

RHEOLOGICAL AND WATER BINDING PROPERTIES
OF A 'FAT-IN-WATER' EMULSION STABILIZED BY STARCH

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Abstract. The rheological and water binding properties of fat-in-water emulsions have been studied by the DMA and NMR methods. Starch has been found to be a very effective stabiliser of fat-in-water emulsions. Even the small addition of just 6-7% has been shown to restore the rheological properties of the system in which over 60% of fat has been replaced with water containing starch added in the procedure of thermal stabilisation. The ability to bind water with emulsions stabilised by starch depends on the availability of the water to bind the hydrogenous centres in the starch. The optimum content of starch ensuring the maximum contribution of bound water is about 7%. At this starch content, water activity in the emulsions studied reached a minimum value of 0.91, which is slightly higher than the water activity in a comparable pure fat phase $A_w = 0.89$.

Key words: Fat-in-water emulsion, DMA, NMR, water activity

INTRODUCTION

In top quality meat products the fat phase is a binding agent ensuring the desired parameters of texture, quality and the micro-biological durability of the product. Increasing demand for low-fat products induces the need to modify product recipes leading to the elimination of fat by, for example, replacing it by water. When the fat is replaced by water to a low degree and the fat phase is a water-in-fat emulsion, the proteins present in the system are able to bind the water so that no significant changes in the quality of the products are observed [7]. In low-fat products when the amount of fat replaced by water exceeds 70% the continuous phase of the product becomes a fat-in-water emulsion losing the rheological properties typical of condensed emulsions [1], which leads to drastic changes in product quality,

especially in its texture and water binding ability [6]. Therefore, water is introduced in combination with structuring and water binding agents. Those agents which meet the required conditions are preparations including proteins, starch and other polysaccharides [3]. Much of the work on the stabilisation of the continuous phase in low-fat meat products has dealt with the properties of the final product, which does not give an insight into the mechanism of the interactions of the additions introduced. In view of the above, the aim of this study was to determine structuring and water-binding effects as related to the introduction of starch into fat-in-water emulsions modelling the continuous phase in low-fat meat products of fine structure.

MATERIALS AND METHODS

The study was performed on mixtures of mechanically homogenised pork fat tissue (fat 93%, water 4%, proteins 3%), water and unmodified wheat starch (Sigma), in proportions corresponding to those in low-fat meat products. The contribution of water in the system was kept constant at 58.3% wt, and the amounts of starch added – 2.1%, 6.4%, 7.5%, 8.6%, 10.7% and 12.8% were compensated for by the elimination of fat, whose contribution was reduced from 40% to 30%. The fat tissue was ground in a grinder with a plate diameter of 3-mm mesh. The fat tissue was completed by a starch-water suspension in the proportions given above. The initial emulsions of the above components in all proportions proved highly unstable and separation into the phases of starch, water and fat took place in a few minutes. For this reason, the mixtures were subjected to thermal treatment – analogous to the pasteurisation of meat products – at 72°C for 20 min, while being stirred continuously. The emulsions were placed in the measurement chambers then gradually cooled by thermostatical systems adequate for DMA and NMR spectrometers and at selected temperatures subjected to DMA [9] and H^1 NMR relaxation measurements. Moreover, the fundamental physical parameters of the texture of the samples (dynamic elasticity modulus (G_1) and loss modulus (G_2), molecular dynamics of water, spin-lattice relaxation rate (R_1) and spin-spin relaxation rate (R_2) at a resonance frequency of 15 MHz were measured. For those samples cooled to 25°C, the activity of water in the emulsions was measured by an MMAW-4, an instrument made by COBRABiD, with forced air flow in the measuring chamber.

RESULTS AND DISCUSSION

Rheological properties

Figures 1 and 2 present the temperature dependencies of the elasticity modulus and loss modulus for the emulsion containing 6.4% of wheat starch.

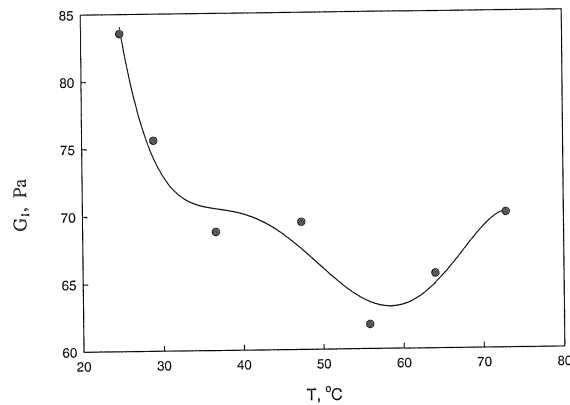


Fig. 1. Temperature dependence of the elasticity modulus for the emulsion containing 6.4% of starch

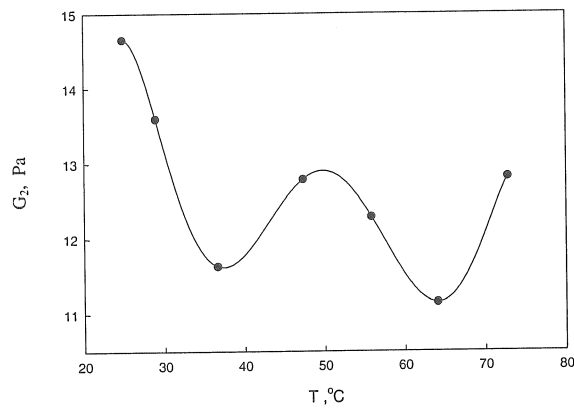


Fig. 2. Temperature dependence of the loss modulus for the emulsion containing 6.4% of starch

When the temperature decreases below 72°C, the values of G_1 and G_2 decrease by several percentage points, which can be related to the phase transition of the protein components of the fat tissue [4]. With a further decrease in temperature the elasticity modulus increases, while the loss modulus reaches the

maximum at about 50°C. This is related to the structuring effect of the starch system observed at the temperature of gelation. A decrease of temperature below 35°C causes a further increase in G_1 and G_2 interpreted as related to solidification of the fat phase in the emulsion studied [9]. For those emulsions with an increased starch content, the character of the temperature dependencies of the moduli is similar. For those emulsions cooled to the ambient temperature, the values of G_1 and G_2 increase with the increasing content of starch in the system (fig. 3, 4).

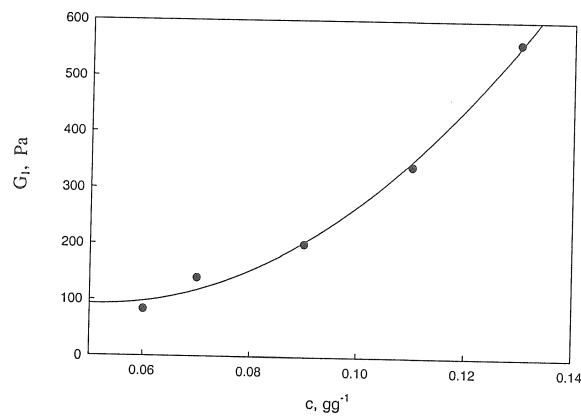


Fig. 3. The elasticity modulus versus the starch content in emulsions at 25°C

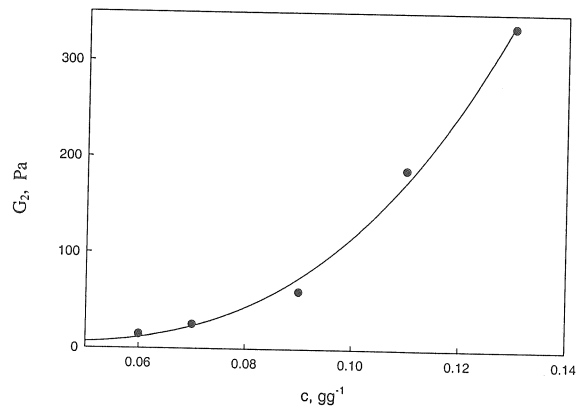


Fig. 4. The loss modulus versus starch content in emulsions at 25°C

The emulsion with the 12.8% starch content is characterised by the elasticity modulus of $G_1 = 560$ Pa and loss modulus of $G_2 = 340$ Pa. These values are much higher than those obtained for pure fat subjected to the same procedure – for fat

systems cooled to ambient temperature, the corresponding values are $G_1 = 100$ Pa and $G_2 = 13$ Pa. It follows from the results of our measurements that starch is a very effective stabiliser of fat-in-water emulsions. By adding 6-7% starch, the rheological parameters of the system are restored with over 60% of the fat being replaced by water with the added starch, gelled in the stabilisation procedure.

Water binding properties

To analyse the mechanism of the water binding in the emulsion structure, temperature measurements of the spin-lattice and spin-spin relaxation rates R_1 (fig. 5) and R_2 (fig. 6) were measured by the NMR method.

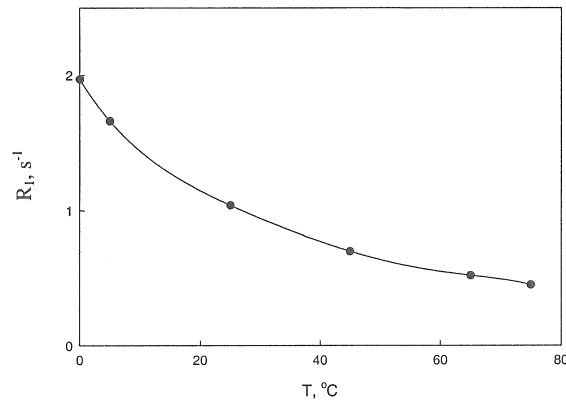


Fig. 5. Temperature dependence of the spin-lattice proton relaxation rate in the emulsion with 6.4% of starch

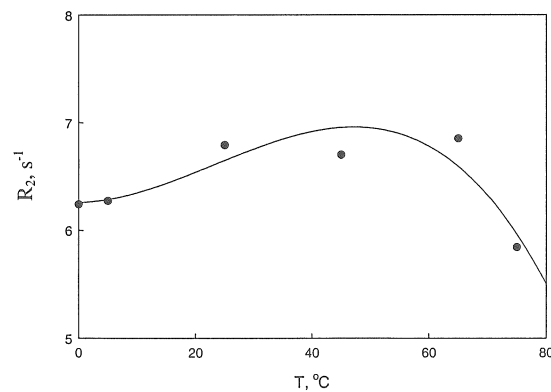


Fig. 6. Temperature dependence of the spin-spin proton relaxation rate in the emulsion with 6.4% of starch

The steady increase of R_1 with decreasing temperatures testifies to the relatively high mobility of the water in the system, typical of the liquid phase. The spin-lattice proton relaxation rate in the emulsions is about three times greater than in free water in which – at 20°C – the relaxation rate is $R_{1F} \approx 0.33 \text{ s}^{-1}$. This fact could be interpreted as a consequence of a significant contribution of hydration water (bound water) in the systems. However, as follows from the calculations assuming the formula [8]:

$$R_1 = C_{HW} (R_{1H} - R_{1F}) + R_{1F}$$

the contribution of hydration water (C_{HW}) in the water contained in the emulsions studied does not exceed 10%, and the significant increase in the relaxation rate is mainly a consequence of the fact that the relaxation rate of the hydration water in the system (R_{1H}) is over 20 times higher than in free water.

A comparison of the temperature courses of the spin-spin (fig. 5) and spin-lattice (fig. 6) relaxation rates suggests that the dominant relaxation mechanism in the hydration layer is not related to changes in the dynamics of the water molecules bound in this layer. If it were, the temperature courses of $R_1(t)$ and $R_2(t)$ should overlap, taking into account that the character of $R_1(t)$ is typical of the liquid state. The weak temperature dependence of R_2 with a small maximum at 50°C suggests that the relaxation mechanism is based on proton exchange, which is typical of biomolecular gels [2] with which water molecules interact through hydrogen bonds. In such systems, the relaxation rate is determined by the water available to the hydrogen bond centres. Figure 7 presents the relative relaxation rate (R_2/R_1), being a measure of static relaxation effects [5] determined by the water binding in the system, as a function of the starch content in the system. In the beginning, the availability of the water-binding centres to water increases because of the increasing content of starch in the system.

After reaching the maximum at $C = 0.07$, a further increase in the starch content leads to a decrease in the availability of the water-binding centres. The similar character of water interactions in the system is indicated by the results of the measurements of water activity (a_w) in the emulsions studied (fig. 8). Initially an increase in the starch content favours an increase in the contribution of the bound water in the system, which leads to a decrease in the water activity to $a_w = 0.91$ at $C = 0.07$. A further increase in the starch content causes an increase in the water activity. This effect can be a result of the evacuation of free water beyond

the starch spherulites undergoing fast re-crystallisation which had previously partly gelled where the starch in the water was excessive.

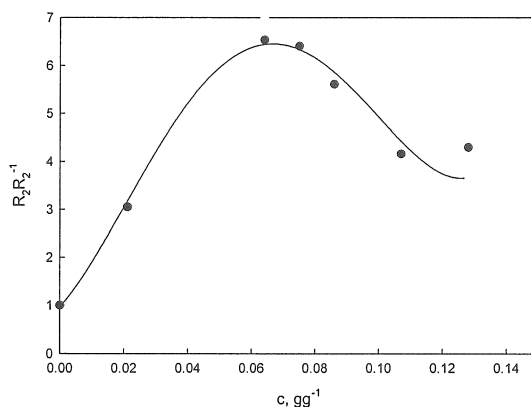


Fig. 7. Relative proton relaxation rate versus the content of starch in emulsions at 25°C

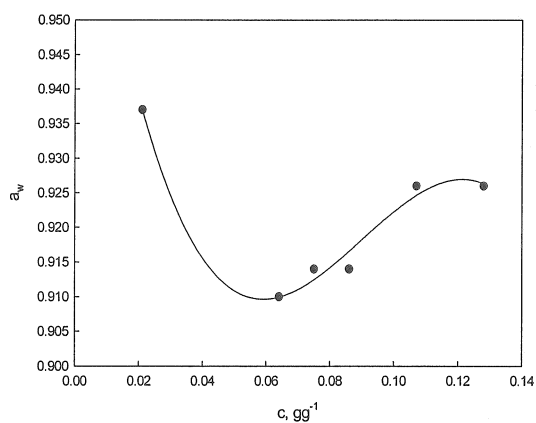


Fig. 8. Water activity versus the content of starch in emulsions at 25°C

CONCLUSIONS

Starch is a very effective stabiliser of fat-in-water emulsions; if just a small amount is added – about 6-7%, the rheological parameters of the system in which over 60% of fat has been replaced by water with the addition of starch gelled in the thermal stabilisation procedure are restored. A further increase in the starch content leads to a significant increase in the rheological parameters of cold emulsions to values many times higher than those obtained in the pure fat phase.

The water binding ability of starch-stabilised emulsions depends on the availability of the hydrogen bond centres to the water molecules in the starch. The optimum content of starch in the system ensures that the maximum contribution of bound water equals ~ 7%. At this starch content, the activity of water in the emulsions studied reaches a minimum value of 0.91, which is slightly higher than that in the pure fat phase which equals 0.89.

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WŁAŚCIWOŚCI REOLOGICZNE I ZDOLNOŚĆ WIĄZANIA WODY EMULSJI TYPU TŁUSZCZ W WODZIE STABILIZOWANYCH SKROBIĄ

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Streszczenie. Właściwości reologiczne i zdolność wiązania wody przez stabilizowane skrobią emulsje typu tłuszcz w wodzie zbadano odpowiednio metodami DMA oraz NMR. Stwierdzono, że skrobia jest bardzo efektywnym stabilizatorem emulsji typu tłuszcz w wodzie i już niewielki jej dodatek w ilości 6 do 7% przywraca parametry reologiczne układu, w którym wyeliminowano ponad 60% fazy tłuszczowej, zastępując ją wodą z dodatkiem skrobi kleikowanej w procedurze stabilizacji cieplnej. Zdolność wiązania wody w stabilizowanych skrobią emulsjach

zależy od dostępności molekuł wody do centrów wiązań wodorowych w skrobi. Optymalna zawartość skrobi w układzie, zapewniająca maksymalny udział wody związanej wynosi około 7%. Przy takiej zawartości skrobi aktywność wody (a_w) w badanych emulsjach osiąga minimalną wartość 0,91, która jest nieco wyższa od aktywności wody w czystej fazie tłuszczowej, gdzie $a_w = 0,89$.

Słowa kluczowe: Emulsje typu tłuszcz w wodzie, DMA, MRJ, aktywność wody

