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Effects of temperature and hydrocolloids on the rheological characteristics of coating batters

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Abstract The rheological properties and water retention capacities of wheat-rice and wheat-corn flour based coating batters with specific hydrocolloids methylcellulose (MC) or hydroxypropyl methylcellulose (HPMC) at different temperatures (5, 15, 25 °C) were determined. All batter formulations showed pseudo-plastic flow behaviour. Consistency index values of wheat-rice and wheat-corn flours were between 10.33 and 81.58 Pa sⁿ; 9.59–80.49 Pa s^n (with MC) and 5.20–20.26 Pa s^n ; 4.74–19.77 Pa s^n (with HPMC) respectively. Wheat-rice flour combination at 5° C and 1.5% MC concentration had the highest water retention capacity (79.36%). The maximum activation energies of MC and HPMC were 47.65 and 23.66 kJ mole−1. Activation energies of batters indicated that MC-samples exhibited the highest temperature dependency.

Keywords Rheology · Hydrocolloids · Batter · Rice flour · Corn flour

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Introduction

A batter could be described as liquid dough containing essentially flour and water. The food product is submerged before cooking process especially by frying. The list of contents can be expanded with the addition of egg, starch, salt and so on. The structure of the batter becomes more complex, as the number of ingredients increase. Mostly, onion rings, vegetables and chicken breast meat are battered, and then prefried and frozen [\[1](#page-6-0)]. The aim of batter coating in fried foodstuffs is to improve texture, volume, aroma of the product $[2]$ $[2]$ and decrease water loss $[3]$ $[3]$.

In the frying process, batter viscosity is an important property in order to identify the activity of coating [\[4](#page-6-3)] and performance of frying [\[5](#page-6-4)]. The viscosity and other rheological features influence physical characteristics of batter coating like pick-up, color and texture [[1,](#page-6-0) [6\]](#page-6-5). Batter pickup is the quantity of batter hanging on to food product and shows difference between the food types [[7\]](#page-6-6). In case of insufficient pick up, the quality characteristics of final product might be at risk [[8\]](#page-6-7). The rheological properties of coating batters are affected by temperature, composition and amount of ingredients in recipe and solid:water rate [\[9](#page-6-8), [10](#page-6-9)]. On the other hand, rate, length and history of shearing have effects on the flow behavior of any fluid system [[11\]](#page-6-10).

Many biopolymers have functional effects on food materials. Using gums in coating batters makes the control of viscosity easier. Thus, the ability of coating improves [\[12](#page-6-11)]. They also develop freeze–thaw stability, taste and textural characteristics and food quality [[6,](#page-6-5) [13](#page-6-12)]. Methylcellulose (MC) and hydroxypropylmethylcellulose (HPMC) are hydrocolloids produced from cellulose by modification $[14]$ $[14]$, classified as dietary fibers $[15]$ $[15]$ and have the capability of decreasing oil intake during frying operations [\[16](#page-6-15)]. Methyl groups in MC and methyl and hydroxypropyl

groups in HPMC are linked to cellulose chain. Hence, these polymers gain perfect hydration-dehydration properties when temperature fluctuates [\[17](#page-7-0)]. If the temperature rises, hydration water leaves the polymer, the viscosity decreases. When the cellulose solution starts cooling, reversible process begins, the viscosity rises [[18,](#page-7-1) [19\]](#page-7-2).

Eyring's theory explains the movement of molecules in fluids. Energy requirement of molecules are supplied from activation energy, molecules move continuously within spaces with this energy. High activation energy means fast fluid flow $[20, 21]$ $[20, 21]$ $[20, 21]$. The value of activation energy decreases considerably when suspended molecules are present in food product like fruit purees. Activation energies of products which show pseudoplastic flow behavior are directly proportional to the flow behaviour index (n) [\[22](#page-7-5)].

Research studies on the rheological behaviour of batter systems are insufficient, as they are mostly focused on different flour combinations [[2,](#page-6-1) [13](#page-6-12), [23](#page-7-6), [24\]](#page-7-7). Limited information is available on the effects of MC or HPMC on batter systems at various temperatures [\[6](#page-6-5), [19](#page-7-2)]. This paper concerns the impact of hydrocolloid type, concentration and temperature on power law fluid parameters and water retention capacity of various batters. Accurate knowledge concerning the performance of cellulose polymers can give idea about oil absorption by batters during frying of coated foods. On the other hand, the possession of rheological inputs will enable the control of food processes, hence flow characteristics influence food quality significantly.

Materials and methods

Batter formulation

The main ingredients of coating batters were wheat flour (W) (Piyale, Ülker, Turkey), corn flour (C) (Piyale, Ülker, Turkey) and rice flour (R) (Piyale, Ülker, Turkey). Compositions of these flours were given in Table [1.](#page-1-0) HPMC (H7509, Sigma Aldrich, USA) or MC (M7027, Sigma Aldrich, USA) (0, 0.5, 1, 1.5%) (w/w) were added into the mixture of wheat flour-corn flour (75–25%; 50–50%; 25–75%) (w/w) or wheat flour-rice (75–25%; 50–50%; 25–75%) (w/w) flour separately. Selected concentrations of hydrocolloids were in agreement with the maximum limits

Table 1 Chemical characteristics of flour samples on dry basis

	Ash $(\%)$	Protein $(\%)$	Fat $(\%)$
Wheat flour (W)	0.47	13,55	2.04
Corn flour (C)	0.62	7.68	3.94
Rice flour (R)	0.55	9.95	1.60

of Natl. Academy of Sciences, Food and Nutrition Board, U.S.A [[15\]](#page-6-14). A total of 48 combinations were studied.

Dry-mix: water ratio was 1:1.2 and each 100 g of formulation contained 2.5 g of table salt (Billur Tuz, İzmir, Turkey) and 3.1 g of baking powder (Dr. Oetker, Torbalı, İzmir, Turkey). All powders were mixed with cold water at room temperature by a kitchen mixer (Rowenta, Germany) for 2 min to obtain a homogeneous batter. The batters were kept in a refrigerator at 4 °C for 30 min before the experiments.

Rheological behavior

Shear stress (τ) and shear rate (γ) played important roles on batter viscosity. Power-law model (Eq. [1\)](#page-1-1) was suitable for both shear thinning and shear thickening fluids.

$$
\tau = K\gamma^n \tag{1}
$$

"K" was the consistency coefficient (Pa sⁿ) and dimensionless "n" was the flow behavior index. At all temperatures, power-law model described the flow behavior of coating batters best. Also, all n values were observed below 1, thus the batters were accepted as "pseudo-plastic" [[25\]](#page-7-8).

Rheological properties of different batter formulations were evaluated using a rheometer (Brookfield DV ІІІ, Brookfield Engineering Laboratories, USA). The temperatures of samples were adjusted to 5, 15 or 25°C with the help of a circulation water bath and sample container (small sample adaptor). Measurements were recorded by Reocalc© software version 1.0 over the range of 0–250 rpm as shear rate, shear stress and torque (%) using SC-27 spindle.

Water retention capacity (WRC)

The WRC of batter samples were determined according to Sanz et al. [[19\]](#page-7-2) with minor modifications. 30 g of coating batter sample were put into a 50 ml centrifuge tube. The temperature of tube was regulated by a water bath $(25^{\circ}C)$ and then, the sample was centrifuged (Hettich Zentrifugen, Tuttlingen) at 10,000×*g* for 15 min. After centrifugation process, the supernatant was separated, measured and WRC value of sample was calculated as the percentage of water released from batters.

Apparent activation energy

The temperature effects on apparent viscosities of coating batters were computed by considering Arrhenius type equation [[26,](#page-7-9) [27\]](#page-7-10);

$$
K = K_0 e^{-E_A / R(1/T_0 - 1/T)}
$$
\n(2)

where K_0 was the consistency factor (Pa s), R was the universal gas constant (kJ/mol K), E_a was the apparent activation energy (kJ/mol) and T was the temperature of batter (Kelvin, K). The reference temperature (T_0) was accepted as 20° C (293.15 K).

Linearization of Eq. (2) (2) is as follows (Eq. (3) (3));

$$
\ln K = \ln K_0 - \frac{E_a}{R} \cdot \left(\frac{1}{T_0} - \frac{1}{T}\right)
$$
 (3)

K₀ and E_a could be calculated from ln K versus $\left(\frac{1}{T_0} - \frac{1}{T}\right)$

plot.

On the other hand, a correlation coefficient (R^2) was computed in order to determine how strong the relationship was between consistency coefficient and activation energy. A correlation >0.8 could be generally described as strong. $R²$ is useful, as it gives the proportion of the variance of one variable that is predictable from the other variable. A total of 12 data was used in order to calculate R^2 for each batter sample.

Statistical analysis

All experiments were performed in triplicate. Statistical analysis on all experimental data was conducted using SPSS software (SPSS Inc., USA—Version 18.0). An analysis of variance (ANOVA) using the general linear model (GLM) procedure was performed to observe the differences in samples with the aim of Tukey's multiple comparison test ($P < 0.05$).

Results and discussion

Effect of MC on batter rheology

Apparent viscosity versus shear rate curves of batters containing wheat-corn flour and wheat-rice flour with MC at 15°C were shown in Figs. [1,](#page-2-1) [2](#page-3-0) and [3.](#page-3-1) Apparent viscosities of all samples prepared with MC decreased, while shear rates were increasing. An orientation effect caused shear thinning flow behavior. At higher shear rates, long polymer chains could not interact with visinal molecules. The viscosity values of samples at these rates can give idea about flow characteristics of food product during some unit operations. Hence, when the viscosity of food increases and shear rate decreases, pumping efficiency may probably decreases [[28\]](#page-7-11). On the other hand, increasing MC concentration increased apparent viscosity as illustrated in Figs. [1,](#page-2-1) [2](#page-3-0) and [3.](#page-3-1) The level of pseudoplasticity could be attributed with polysaccharide (hydrocolloid) concentration and interfacial film formation and molecular movements mainly lead to raise in viscosity [\[29](#page-7-12)].

For all samples, when temperature rose, apparent viscosity values dropped. Many researchers reported that

Fig. 1 Apparent viscosity changes of batters containing hydrocolloids at 15°C **a** 75% W–25% C **b** 75% W–25% R (*MC* methylcellulose, *HPMC* hydroxyprophylmethlycellulose, *W* wheat flour, *C* corn flour, *R* rice flour)

temperature had a negative effect on viscosity [[26,](#page-7-9) [30](#page-7-13), [31](#page-7-14)]. Because of thermal expansion in higher temperatures, distances between molecules increases resulting from intermolecular forces and this effect is reversible [[28\]](#page-7-11).

Rice or corn flour addition into batters caused decrease of K values. Consistency index levels of batters including corn flour-MC were in between 9.59 and 80.49 Pa sⁿ, containing rice flour-MC ranged between 10.33 and 81.58 Pa sⁿ respectively. Corn flour replacement with rice flour caused higher viscosity in samples with MC. Because batters based on corn starch needs perpetual mixing to prevent settling out the solid particles. Also, diameters and shapes of particles could be different [\[1](#page-6-0), [32,](#page-7-15) [33](#page-7-16)]. Approximate values were reported for low caloric desert gels containing inulin, powder milk and a hydrocolloid (xantham gum, agar–agar or guar gum) [\[34](#page-7-17)]. In that study, K values were in the range of $13.59 - 71.79$ Pa sⁿ.

For all flour blends studied, temperature rise produced a decrease in flow behaviour index value. Dimensionless "n" ranged between 0.50 and 0.71 for samples with corn flour and 0.41–0.77 for rice flour. If flow behaviour index goes below 0.6, a Non-Newtonian behaviour becomes significant [\[28](#page-7-11)]. Because mostly in emulsions, it means that gravitational separation does not be harmful for oil and/or

Fig. 2 Apparent viscosity changes of batters containing hydrocolloids at 15°C **a** 50% W–50% C **b** 50% W–50% R (*MC* methylcellulose, *HPMC* hydroxyprophylmethlycellulose, *W* wheat flour, *C* corn flour, *R* rice flour)

water droplets [\[35](#page-7-18)]. Also, slimy taste in mouth could not be felt below 0.6 [\[36](#page-7-19)]. Thus, especially at 1.5% MC concentration and 25° C, for all flour combinations, the highest pseudo-plasticity was observed and this was required for good sensory properties [[33,](#page-7-16) [37\]](#page-7-20).

Effect of HPMC on batter rheology

Differences in apparent viscosity values of samples produced with wheat flour-corn flour-HPMC or wheat flourrice flour-HPMC at changing shear rates were demonstrated in Figs. [1](#page-2-1), [2,](#page-3-0) [3](#page-3-1) (15 °C). As can be seen from Figs. 1, [2](#page-3-0) and [3](#page-3-1), the apparent viscosities of batters containing HPMC increased with decreasing shear rates. Adding HPMC enhanced the apparent viscosities of all batters because of excessiveness of chain–chain interactions occurred in aqueous solutions of this hydrocolloid. If there is HPMC in the medium of batter, any type of flour and HPMC tend to gain water, a molecule-to-molecule affiliation arises, hence consistency increases $[38]$ $[38]$. As such in MC, when the amount of rice or corn flour in batter with HPMC increased, consistencies of samples dropped to lower levels. Because, wheat flour was more effective on viscosity than any other

Fig. 3 Apparent viscosity changes of batters containing hydrocolloids at 15°C **a** 25% W–75% C **b** 25% W–75% R (*MC* methylcellulose, *HPMC* hydroxyprophylmethlycellulose, *W* wheat flour, *C* corn flour, *R* rice flour)

flours. Corn and rice flour diluted the strengthening effect of gluten matrix [\[39](#page-7-22)]. The similar results were also reported for batter systems with different flour concentrations [\[2](#page-6-1)].

The highest apparent viscosities were seen at the rate of 1.5% and at 5 °C for all samples. Batter consistencies including corn flour-HPMC were in between 4.74 and 19.77 Pa sⁿ, containing rice flour-HPMC ranged between 5.20 and 20.26 Pa s n . Viscosities of MC added samples were relatively higher than samples with HPMC at the same ratio. This difference could be attributed to water binding capacities of hydrocolloids due to the different ratios of methyl and hydroxypropyl substitutions, as well as hydrophobic interference between molecules including methoxyl groups [\[40](#page-7-23)]. When a hydrocolloid holds a significant amount of water, the viscosity of batter rises. Since, the solubility of HPMC was greater than MC, the samples containing HPMC had lower apparent viscosities [\[5](#page-6-4)].

Shear-thinning behavior $(n < 1)$ of HPMC added batters was only influenced by temperature according to results of a univariate analysis of variance $(P<0.05)$. The increment of temperature reduced flow indices. Minimum values of "n" were 0.52 and 0.49, maximum values were 0.75 and 0.63 for corn and rice flour enhanced batters respectively between 5 and 25 °C. Flour blends with rice were more pseudo-plastic than batters with corn flour because of having lower flow indices. Dimensionless "n" of HPMC-batters demonstrated similarities with 1%-2%-3% carrageenan at different temperatures [\[37](#page-7-20)]. Baixauli et al. [\[41](#page-7-24)] also claimed that temperature control was significant for batters handling in terms of the analysis results of their research. They found that in $5-40\degree$ C range, important decreases occurred in flow behavior indices of batters with different dried egg or dextrin concentrations when temperature rose. On the other hand, in an another research, it was emphasized that, flow index values of salep (which is a milk beverage obtained from dried tubers of *Orchis mascula* and contained glucomannose and starch) with 100–0% soy milk ranged between 0.41 and 0.73 respectively and these levels were in line with the current study. Thus, it can be said that rice or corn batters with MC or HPMC had similar flow characteristics with traditional Turkish beverage "salep" which contained soy milk [[42\]](#page-7-25).

Water retention capacity (WRC)

Temperature and hydrocolloid concentration effects on WRC were presented in Table [2.](#page-5-0) In all samples, MC and HPMC enhanced the WRC of batters. The highest water retention capacity was observed in 75% W–25% R sample containing 1.5% MC at 5° C (79.36%) and the lowest was 38.95% which belonged to 25% W–75% C batter with 0.5% HPMC at 25° C (except control sample). The minimum WRC value of MC-batter was 44.58% (25% W–75% C batter at 0.5% concentration and 25° C) and the maximum WRC value of HPMC-batter was 65.02% (75% W–25% R batter at 1.5% and 5° C).

When a hydrocolloid concentration increased, the demand of holding water of hydrocolloid chains also raised [\[19](#page-7-2)]. Water holding capacities of MC-samples were higher than HPMC-samples distinctly. Because, WRC is primarily pertinent to viscosity within the batter. Greater viscosity of MC clarified higher amount of water hold [[23\]](#page-7-6). On the other hand, HPMC contained protruded hydroxypropyl ether groups and these molecules inhibited the interaction of hydrocolloid chains with other molecules like H_2O , thus, the lower WRC of HPMC in comparison with MC may probably be originated from this situation [\[38](#page-7-21)]. Also, in viscosity development, molecular structure and molecular weight of hydrocolloid played an important role [\[18](#page-7-1)].

Wheat and rice flour combined batters showed greater water holding capacities than batters with wheat and corn flour, as expected. The high water absorption level of these coating batters may be due to the starch structure and content of rice flour [\[43](#page-7-26), [44](#page-7-27)]. Starch is elementarily related with rheological properties and moisture content of a material. Amylose level, granule size, shape and volume fraction were significant in contributing to starch [[45,](#page-7-28) [46](#page-7-29)].

Şümnü [[44\]](#page-7-27) stated that high water retention rates of rice and wheat flour and their combinations could account for much governance on moisture transfer in weight loss values of microwave baked cakes. On the other hand, starch made an improvement in rheological characteristics of yoghurt samples that contained blueberry, because of high waterbind capacity and high molecular weight [[34\]](#page-7-17).

Apparent activation energy

Activation energies, consistency factors and the coefficients of correlation were calculated and shown in Table [3.](#page-6-16) Rise in temperature causes a change in consistency index. Decreased consistency index forms resistance to flow [\[47](#page-7-30)]. Sensibility of viscosity incident to temperature is stated with Arrhenius equation [\[26](#page-7-9)]. High R^2 values referred that consistency factors of batters in relation with temperature obeyed the Arrhenius type model equation. \mathbb{R}^2 levels were between 0.80 and 1.00 for all types of batters indicating the strong relationship of the Arrhenius model to describe the temperature dependencies of samples with hydrocolloids.

The highest activation energy $(47.65 \text{ kJ mole}^{-1})$ belonged to 75% W–25% C batter mix with 1% MC which was similar with the activation energy of carregenaan reported by Marcotte et al. [\[37](#page-7-20)]. There is no information about activation energies of selected hydrocolloids for comparison. On the other hand, activation energy values of all samples (apart from controls) with HPMC were below 23.66 kJ mole⁻¹. This value was pertained to wheat-corn flour batter mix (25% W–75% C) at 1.5% concentration. A higher E_a value means that, quick changes in viscosity can be observed [\[48](#page-7-31)]. Therefore, the control of temperature was important for both MC and HPMC hydrocolloids at 1% and above concentrations while using especially with corn flour. Activation energies of HPMC with different flour compositions at different concentrations were always smaller than samples with MC. Hence, the control of viscosities of MC-batters could be harder than HPMC samples. Mostly, there was a high dependency between apparent viscosity and hydrocolloid concentration for both hydrocolloids (Table [3\)](#page-6-16).

The activation energy was related to hydrocolloid concentration and ingredients of product [\[22\]](#page-7-5). Activation values of coating batters with MC or HPMC increased when cellulosic polymer concentration was enhanced up to 1% for all flour compositions. After this percentage, energy levels mostly decreased. These results were partially compatible with the results stated for *Alyssum homolocarpum* seed gum and tomato ketchups [\[33,](#page-7-16) [49](#page-7-32)]. An increase in hydrocolloid amount caused a decrease in activation energy in specified studies previously. This may be due to the different starch and pectin (hydrocolloids) contents $(>1\%)$. It could be inferred that, up to

Table 2 Water retention capacities (WRC) of coating batters

Different small letters indicate significant differences between temperatures of each hydrocolloid concentration in own column (P < 0.05) Different capital letters show significant differences between average hydrocolloid concentrations in same column $(P<0.05)$

MC methylcellulose, *HPMC* hydroxyprophylmethlycellulose, *W* wheat flour, *C* corn flour, *R* rice flour)

1% hydrocolloid concentration, activation energy levels were directly proportional with MC or HPMC amount, but after this stage, there was an inverse proportion. Further studies which focused on varied MC and/or HPMC concentration(s) $(>1.5\%)$ should be needed.

Conclusion

This study indicated that rheology of coating batters could be successfully developed by the supplementation of MC or HPMC with the suitable temperature control. The effect of temperature on apparent viscosity was depicted evidently by Arrhenius equation. Nevertheless, the composition of batter and hydrocolloid concentration were two of

MC methylcellulose, *HPMC* hydroxyprophylmethlycellulose, *W* wheat flour, *C* corn flour, *R* rice flour)

the most important factors. Rheological behaviour of batter was a crucial point for pick up and so for food quality especially the battered and/or prefried products. Power-law model ensured good fitting for flow properties of all batter formulations. Batters containing the highest amounts of any hydrocolloid showed the highest apparent viscosity at all flour compositions. Increase in temperature caused a decrease in apparent viscosity of all samples. The influence of wheat flour on viscosity was greater than corn and rice flours. MC had more additive effect on viscosity, WRC and activation energy than HPMC.

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