 26°C.

A rotationary viscometer Rheotest RV2-type with S/S_2 cylinder coupling was used for the measurements. For all the samples and irradiation doses, shear stress, τ (mPa) and apparent viscosity, η_a (mPa s) were determined for twelve shear rate values, D_r (s^{-1}) in the range of 1.0-437.4 s^{-1} specific to the viscometer type [1,6]. All the samples were measured in triplicate. The results represent arithmetic mean of direct measurements.

An important assumption is that viscometric parameter variation in relation to irradiation should be related to starch degradation and the number of molecules or chemical bonds damaged presents an exponential variation in relation to the irradiation dose [1,5,10]. As rheoviscometric parameters should be related to the number of damaged or undamaged starch molecules, relationship between these viscometric parameters and the irradiation dose can be established.

The experimental data were used to analyse the variation of shear stress and apparent viscosity by irradiation dose, for different shear rate values i.e., $\tau(D)$ and $\eta_a(D)$, respectively. On this basis, by usual methods of regression analysis and linearisation dose-effect relationship and related curves were established.

RESULTS

The results of rheoviscometric measurements for corn starch are presented in graphical form in Figs 1 and 2. The first illustration (Fig.1) presents the variation of the shear stress with the irradiation dose, $\tau(D)$ for the different values of the shear rate, D_r = 48.6-437.4 s^{-1} for corn starch suspension of approximately 3% w/v concentration.

Figure 2 presents variation of the apparent viscosity by dose, $\eta_a(D)$ with the same values of

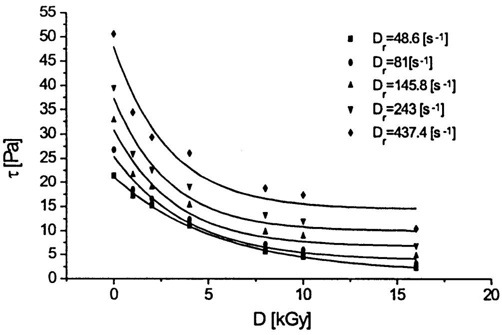

Fig. 1. The variation of shear stress, τ (mPa) with the irradiation dose, D (kGy) for corn starch suspension (2.5% w/v concentration) at differnet shear rates, D_r (s^{-1}).

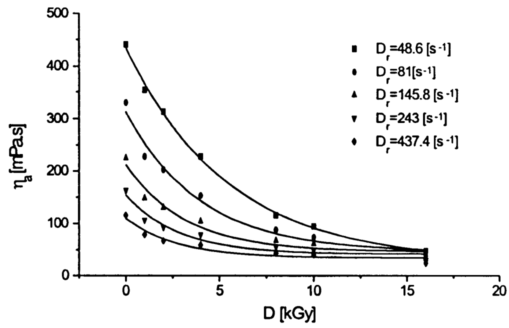

Fig. 2. The variation of apparent viscosity η_a (mPa s) with the irradaition dose, D (kGy) for corn starch suspension (2.5% w/v concentration) at different shear rates, D_r (s^{-1}).

shear rate, D_r and for the same corn starch suspension.

In the first case, the equation obtained from the experimental data presented in Fig. 1 for the shear stress, $\tau(D)$ has an exponential form:

$$\tau = a \exp(-b D). \qquad (1)$$

Therefore, in the logarithmic form:

$$\ln \tau = \ln a - b\ D \qquad (2)$$

it represents a linear variation of $\ln \tau(D)$ with a negative slope. By regression analysis parameters $\ln a$ and b (which give the slope) presented in Table 1 together with the correlation coefficients for different values of the shear rate, D_r are obtained.

From these data, it is clear that $\ln a$ depends linearly on D_r, for $D_r \geq 27.0\ s^{-1}$ and should be written as:

$$\ln a = c D_r + d \qquad (3)$$

where, using the least squares method, we obtain: $c = 159 \cdot 10^{-5}$, $d = 2.867$ with a correlation coefficient r = 0.995.

For the parameter b of Eqs (1) and (2) a variation with D_r values, may be observed, but the relationship is more complex and could be written as:

$$b = b_0 + b_1 (1 + D_r^{1/2})^{-1} \qquad (4)$$

with $b_0 = 0.05$ and $b_1 = 0.6779$.

These equations fit the experimental data and describe the relation between shear stress and apparent viscosity of the starch suspensions and irradiation dose, D.

For the black pepper alkalinized suspensions, the experimental data are presented in Fig. 3 as apparent viscosity by dose, $\eta_a(D)$ for the six values of shear rate, $D_r = 27.0\text{-}437.4\ s^{-1}$ for the particle size $\Phi_1 \leq 125\ \mu m$.

Experimental data show the same variation of apparent viscosity by irradiation dose, $\eta_a(D)$ also for the other two granulation levels of black pepper, $\Phi_2 \leq 250$ and $\Phi_3 \leq 500\ \mu m$, respectively. Therefore, the relation of apparent viscosity and irradiation dose, $\eta_a(D)$ should be expressed, in terms of the so-called "dose-effect relationship" by an exponential equation:

Table 1. The parameter values and the values of correlation coefficient, r for the equation describing the variation of starch shear rate by irradiation dose (Eqs (1) and (2))

Parameter	Share rate, D_r (s^{-1})								
	5.4	9.0	16.2	27.0	48.6	81.0	145.8	243.0	437.4
$\ln a$	2.681	2.803	2.938	2.917	2.917	2.983	3.116	3.289	3.542
b	0.178	0.177	0.180	0.159	0.134	0.118	0.098	0.084	0.074
r	0.999	0.999	0.999	0.995	0.994	0.997	0.997	0.998	0.998

$$\eta_a = A \exp(-k\,D) \qquad (5)$$

where the two coefficients, A and k, depend both on the shear rate, D_r and the particle size, Φ.

By analysis of the experimental data a direct relationship between the coefficient A and the shear rate value was obtained. It means the variation of $A(D_r)$, given by the equation:

$$A = p\,D_r^{-1} + q \qquad (6)$$

where p and q depend on the particle size. Whereas, variation of the coefficient k by shear rate, $k(D_r)$ cannot be expressed in a satisfactory manner.

Figure 4 presents variation of apparent viscosity of black pepper suspensions in relation to shear rate values higher than 48.6 s^{-1} for all three particle sizes and irradiated at 10 kGy. This figure presents the influence of particle size on the apparent viscosity in a more detailed way.

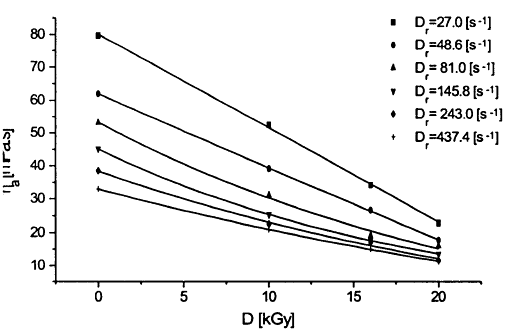

Fig. 3. The variation of apparent viscosity η_a (mPa s) with the irradaition dose, D (kGy) for black pepper alkalised suspensions (~2.5% w/v concentration as starch equivalent) at different shear rates, D_r (s^{-1}, $D_r \geq 27.0$ s^{-1}).

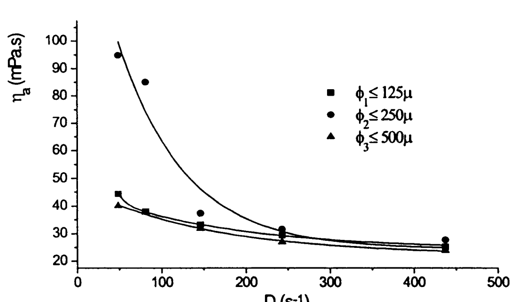

Fig. 4. The variation of apparent viscosity with the share rate, D_r (s^{-1}, $D_r \geq 48.6$ s^{-1}) for the black pepper alkalised suspensions (~2.5% w/v concentration as starch equivalent) obtained from ground pepper at particle size, $\Phi_1 \leq 125$ μm.

DISCUSSION

For both considered materials the values of apparent viscosity for non-irradiated samples is significantly higher than for the irradiated ones, when the values of share rate are $D_r \geq 27.0$ s^{-1}. For the shear rate values lower than $D_r \leq 27.0$ s^{-1} and for the lower doses (D = 0, 1, 2, 4 kGy) the difference between apparent viscosity and shear stress values of different samples were not very clear and reproducible (Figs 1-3).

As expected, apparent viscosity, η_a decreased with increasing irradiation dose, as shown in Figs 2 and 3. Variation of apparent viscosity by dose is described by an exponential equation as in the case of shear stress variation by dose (Eqs (1), (2) and (5)). These equations represent the dose-effect relationships in the case of rheoviscometric properties of corn starch and ground black pepper.

The influence of experimental conditions, mainly of the shear rate value, D_r on the rheoviscometric measurements is proved by all the experimental data shown in Figs 1-4 and it is also presented in the equations which describe variation of shear stress and apparent viscosity by dose. The relation between rheoviscometric equation coefficients and shear rate values are described by Eqs (3), (4) and (6) in both cases, for corn starch and black pepper.

It is obvious from the experimental data presented in Figs 3 and 4 that particle size significantly influences rheoviscometric properties of ground black pepper suspensions.

By rheoviscometric measurements and data analysis all the coefficients of the equations which describe rheological behaviour of corn starch and black pepper under irradiation and their relations can be established.

The rheograms for both corn starch and ground pepper are clear enough, for $D_r \geq 27.0$ s^{-1} to differentiate between irradiated and non-irradiated samples and to be used as an identification method of the ionising treatment applied to these materials.

CONCLUSIONS

Corn starch and black pepper obviously present the same rheoviscometric behaviour under irradiation and this fact should be attributed to starch degradation and depolymerization due to ionising radiation and confirm one of main assumption of this study.

For both materials the variation of apparent viscosity by irradiation dose is described by exponential equations and the apparent viscosity decreases by dose. These equations fit the experimental data for both corn starch and ground black pepper well, the correlation coefficient values being, $r \geq 0.93$ for all the cases and represent the dose-effect relationships for corn starch and ground black pepper suspensions.

The coefficients of these equations could also be obtained by analysing data from viscometric measurements and they strongly depend on the shear rate values.

Some of the experimental conditions, like sample preparation procedure or the particle size, have a significant influence on the rheological parameters and on their variation by dose.

In all the cases ionising treatment showed relation to the irradiation dose by viscometric measurements and the rheological parameters of the considered materials. For shear rate values, $D_r \geq 27.0\ s^{-1}$ all the dose-effect curves are clear enough to differentiate between the non-irradiated and irradiated samples.

Therefore, the variation of rheological parameter values by the irradiation dose could be used as the basis for setting up a simple and reliable method to identify and control the ionising treatment applied to different dehydrated starch-containing food materials and foodstuffs.

REFERENCES

1. **Casandroiu T., Oprita N., Ferdes O.:** On the gamma-irradiated black pepper rehoviscometric identification possibility. Romanian J. Biophys., 7(1-2), 141-151, 1997.
2. **Dood N.J.F., Lea J.S., Swallow A.J.:** The ESR detection of irradiated food. Appl. Radiat. Isot., 40, 1211-1214, 1989.
3. **Duliu O.G., Grecu V.V., Ferdes O.:** Preliminary EPR studies on some irradiated food components and foodstuffs. J. Food Physics, suppl., 66-70, 1996.
4. **Farkas J.:** Irradiation of Dry Food Ingredients. CRC Press Inc., Boca Raton, Florida, USA, 1988.
5. **Farkas J., Sharif M.M., Barabasassy S.:** Analytical studies into radiation-induced starch damage in black and white peppers. Acta Alimentaria, 19(3), 273-279, 1990.
6. **Ferdes O., Casandroiu T., Oprita N.:** Rheoviscometric technique in identification, control and quality evaluation of some irradiated food ingredients. Acta Alimentaria, 25(4), 375-380, 1996.
7. **Hayashi T., Todoriki S.:** Detection of irradiated peppers by viscosity measurement at extremly high pH. Radiat. Phys. Chem., 48(1), 101-104, 1996.
8. **Kispeter J., Delincee H., Kiss L.:** Influence of mineral composition on thermoluminescence of irradiated foodstuffs. Acta alimentaria, 25(4), 199-202, 1996.
9. **Kiss I., Farkas J.:** Irradiation as a method for decontamination of spices. Food Rev. Int., 4(1), 77-92, 1988.
10. **Raffi J., Agnel J-P.:** Influence of the physical structure of the irradiated starches on their ESR spectra kinetics. J. Phys. Chem., 87, 2369-2373, 1983.
11. **Sanderson D.C.W., Slater C., Cairns K.J.:** Thermoluminescence of foods: origins and implications for detecting irradiation. Radiat. Phys. Chem., 34, 915-924, 1989.
12. **Schreiber G.A., Helle N., Bogl K.W.:** Detection of irradiated food-methods and routine applications. Int. J. Radiat. Biol., 63(10), 105-130, 1993.
13. **Schreiber G. A., Leffke A., Mager M., Helle N., Bogl K.W.:** Viscosity of alkaline suspensions of black and white pepper samples: an indication or an identification of high dose radiation treatment. Radiat. Phys. Chem., 44(5), 467-472, 1994
14. **Singh L., Mohan M.S., Padwal-Desai S.R., Sankaran R., Sharma, T.R.:** The use of gamma irradiation for imporving microbiological qualities of spices. J. Food Sci. Technol., 25, 357-360, 1988.
15. W.H.O.: Food Irradiation: a technique for preserving and improving the safety of food. W.H.O., Geneva, 1988.
16. W.H.O: Safety and nutritional adequacy of irradiated food. W.H.O., Geneva, 1994.
17. **Williams P.C., Fegol K.S.W.:** Colorimetric determination of damaged starch in flour. Cereal Chem., 46, 56-62, 1969.