Determination of Surface Tension Properties of Wheat Endosperms, Wheat Flours, and Wheat Glutens

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ABSTRACT

During wheat dough processing, a large part of the interactions with water are governed by wettability properties of flour. The wettability properties of wheat materials (flat slices of wheat endosperm, flour-based pellets, and gluten-based pellets) were assessed by the measurement of contact angles of a sessile drop of three reference liquids (water, diiodomethane, and formamide) and estimated by equilibrium properties (contact angles and surface tension properties) and drop penetration rates. The surface tension (γ_s) of wheat materials was measured between 49.6 and 55.3 mJ/m^{-2}. The present work permitted the evaluation of specific wheat types (hard wheat vs. soft wheat) and evaluation of the influence of material structure (flat slices of endosperm vs. flour-based pellets), and material nature (flour-based pellets vs. gluten-based pellets) on the wettability properties. The surface tension properties were considered with regard to the nonideal structure of sample surfaces by considering surface roughness and material porosity.

During wheat-based product processing, mixing of flour and ingredients is a critical point that governs the machinability of the dough as well as the quality of end-products. Extensive literature is available on mechanisms leading to the development of a dough through mechanical energy input. Nevertheless, extensive understanding of the physicochemical mechanisms involved in the first moments of particle agglomeration in the presence of water still remains incomplete.

In many food wet-granulation processes, a large part of the interactions with liquid are governed by the wettability properties of the powder. In a recent review, Iveson et al (2001) evaluated the current understanding of wet-granulation processes. Whether or not wetting is energetically favorable is driven by two thermodynamic parameters: the solid-liquid contact angle and the surface free energies. Studies of wettability can be achieved by the determination of the surface energies of the solid and of the liquid (Buckton 1990, 1993; Planisek et al 2000; Zhang et al 2002). On powdered solids, the determination of surface tension is more difficult than on a flat nonporous solid (Buckton et al 1995). Most of the techniques for surface tension determination on powders rely on the direct (or indirect) determination of contact angles. Contact angles can be determined by the capillary rise technique (using the Washburn equation), by isothermal microcalorimetry, or by inverse gas chromatography. Galet et al (1999) used the capillary rise technique to determine the contact angle of water on durum wheat semolina. Nevertheless, this approach was hampered by the high swelling behavior of semolina particles with water that obstructed the progression of water. Roman-Gutierrez et al (2003) measured the initial contact angles of water drops deposited on pellets based on flours or flour components.

The aim of the present work was the evaluation of specific wheat types (hard wheat vs. soft wheat), the influence of material structure (flat slices of endosperm vs. flour-based pellets), and material nature (flour-based pellets vs. gluten-based pellets) on the wettability properties of wheat materials. The wettability properties were assessed by measurement of contact angles of a sessile drop of three reference liquids (water, diiodomethane, and formamide) and estimated by the determination of two kinds of parameters (equilibrium properties [with contact angles and tension surface properties] and drop penetration rates).

THEORY

The theoretical approach for surface tension determination is based on the well-known Young equation (Equation 1) that describes the equilibrium of a drop of liquid placed on the surface a solid and surrounded by air

$$\gamma_{SV} = \gamma_{SL} + \gamma_{LV} \cos\theta \tag{1}$$

where θ is the contact angle between the solid and the liquid (°); γ_{SV} is the interfacial tension between the solid and air (mJ/m^{-2}); γ_{SL} is the interfacial tension between the solid and the liquid (mJ/m^{-2}); and γ_{LV} is the interfacial tension between the liquid and air (mJ/m^{-2}).

It is usually assumed that $\gamma_{LV} = \gamma_L$ because the liquid is always surrounded by its saturated vapor. The superficial tension of the liquid (γ_L) is an intrinsic characteristic of the liquid. The surface tension of the solid (γ_S) is given as $\gamma_S = \gamma_{SV} + \pi_e$, but it is generally assumed that $\gamma_{SV} = \gamma_S$. According to Yildirim (2001), the film pressure on the solid π_e can be neglected when $\gamma_L > \gamma_S$ and when there are no vapors of low-energy substances surrounding the drop of liquid. The surface tension of the solid (γ_S) is given as

$$\gamma_S = \gamma_{SL} + \gamma_L \cos\theta \tag{2}$$

The superficial tension γ_L is known for several reference liquids and θ can be experimentally measured. γ_{SL} cannot be directly measured (Sharma and Hanumantha Rao 2002). The surface tension component approach was used to estimate γ_{SL} because this approach has been widely utilized for biological materials in the past few years (Mavon et al 1997, 1998; Doscolis et al 2000; Wålinder 2000; Sharma and Hanumantha Rao 2002; Bialopiotrowicz 2003). However, debates still exist between different approaches proposed to estimate γ_{SL} (Kwok et al 2000; Chibowski et al 2002). In the surface tension component approach, surface tensions of solids and liquids can be split in three surface tension components (van Oss 1996) described as

$$\gamma_i = \gamma_i^{LW} + 2\sqrt{\gamma_i^{+}\gamma_i^{-}} \tag{3}$$

where i = S (solid) or L (liquid); γ_i^{LW} is the Lifshitz-van der Waals component (apolar component); γ_i^{+} is the electron-donor component and γ_i^{-} is the electron-acceptor component. The interfacial energy between the solid and the liquid (γ_{SL}) is linked to the superficial tension of the liquid and to the surface tension of the solid (van Oss 1996) as

$$\gamma_{SL} = \left(\sqrt{\gamma_S^{LW}} - \sqrt{\gamma_L^{LW}}\right)^2 + 2\left(\sqrt{\gamma_S^{+}} - \sqrt{\gamma_L^{+}}\right)\left(\sqrt{\gamma_S^{-}} - \sqrt{\gamma_L^{-}}\right) \tag{4}$$

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Equations 5a–c were obtained by combining Equations 2–4 with three different reference liquids (L_1, L_2, and L_3)

$$\left(1 + \cos\theta_1\right)\gamma_{L_1} = 2\left(\sqrt{\gamma_S^{LW}\gamma_{L1}^{LW}} + \sqrt{\gamma_S^{+}\gamma_{L_1}^{-}} + \sqrt{\gamma_S^{-}\gamma_{L_1}^{+}}\right) \quad (5a)$$

$$\left(1 + \cos\theta_2\right)\gamma_{L_2} = 2\left(\sqrt{\gamma_S^{LW}\gamma_{L2}^{LW}} + \sqrt{\gamma_S^{+}\gamma_{L_2}^{-}} + \sqrt{\gamma_S^{-}\gamma_{L_2}^{+}}\right) \quad (5b)$$

$$\left(1 + \cos\theta_3\right)\gamma_{L_3} = 2\left(\sqrt{\gamma_S^{LW}\gamma_{L3}^{LW}} + \sqrt{\gamma_S^{+}\gamma_{L_3}^{-}} + \sqrt{\gamma_S^{-}\gamma_{L_3}^{+}}\right) \quad (5c)$$

The three parameters characterizing the surface tension of the solid (γ_S^{LW}, γ_S^+, γ_S^-) can thus be determined by solving Equations 5a–c with the measured values of contact angles (θ_1, θ_2, and θ_3) for three selected reference liquids of known surface tension components (γ_L^{LW}, γ_L^+, γ_L^-). The choice of reference liquids is very important. Kwok et al (2000) point out that the reference liquids should satisfy the condition $\gamma_L > \gamma_S$. Shalel-Levanon and Marmur (2003) demonstrated mathematically that minimal errors on the determination of γ_S are obtained when one of the three liquids is apolar and when the two other liquids are monopolar ($\gamma_L^+ = 0$ or $\gamma_L^- = 0$) with different polarities.

We selected three reference liquids for the present study: water, formamide, and diiodomethane (Table I). The condition $\gamma_L > \gamma_S$ is satisfied for water and formamide. One of the three liquids is apolar but the two other liquids are not monopolar. Thus, the choice of reference liquids was based on a compromise considering the above-mentioned conditions and considering the range of liquids of known surface tension components.

MATERIALS AND METHODS

Raw Materials

Eight pure wheat cultivars (ITCF-Arvalis, France) were selected: five hard wheat cultivars (Aztec, Isengrain, Orvantis, Qualital, Soissons) and three soft wheat cultivars (Crousty, Scipion, Sideral). The grains were tempered at 17% (wet basis) for 15 hr before milling. The flours were obtained from a conventional milling process performed in a Bühler mill (MLU-202) by the same operator. The milling process consists of three stages on ridged break rolls and three stages on smooth reduction rolls. Each of these stages is followed by a sieving stage on plansifters. The flour milling yields are expressed in percentage (wet basis).

The glutens were extracted from the flours by washing out developed doughs. For each flour, 500 g of flour were mixed with 400 g of deionized water in a food processor (Kenwood KM 221), until the dough mass stuck to the blades. Sticking of the dough to the blades was used as the point at which the dough was assumed to be sufficiently developed. The developed dough was then mixed carefully with a batter in an excess of deionized water (2L) for 10 min. The washed dough was rinsed on a 200-µm sieve. The underlying gluten was collected and kneaded by hand (with plastic gloves) under a flow of deionized water until the water ran clear. The gluten was then lyophilized, ground, and stored in hermetic pans until needed.

The moisture content of the flours was determined from three measurements according to Approved Method 44-15A (AACC 2000). The ash content of the flours was determined from two measurements by differential weighing of samples before and after heating at 900°C for 2 hr according to French method NF V 03-720 (AFNOR 1997). The damaged starch content of the flours was determined from one measurement according to Approved Method 76-31 (AACC 2000) using a starch damage assay kit (Megazyme International Ireland Ltd., Ireland). The protein content of the flours and glutens was determined from one measurement by the Kjeldhal method according to the French method NF C 03-050.

The selected reference liquids were ultrapure water (18.2 MΩ.cm), diiodomethane (99%), and formamide (Acros Organics, Geel, Belgium).

Preparation of Pellets and Flat Slices of Endosperm

Before the preparation, the pellets, flour, and gluten powders were equilibrated at 81% rh (in the presence of KBr-saturated solutions) for seven days. The pellets (1.80 mm thick and 11.28 mm diameter) were prepared by pressing ≈340–380 mg of powder using a press (ED Fogerais, Vitry sur Seine) in the manual mode, at a pressure of 140 MPa (±5%) and room temperature.

The flat slices of wheat grain endosperm were prepared by direct abrasion of wheat grains with glasspaper (no. 600). The surface of the endosperm was finally smoothed with a scalpel previously washed with ethanol.

Physical Properties

The particle size distribution of wheat flours was determined by laser granulometry (Beckman Coulter LS 230). The particle size distribution was defined by the median diameter (d_{50}) and size dispersion ($(d_{90} - d_{10})/d_{50}$). One measurement was made for each product.

TABLE I
Surface Tension Components of Liquids at 20°C (from Van Oss 1996)

	Surface Tension Components (mJ/m^{-2})			
	γ_L	γ_L^{LW}	γ_L^+	γ_L^-
Diiodomethane	50.8	50.8	0	0
Water	72.8	21.8	25.5	25.5
Formamide	58	39	2.28	39.6

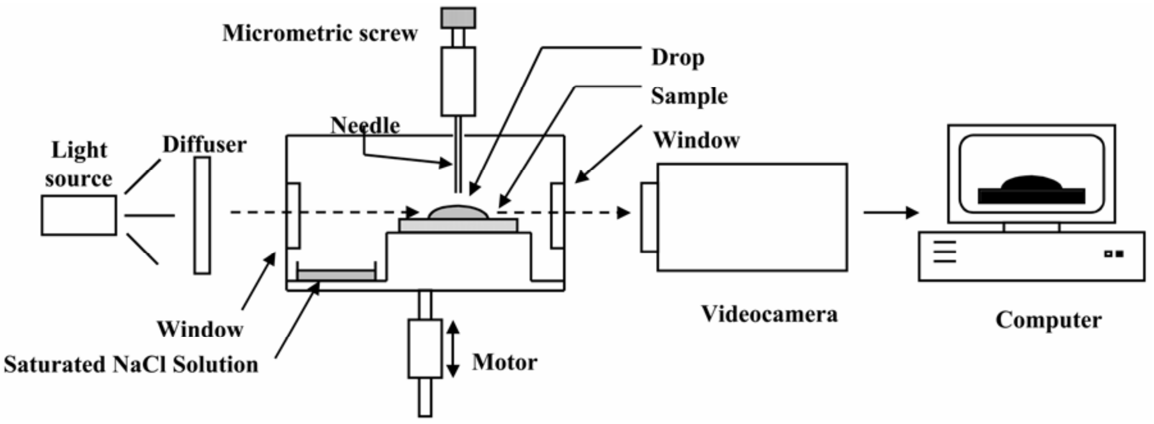

Fig. 1. Experimental set-up.

The porosity and median pore size of pellets were determined using a mercury porosimeter (Autopore II 9215, Micrometrics).

This method takes into account open porosity with pore sizes of 0.05–400 µm. One measurement was made on pellets. Sample weight for porosity measurements was 1 g (±0.1 g). Theoretical value (Micrometrics data) of the contact angle of a mercury drop on starch-based material (147°) was used for the calculation of the median pore size.

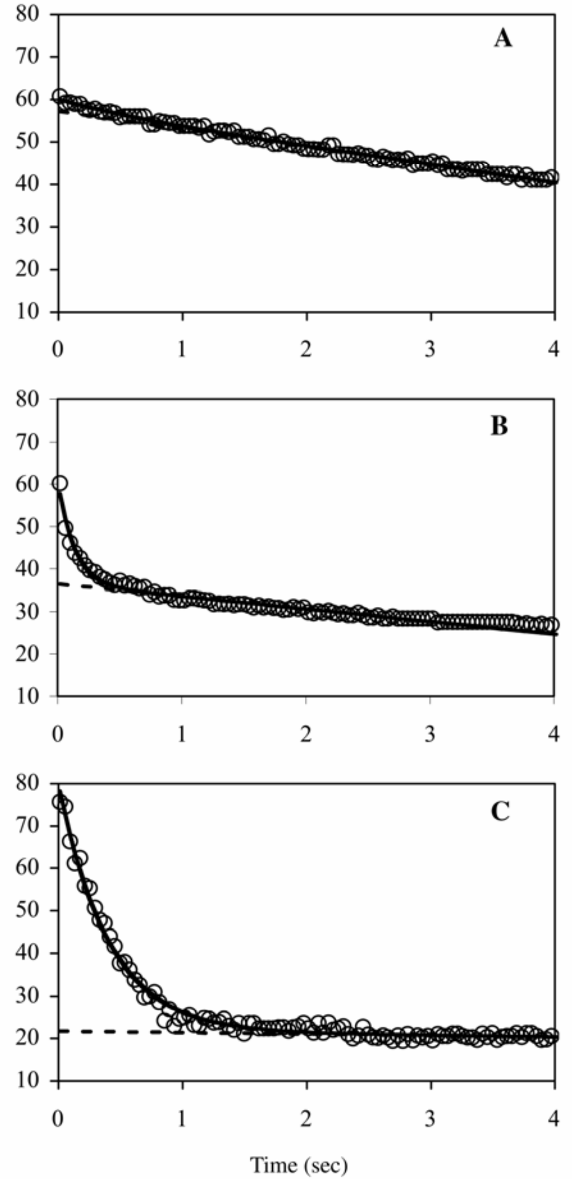

Fig. 2. Contact angle evolution with time of diiodomethane (**A**), water (**B**), and formamide (**C**) drops deposited on flour pellets of Crousty (○ experimental data; solid lines data obtained from Equation 6; dashed lines data obtained from Equation 7).

Contact Angle Measurements

Before contact angle measurements, pellets and endosperm samples were equilibrated at 59% rh (in the presence of saturated NaBr solutions) for seven days. Contact angle measurements were made with a goniometer (Digidrop, GBX, France) equipped with a diffuse light source, a CCD camera (25 frames/sec), and a closed chamber with controlled temperature (23°C ± 1) and relative humidity (59%) in the presence of NaBr-saturated solution) (Fig. 1). The chamber is mounted on a vertical motor-driven plate that allows the sample to be raised in contact (at 12 mm/min) with the pendant drop (formed with a micrometric screw). The goniometer, the liquids (pure water, diiodomethane, and formamide), the chamber, and samples were placed in a thermostated room (23°C) at least 24 hr before measurements. Two types of needles were used: a stainless steel needle (0.45 mm external diameter) for measurement on flat slices of endosperm samples and a Teflon needle (0.73 mm external diameter) for measurement on pellets. When in contact with the sample, the drop immediately detached from the needle, started spreading, and was filmed. The film was analyzed frame-by-frame with the GBX software (Windrop, GBX, France) to determine the contact angle, drop height, and base diameter. At least three measurements were performed on each sample.

Data Analysis

Experimental data were analyzed by ANOVA (Statgraphics Plus v. 5.0 for Windows) and means were separated by Student-Newman-Keuls multiple range test whenever there was a significant difference between the means. Significance was defined at $P < 0.05$. For two samples, comparisons of a *t*-test was run with a significance level at $P < 0.05$.

Modeling the contact angle kinetics was achieved using Equation 6, an empirical function derived from those proposed by Link and Schlünder (1996)

$$f_1(t) = \theta_1 \exp(-k_{\text{spread}}\, t) + \theta_2 - K_{\text{abs}}\, t \tag{6}$$

Parameters θ_1 (°) and k_{spread} (sec^{-1}) describe the exponential part of the spreading stage. Parameters θ_2 (°) and K_{abs} (°/sec^{-1}) describe the linear part of the absorption stage. Parameter K_{abs} represents the contact angle diminution rate during the absorption stage. It was supposed that swelling of the solid materials did not occur during the experiments.

Contact angles were determined at apparent equilibrium conditions by considering the intersection between the initial spreading stage and the absorption stage. The time at the intersection point (t_{equ}) was evaluated when the difference between fitted contact angle values (Equation 6) and values from the linear absorption equation (Equation 7) is <3%.

$$f_2(t) = \theta_2 - K_{\text{abs}}\, t \tag{7}$$

TABLE II
Milling Yields, Moisture Contents, Ash Contents, and Particle Size Distributions of Selected Wheat Flours

		Milling Yield (%)	Flour Composition				Particle Size Distribution (µm)			
			Moisture (%)	Damaged Starch (%db)	Protein (%db)	Ash (%db)	d_{10}	d_{50}	d_{90}	Disp[a]
Crousty	Soft	59.8	15.1	2.6	9.1	0.38	5.3	56.3	162.6	2.8
Scipion	Soft	72.9	14.8	5.6	10.9	0.28	5.0	54.9	158.0	2.8
Sideral	Soft	71.7	13.3	3.5	9.0	0.38	5.0	52.6	164.6	3.0
Aztec	Hard	71.8	14.3	5.8	12.1	0.34	18.7	92.4	171.3	1.7
Isengrain	Hard	75.6	14.6	6.0	10.1	0.34	14.0	88.6	171.1	1.8
Orvantis	Hard	71.8	13.9	6.9	10.0	0.33	19.7	98.5	184.7	1.7
Qualital	Hard	73.6	14.8	7.4	13.2	0.46	18.2	95.1	178.0	1.7
Soissons	Hard	76.9	14.5	4.1	10.2	0.38	23.7	108.3	193.1	1.6

[a] Disp = size dispersion ($[d_{90} - d_{10}]/d_{50}$).

The fitting of parameters θ_1, θ_2, K_{abs}, and k_{spread} of Equation 6 was achieved through minimization of the sum of square deviations between the model and experimental values. All calculations used the solver function of the Excel software (v. 98). Fitting was made on experimental values recorded at 0–4 sec. The quality of fitting was evaluated by square linear regression coefficient (R^2) and root mean square deviation between model and experimental values.

RESULTS

Flours and Gluten Characteristics

The milling yield and the moisture content of the flours are presented in Table II. The flour milling yields range from 71.7% to 76.9%, except for the Crousty cultivar (59.8%) because the flour plugged up the sieves of the plansifter. The ash content is low for all flours (0.28–0.46%). The particle size distributions of wheat flours are presented in Table II. As expected, soft wheat flours contain more small particles (free starch granules generated during milling) than hard wheat flours. The median particle diameter (d_{50}) of soft wheat flour particles had a range of 52.6–56.3 µm, whereas the median diameter of hard wheat flour particles had a range of 88.6–108.7 µm. Biochemical composition of flours is presented in Table II.

The damaged starch content is lower for soft wheat flours (2.6–5.6%) than for hard wheat flours (5.8–7.4%), except for Soissons flours (4.1%). Protein content is generally slightly lower for soft wheat flours (9.0–10.9%) than for hard wheat flours (10.0–13.2%).

The protein content of the glutens extracted from Scipion and Soissons flours are 64.1 and 66.5%, respectively. A significant part of the starch is still present in the glutens. However, we considered that the wettability properties of gluten pellets describe the behavior of the protein fraction of flours.

Modeling Kinetics of Contact Angle Evolution

Spreading kinetics of the three reference liquids (diiodomethane, water, and formamide) on flour-based pellets based on Crousty wheat are presented as typical examples in Fig. 2. Two stages are observed in the contact angle evolution. The first stage corresponds to a steep decrease in contact angle along with a decrease in height and an increase in base diameter due to spreading of the drop on the solid. The drop rapidly reaches (<1 sec) an apparent equilibrium stage, immediately followed by the absorption stage. During the absorption stage, the drop base diameter does not increase noticeably, and the contact angle decreases linearly with time, due to capillarity penetration of liquid into the pellet. It takes ≈8 sec for water and diiodomethane drops to disappear completely into the pellet and >8 sec for formamide drops. Link and Schlünder (1996), Martic et al (2003), and Sharma and Hanumantha Rao (2002) have previously reported similar behaviors on other materials.

The kinetics of contact angle evolution were modeled using Equation 6. Analyses of experimental data showed that it suitably fits the spreading kinetics of the three reference liquids on flat slices of endosperm, flour-based pellets, and gluten-based pellets (90% R^2 >0.8 and 90% of root mean square deviations between the model and experimental values are <1.49°).

Equilibrium Contact Angles and Surface Tensions

The equilibrium contact angles of drops directly deposited on the flat slices of endosperm were calculated using Equations 6 and 7 and are presented in Table III. Equilibrium contact angles are significantly different ($P < 0.05$) between Scipion and Soissons flat slices of endosperm for diiodomethane (42.1 vs. 58.5°) and water (20.4 vs. 53.3°) drops. They are not significantly different ($P > 0.05$) considering the formamide drop (22.2 vs. 16.0°). The surface tension components of Scipion and Soissons flat endo-

TABLE III
Equilibrium Contact Angles (Mean ± Standard Deviation) of Drops from Reference Liquids and Calculated Surface Tension Components Measured on Flat Endosperm Samples[a]

		Contact Angle (°)			Surface Tension Components (mJ/m^{-2})			
		Diiodomethane	Water	Formamide	γ_S	γ_S^{LW}	γ_S^+	γ_S^-
Scipion	Soft	42.1 ± 3.6a	20.4 ± 5.8a	16.0 ± 5.6a	55.3	38.5	1.4	49.5
Soissons	Hard	58.5 ± 9.1b	53.3 ± 2.9b	22.2 ± 4.6a	49.6	29.4	6.5	15.7

[a] Within a column, means followed by the same letter are not significantly different, $P \leq 0.05$.

TABLE IV
Equilibrium Contact Angles (Mean ± Standard Deviation) of Drops from Reference Liquids and Calculated Surface Tension Components Measured on Flour Pellets[a]

		Contact Angle (°)			Surface Tension Components (mJ/m^{-2})			
		Diiodomethane	Water	Formamide	γ_L	γ_L^{LW}	γ_L^+	γ_L^-
Crousty	Soft	57.3 ± 1.3a–c	32.9 ± 3.5a	22.1 ± 0.9a	54.3	30.1	3.7	39.1
Scipion	Soft	58.6 ± 0.4bc	33.3 ± 0.9a	23.7 ± 2.9a	53.8	29.4	3.8	39.4
Sideral	Soft	61.0 ± 1.1c	32.1 ± 2.1a	23.8 ± 0.8a	54.1	28.0	4.2	40.7
Aztec	Hard	58.1 ± 0.4bc	31.2 ± 3.3a	22.2 ± 1.2a	54.4	29.7	3.7	41.0
Isengrain	Hard	55.8 ± 1.2ab	29.7 ± 1.8a	22.9 ± 0.5a	53.9	31.0	3.0	43.4
Orvantis	Hard	53.8 ± 3.3a	29.6 ± 3.8a	21.6 ± 1.5a	54.3	32.1	2.9	42.7
Qualital	Hard	58.3 ± 1.6bc	34.5 ± 1.1a	23.4 ± 1.4a	53.8	29.5	3.9	37.9
Soissons	Hard	57.4 ± 0.4a–c	32.3 ± 2.6a	23.6 ± 1.7a	53.8	30.1	3.5	40.5

[a] Within a column, means followed by the same letter are not significantly different as determined by Student-Newman-Keuls' multiple range test, $P \leq 0.05$.

TABLE V
Equilibrium Contact Angles (Mean ± Standard Deviation) of Drops from Reference Liquids and Calculated Surface Tension Components Measured on the Gluten Pellets[a]

		Contact Angle (°)			Surface Tension Components (mJ/m^{-2})			
		Diiodomethane	Water	Formamide	γ_S	γ_S^{LW}	γ_S^+	γ_S^-
Scipion	Soft	58.6 ± 1.9a	38.0 ± 0.9a	23.1 ± 0.9a	53.5	29.4	4.3	33.6
Soissons	Hard	52.4 ± 2.4b	37.9 ± 0.6a	24.9 ± 0.1b	52.7	32.9	2.8	35.0

[a] Within a column, means followed by the same letter are not significantly different, $P \leq 0.05$.

sperm samples were calculated using Equation 5a–c and are presented in Table III. The equations were solved numerically. There are large differences between Scipion and Soissons concerning the apolar component γ_S^{LW} (38.5 vs. 29.4 mJ/m^{-2}), the acid component γ_S^+ (1.4 vs. 6.5 mJ/m^{-2}), the basic component γ_S^- (49.5 vs. 15.7 mJ/m^{-2}), and thus, the total surface tension γ_S (55.3 vs. 49.6 mJ/m^{-2}).

The equilibrium contact angles of drops deposited on the flour-based pellets are presented in Table IV. For water, the contact angle ranges between 29.6° (Orvantis) and 34.5° (Qualital), without significant difference ($P > 0.05$). For formamide, the contact angle range is between 21.6° (Orvantis) and 23.8° (Sideral) without significant difference ($P > 0.05$). For diiodomethane, significant differences ($P < 0.05$) can be observed between the contact angle values between 53.8° (Orvantis) and 61.0° (Sideral) wheat cultivar. Nevertheless, it was not possible to clearly discriminate the two wheat types considering the contact angles with diiodomethane. The calculated surface tension components of the flour-based pellets are presented in Table IV. The surface tension values (γ_S) of the flour pellets were 53.8–54.4 mJ/m^{-2}. The apolar component (γ_S^{LW}) was 28.0–32.1 mJ/m^{-2}. The acid component (γ_S^+) was 2.9–4.2 mJ/m^{-2}. The basic component (γ_S^-) was 37.9–43.4 mJ/m^{-2}. Only little differences are observed between the flour-based pellets concerning the calculated surface tension components.

The measured values of equilibrium contact angles of drops deposited on gluten-based pellets are presented in Table V. The contact angles for Scipion gluten-based pellets are significantly different ($P > 0.05$) than those for Soisssons gluten-based pellets, when using diiodomethane (58.6 vs. 52.4°) and formamide (23.1 vs. 24.9°). No significant difference is observed between contact angles values when using water (38.0 vs. 37.9°). The surface tension components were calculated for the gluten-based pellets (Table V). Surface tension components for the Scipion and Soissons gluten-based pellets are close one to another, considering γ_S^{LW} (29.4 vs. 32.9 mJ/m^{-2}), γ_S^{LW} (4.3 vs. 2.8 mJ/m^{-2}), γ_S^-(33.6 vs. 35.0 mJ/m^{-2}) and γ_S (53.5 vs. 52.7 mJ/m^{-2}).

TABLE VI
Penetration Rates (K_{abs} Parameters) of Diiodomethane, Water, and Formamide into Flat Endosperm Samples (Mean ± Standard Deviation)[a]

		K_{abs} (°/sec)		
		Diiodomethane	Water	Formamide
Scipion	Soft	1.0 ± 0.9a	1.7 ± 0.4a	0.5 ± 0.4a
Soissons	Hard	0.3 ± 0.4a	0.6 ± 0.3b	0.1 ± 0.3a

[a] Within a column, means followed by the same letter are not significantly different, $P \leq 0.05$.

TABLE VII
Penetration Rates (K_{abs} Parameters) of Diiodomethane, Water, and Formamide into Flour Pellets (Mean ± Standard Deviation)[a]

		K_{abs} (°/sec)		
		Diiodomethane	Water	Formamide
Crousty	Soft	4.3 ± 0.1a	2.3 ± 0.6ab	0.4 ± 0.1a
Scipion	Soft	4.7 ± 0.7ab	2.0 ± 0.3a	0.5 ± 0.3a
Sideral	Soft	5.2 ± 0.3ab	3.0 ± 1.1ab	0.9 ± 1.2a
Aztec	Hard	12.0 ± 2.2c	2.7 ± 0.3ab	0.0 ± 0.0a
Isengrain	Hard	6.0 ± 1.1ab	3.0 ± 0.5ab	0.0 ± 0.0a
Orvantis	Hard	9.1 ± 0.4bc	4.7 ± 1.0c	0.3 ± 0.2a
Qualital	Hard	10.1 ± 3.2c	4.0 ± 0.4bc	0.0 ± 0.0a
Soissons	Hard	11.1 ± 0.7c	5.0 ± 1.5c	0.5 ± 0.5a

[a] Within a column, means followed by the same letter are not significantly different as determined by Student-Newman-Keuls' multiple range test, $P \leq 0.05$.

TABLE VIII
Penetration Rates (K_{abs} Parameters) of Diiodomethane, Water, and Formamide into Gluten Pellets (Mean ± Standard Deviation)[a]

		K_{abs} (°/sec)		
		Diiodomethane	Water	Formamide
Scipion	Soft	3.2 ± 0.6a	0.4 ± 0.2a	0.0 ± 0.0a
Soissons	Hard	6.8 ± 0.4b	0.5 ± 0.3a	0.0 ± 0.0a

[a] Within a column, means followed by the same letter are not significantly different, $P \leq 0.05$.

Penetration Rates of Liquids

Penetration of reference liquid into flat slices of endosperm, flour-based pellets, and gluten-based pellets occurs after the initial drop spreading stage. The penetration rate of reference liquids was evaluated using Equation 6. The penetration rates of the three reference liquids into the flat slices of endosperm are presented in Table VI. The penetration rates of diiodomethane and formamide into the two wheat types (Scipion vs. Soissons) flat slices of endosperm are not significantly different ($P > 0.05$). On the other hand, the penetration rate of water into Scipion flat slices of endosperm (1.7°/sec) is significantly higher ($P < 0.05$) than the one for Soissons (0.6°/sec). The penetration rate of water thus discriminates wheat types (soft vs. hard) for the flat slices of endosperm.

The penetration rates of the three reference liquids into the flour pellets are presented in Table VII. The penetration rates of formamide are 0.0–0.9°/sec and are not significantly different ($P > 0.05$). The penetration rate of diiodomethane is lower for soft (4.3–5.2°/sec) than for hard (6.0–12.0°/sec) wheat flour-based pellets. It should be pointed out that the penetration rate of diiodomethane is significantly higher ($P < 0.05$) for the pellets based on Aztec, Soissons, and Qualital hard wheats than for the pellets based on Sideral, Scipion, and Crousty soft wheats. The penetration rate of water into the flour pellets (Table VII) is slightly lower for soft wheat (2.0–3.0°/sec) than for hard wheat (2.7–5.0°/sec). However, it was only possible to significantly discriminate ($P < 0.05$) the Soissons and Orvantis hard wheat from the Scipion soft wheat. It is thus possible to discriminate the soft and hard wheat with water penetration rates, although less clearly than with diiodomethane.

The penetration rates of the three reference liquids into the gluten-based pellets are presented in Table VIII. The penetration rate of diiodomethane is significantly lower ($P < 0.05$) for Scipion (3.2°/sec) than for Soissons (6.8°/sec). The penetration rates of water and formamide in gluten-based pellets are not significantly different ($P > 0.05$) between Scipion and Soissons. Thus, it was possible to discriminate the soft and hard wheat gluten-based pellets with the penetration rate of diiodomethane, whereas it was not possible with water and formamide.

DISCUSSIONS

The present work determined some physical properties of wheat materials in regards to the surface tension properties. The wettability properties of wheat materials were assessed with three reference liquids (diiodomethane, water, and formamide) and estimated by the determination of two types of parameters: equilibrium properties (with contact angles and surface tension properties), and drop penetration rates.

Our results indicate that surface tension (γ_S) of wheat materials has a range of 49.6–55.3 mJ/m^{-2} (Tables III–V). We observed that irrespective of material type (flat slices of endosperm, flour-based pellets, or gluten-based pellets), the acid component (γ_S^+) was systematically lower than the basic (γ_S^-) component, as often mentioned in the literature. The surface tension properties of wheat materials are in accordance with those given by van Oss (1996) for potato amylose (γ_S = 52.6 mJ/m^{-2}; γ_S^{LW} = 42.3 mJ/m^{-2};

$\gamma_S^+ = 0.64$ mJ/m^{-2}; $\gamma_S^- = 41.4$ mJ/m^{-2}) and corn amylopectin ($\gamma_S = 48.4$ mJ/m^{-2}; $\gamma_S^{LW} = 40.1$ mJ/m^{-2}; $\gamma_S^+ = 0.74$ mJ/m^{-2}; $\gamma_S^- = 23.4$ mJ/m^{-2}).

The present work evaluates specific wheat types (hard wheat vs. soft wheat) in regard to their wettability properties. Considering the equilibrium properties, there is slight influence of the wheat type on contact angle values when measured on flour-based pellets or gluten-based pellets (Tables IV–V). Similar trends are observed when regarding the surface tension properties. Similar behaviors have been reported by Roman-Gutierrez et al (2003), who did not demonstrate significant difference between hard and soft wheat with regard to water drop contact angles values on flour-based pellets. On the other hand, wheat type has a marked influence on contact angles when measured on flat slices of endosperm (Table III). Significant differences in total surface tension and in apolar, acid, and basic components were only reported on the flat slices of endosperm (Table III).

Considering the penetration rates (Fig. 3), it is possible to discriminate the hard or soft wheat types when characterized on flour-based pellets with diiodomethane or water drops (Table VII) and on gluten-based pellets with diiodomethane drops (Table VIII). On the other hand, there is no significant influence of wheat type on penetration rates for the flat slices of endosperm (Table VI).

The results can also be analyzed to evaluate the influence of material nature (flour-based pellets vs. gluten-based pellets) on wettability properties. Considering the equilibrium properties, we observed a slight influence of material nature when comparing the values of contact angles and surface tensions between flour-based pellets (Table IV) and gluten-based pellets (Table V). For Scipion and Soissons, the total surface tensions of flour-based pellets (53.8 and 53.8 mJ/m^{-2}) are close to those of gluten-based pellets (53.5 and 52.7 mJ/m^{-2}). The equilibrium wettability properties appeared not to be really affected by the nature of materials (flour vs. gluten). On the other hand, Roman-Gutierrez et al (2003) observed significant differences between flour-based pellets and industrial gluten-based pellets considering the initial contact angles of water drops. The gluten-based pellets were characterized by higher contact angles for water drops.

Nevertheless, one has to take into account that the differences (or absence of differences) between contact angles measured on flour-based or gluten-based pellets may arise from physical differences between the pellets and not because of chemical differences. Indeed, the ways flour and gluten pellets were prepared may be assumed not to be identical.

Considering the penetration rates, we observed significant difference between flour-based pellets and gluten-based pellets (Tables VII–VIII). For instance, with Scipion wheat, the penetration rates with diiodomethane, water, or formamide are higher in flour pellets (4.7, 2.0, and 0.5°/sec) than in gluten pellets (3.2, 0.4, and 0°/sec).

The present work also evaluated the influence of material structure (flat slices of endosperm vs. flour-based pellets) on wettability properties of wheat materials. Considering the equilibrium properties, we observed a significant influence of material structure when comparing the values of contact angles and surface tensions between flat slices of endosperm (Table IV) and flour-based pellets (Table V). For Scipion and Soissons, the total surface tensions of flat slices of endosperm (55.3 and 49.6 mJ/m^{-2}) are significantly different from those of flour-based pellets (53.8 and 53.8 mJ/m^{-2}). The transformation of wheat endosperm in flour-based pellets induced an increase in surface tension (49.6 to 53.8 mJ/m^{-2}) for the hard wheat (Soissons), while it induced a decrease in surface tension (55.3 to 53.8 mJ/m^{-2}) for the soft wheat (Scipion). The equilibrium wettability properties are thus greatly affected by structure of materials (flat endosperm vs. flour pellets).

TABLE IX
Porosity and Median Pore Diameter of the Flour and Gluten Pellets

		Porosity	Median Pore Diameter (μm)
Flour pellets			
Scipion	Soft	0.21	1.4
Soissons	Hard	0.20	2.6
Gluten pellets			
Scipion	Soft	0.17	1.6
Soissons	Hard	0.18	2.2

Considering the penetration rates, the transformation of wheat endosperm into flour-based pellets induced significant increases in values. For instance, with Soissons wheat, the penetration rates increased with diiodomethane (0.3 to 11.1°/sec), water (0.6 to 5.0°/sec), or formamide (0.1 to 0.5°/sec).

Interpretation of equilibrium contact angles when measured on nonideal material surfaces is still subject to discussion and the calculated surface tension can only be considered as an apparent physical property. In fact, the measured contact angle depends not only on the surface tension of the solid but also on the structure of the solid surface. Two structure parameters can be considered: surface roughness and material porosity (Buckton 1990; Buckton et al 1995; Kwok and Neumann 1999; Popovich et al 1999; Yildirim 2001; Yu et al 2001; Muster and Prestidge 2002). It is known that equilibrium contact angles (<90°) are underestimated on rough surfaces when compared with a perfectly smooth surface made of the same material (Uelzen and Müller 2003).

In the scope of this study, it can be said that when comparing contact angles on pellets prepared under similar conditions (for example, flour-based pellets), one is more likely to assess real differences in surface tension properties than when comparing contact angles on pellets prepared under different conditions (for example, flour-based vs. gluten-based pellets or flat slices of endosperm vs. flour-based pellets). In the latter case, there may be uncontrolled effects due to structure parameters (roughness and porosity).

It was not possible to evaluate the roughness of the flat endosperm samples, the flour pellets, or the gluten pellets using atomic force microscopy (AFM) measurements because of a too high macroscopic roughness of samples.

The porosity of flour and gluten-based pellets was determined using mercury porosimetry. Measurements were made on two wheat cultivars (Table IX). Similar values of porosity were observed for the two selected hard and soft wheat flour-based pellets (0.20–0.21). It should be noted that porosity of flour pellets is slightly higher than that measured for the gluten pellets (0.17–0.18). It is known that open porosity tends to lower the values of

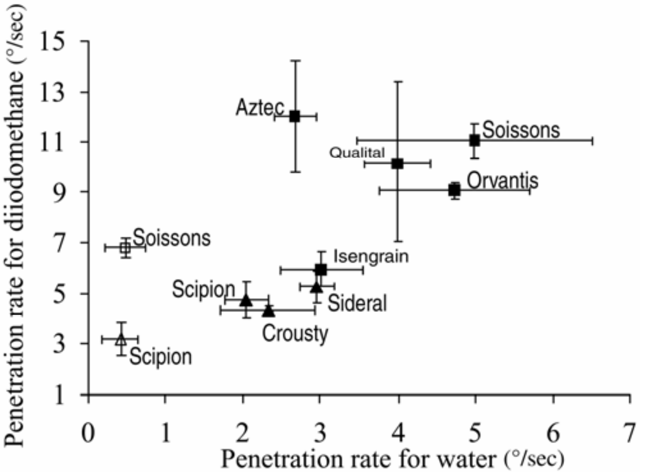

Fig. 3. Penetration rates (K_{abs} parameters) of diiodomethane and water into flour and gluten pellets (■ hard wheat flour; ▲ soft wheat flour; □ hard wheat gluten; Δ soft wheat gluten).

contact angles because the drop basis area is not only in contact with the solid but also with the pores filled with liquid (Buckton et al 1995; Yu et al 2001).

It was not possible to directly measure the porosity of the flat slices of endosperm using mercury porosimetry because of a too high sample weight (≤1 g) required for measurements (≈20 min are needed to prepare a flat slice of endosperm of 20 mg). Dobraszczyk et al (2002) estimated the apparent porosity of soft and hard wheat endosperm from density measurements by considering that the difference in density values are attributable to the presence of void and not to variation in the density of the solid phase. The broad distribution of measured density for soft wheat varieties induced a correspondingly large spread in porosity of 3–13%, whereas the narrower distribution of density within hard wheats showed porosity of 2–8% (Dobraszczyk et al 2002). These apparent large differences in porosity of hard and soft wheat endosperm can then be supposed to significantly contribute to marked differences in contact angles and surface tensions properties.

A more detailed analysis of the drop penetration rates (Tables VI–VIII) in wheat material was proposed by taking into consideration structural parameters. The penetration rates of a liquid into a porous material consisting of particles depend on three parameters: intrinsic contact angle between solid and liquid, material porosity, and pore diameter. Freudig et al (1999), citing Schubert (1993), proposed a model to describe the penetration time of a liquid into a porous material

$$t = \frac{15\,(1 - \varepsilon)\,\eta_L\,h^2}{\varepsilon\,x\,\gamma_L\,\cos\theta} \tag{8}$$

where t is the penetration time (sec), x is the particle diameter (mm), ε is the porosity, η_L is the liquid viscosity (Pa.sec), h (mm) is the height of material, γ_L is the liquid superficial tension (mJ/m^{-2}), and θ is the intrinsic contact angle between solid and liquid (°).

Because the porosities of Scipion and Soissons flour-based pellets are similar (Table IX), it can thus be inferred that the differences of penetration rates of water or diiodomethane drops measured between hard and soft flour-based pellets (Table VII) are partly due to differences in pore size in pellets. Indeed, the median pore diameter in flour-based pellets (Table IX) was lower for Scipion wheat (1.4 μm) than for Soissons wheat (2.6 μm). Using Equation 8, it becomes clear that the differences in penetration rates observed for the flour-based pellets are mainly due to differences in pellet structure and not in surface tension properties.

CONCLUSIONS

The main objective of this work was the determination of surface tensions of wheat materials (wheat endosperm, wheat flours, and wheat glutens) by the measurement of contact angles of a sessile drop of reference liquids.

The materials studied here show nonideal surfaces due to macroscopic roughness and porosity. Therefore, the measured contact angles depend not only on the surface tension of the material but also on the structure of its surface and on its porosity. Considering this, the results of contact angle measurements can be compared most reliably in terms of surface tension properties for materials prepared under the same conditions (for example, flour-based pellets).

No influence of wheat type on contact angles (hard vs. soft) and surface tensions was reported for flour-based pellets. Nevertheless, it was possible to discriminate between flour-based pellets derived from hard or soft wheat considering the penetration rates of water and diiodomethane. Taking into account the structural parameters of the flour-based pellets, the differences in penetration rates seem to lie mainly in differences in the physical structure of the pellets (especially the type of porosity) rather than in their surface tension properties.

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