

## Release of Isoamyl Acetate from Starch Pastes of Various Structures: Thermodynamic and Kinetic Parameters

NATHALIE CAYOT,<sup>\*,†</sup> FANNY PRETOT,<sup>†</sup> JEAN-LOUIS DOUBLIER,<sup>§</sup>  
JEAN-MARIE MEUNIER,<sup>†</sup> AND ELISABETH GUICHARD<sup>†</sup>

Unité Mixte de Recherche "Arômes" INRA/ENESAD, 17 rue Sully, B.P. 86510,  
21079 Dijon Cedex, France, and LPCM INRA, Rue de la Géraudière, B.P. 71627,  
44316 Nantes Cedex 03, France

The release of isoamyl acetate from starch-based matrices was studied on the basis of a cumulative dynamic headspace analysis. Two corn starches were compared, which are known to yield pastes and gels differing in their structures and properties. These properties were assessed by viscometry and viscoelastic measurements. Aroma release was discussed as a function of the structure and texture parameters of the matrix. The release curves obtained from water and from the various starch-based matrices at 25 °C showed similar patterns but differed in their initial slopes and in the final plateau values. The lowest initial slopes were obtained for the normal starch dispersions that formed gels due to amylose gelation. The aroma compound was entirely released from water and from the waxy starch pastes. A significant amount of isoamyl acetate remained trapped in the normal starch dispersions.

**KEYWORDS:** Starch paste; flavor release; structure; texture; interactions

### INTRODUCTION

It is now well-known that the release of aroma compounds from food matrices is mainly governed by two phenomena: on the one hand, the physicochemical interactions between the aroma compounds and some food ingredients may decrease the availability of the aroma in the gas phase (thermodynamic characteristics); on the other hand, the structural characteristics of the food matrix may influence diffusion phenomena and hence kinetic parameters (1–3). Guinard and Marty (4) followed the aroma release in gelatin gels,  $\iota$ -carrageenan gels, and starch gels by time–intensity measurements. They reported a correlation between the rigidity of the gels and aroma release except in the case of starch gels. Other authors studied the release of various aroma compounds with various matrices and reported an effect of the viscosity on flavor release and perception (3, 5, 6).

Both molecular interactions and structure–texture properties are particularly important in the case of starchy products because starch is often used for its thickening or gelling properties. Moreover, amylose was proved to develop specific physicochemical interactions with some aroma compounds (7). It is therefore useful to quantify the respective impact of structure and of molecular interactions on aroma release in starchy products.

Different studies have been performed on the release of aroma compounds from starchy products in a static way (8, 9). This

approach allowed one to establish and quantify the physicochemical interactions between starch and aroma compounds and provided thermodynamic data. This did not provide, however, a thorough understanding of the different perceptions observed with starch-based products. Some studies deal with the dynamic aspects of aroma release. For example, Van Ruth and King (10) used a model mouth device to follow the aroma release from aqueous model foods containing increasing concentrations of starch. Comparing data obtained by equilibrium headspace analysis and data obtained by flavor release, they concluded that the kinetic component of flavor release was of greater importance than the thermodynamic component.

The aim of the present study was thus to monitor the release of a common flavoring compound from starch dispersions with constant concentrations in starch but differing in their textures. Isoamyl acetate was chosen as aroma compound because it does not form any complex with amylose (11) and therefore could be used with starch of various amylose contents. The structure/texture parameters of the starch pastes were varied by changing the type of starch and the shearing conditions during the pasting process.

### MATERIALS AND METHODS

**Materials.** Two corn starches were kindly provided by Roquette (Lestrem, France): a normal corn starch containing 26% (w/w) of amylose and a waxy corn starch containing <1% (w/w) of amylose.

Isoamyl acetate (CAS Registry No. 123-92-2) was purchased from Aldrich (purity > 99%). Methyl heptanoate (Sigma, purity ≈ 99%) and ethyl hexanoate (Sigma, purity ≈ 99%) were used as extraction and chromatography standards, respectively.

\* Corresponding author (e-mail n.cayot@enesad.fr).

<sup>†</sup> Unité Mixte de Recherche "Arômes" INRA/ENESAD.

<sup>§</sup> LPCM INRA.

**Table 1.** Operating Conditions for the Preparation of the Starch Pastes

	normal corn starch: 26% amylose	waxy corn starch: <1% amylose
normal stirring	normal starch paste (NSP)	waxy starch paste (WSP)
normal stirring + extra shearing	sheared normal starch paste (SNSP)	sheared waxy starch paste (SWSP)

**Preparation of Starch Pastes.** Starch suspensions were prepared by dispersing 7.5% (w/w) of starch in deionized water at ambient temperature. This blend was poured into an IKA LR 2000 V reactor (Staufen, Germany) and then cooked. Just before heating, the aroma compound was added [ $1.75 \cdot \text{ppm}(\text{w})$  of suspension]. The temperature inside the cooking device was regulated ( $\pm 0.1$  °C precision) using a laboratory thermostat via the double jacket (Lauda C6CS, temperature sensor PT 100). The oil contained in the double-walled vessel had been previously heated to 120 °C to ensure a reproducible heating. The temperature of the product was 25 °C at the beginning of the cooking process and raised asymptotically to 98 °C. Then the product was maintained at the set point for 15 min.

During the cooking time (35 min in all), the starch paste was stirred using an anchor-shaped stirrer, at a rate of 50 rpm. When extra shearing was applied, this was performed using an Ultra-Turrax homogenizer (T25, IKA, S25-KV-18G). The speed was 8000 rpm (without load) and was applied during the last 15 min of the heating process. By varying the starch quality and the shearing process, we obtained four different matrices as reported in **Table 1**.

For dynamic headspace analysis, the starch pastes were sampled immediately after cooking. An aliquot of 1.5 g of starch slurry was poured into 40 mL glass tubes. The tubes were hermetically sealed and stored at 6 °C 24 h before analysis. The amount of paste in the tubes and the time of storage had been determined in preliminary studies to obtain a good reproducibility. An aliquot of the starch pastes was also taken to measure the aroma concentration remaining in the starch pastes after the cooking process.

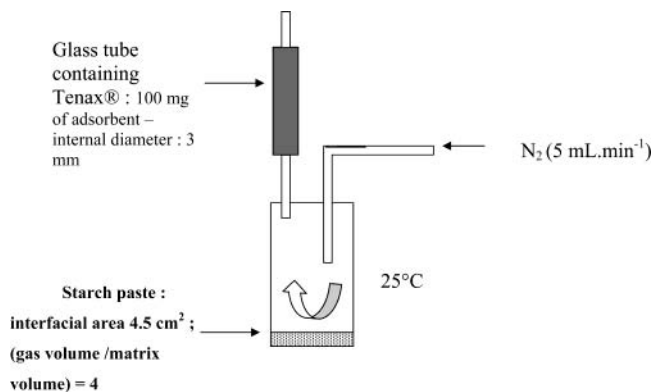
**Rheological Characterization.** Rheological measurements were performed using a SR5 rheometer (Rheometrics). A cone-plate geometry (4 cm diameter, angle 2°) was used to describe the rheological behavior of the various starch pastes immediately after cooking. The temperature during measurement was regulated by a Peltier device attached to the plate of the rheometer.

The flow behavior of the starch pastes was established through a flow curve at 60 °C from 0 to 70  $\text{s}^{-1}$ . The increase in shear stress was applied in the linear mode. The obtained flow curves were modeled between 10 and 60  $\text{s}^{-1}$  by the Ostwald de Waele equation.

The product then underwent a rapid decrease in temperature from 60 to 5 °C, and a dynamic time sweep test was performed. The applied stress was 2.5% at a 1  $\text{rad}\cdot\text{s}^{-1}$  frequency. The values of  $G'$  and  $G''$  were recorded thanks to the Orchestrator software (Rheometrics) during 9 h for the normal starch suspensions and during 15 min for the waxy starch pastes. The structure of the starch dispersions was then assessed by a frequency sweep test.

**Determination of Aroma Content.** Quantification was made in the cooled products by extracting the aroma compounds with a Likens–Nickerson apparatus (12). The extracts were analyzed using a GC with FID. After 1 day at 6 °C, 40 g of the starch paste was dispersed in 100 mL of pure water, saturated with NaCl (360  $\text{g}\cdot\text{L}^{-1}$ ). Methyl heptanoate was used as the extraction standard; it was added to the solution at a concentration of 2.5  $\text{mg}\cdot\text{L}^{-1}$ . This solution was extracted by 25 mL of dichloromethane, during 30 min after the boiling point had been reached. These extractions were made in triplicate, and we added ethyl hexanoate to the extracts as the chromatography standard.

The obtained extracts were analyzed with an HP 6890 gas chromatograph fitted with a split/split less injector (230 °C) and with a flame ionization detector (250 °C;  $\text{H}_2$ , 30  $\text{mL}\cdot\text{min}^{-1}$ ; air, 300  $\text{mL}\cdot\text{min}^{-1}$ ; makeup, 25  $\text{mL}\cdot\text{min}^{-1}$   $\text{N}_2$ ). It was equipped with a high-resolution gas chromatography column DB-FFAP (J&W Scientific) of 30  $\text{m} \times 0.32$  mm (i.d.). Film thickness was 0.25  $\mu\text{m}$ . Nitrogen was used as vector

**Figure 1.** Schematic view of the aroma-trapping device.

gas, at a rate of 1  $\text{mL}\cdot\text{min}^{-1}$ . Extracts were injected automatically using an HP6890 injector in splitless mode (opening after 0.3 min). The temperature of the oven increased from 40 to 200 °C at a 5 °C $\cdot\text{min}^{-1}$  rate.

**Dynamic Headspace Analysis.** The glass vials containing the samples were purged by  $\text{N}_2$  at a 5  $\text{mL}\cdot\text{min}^{-1}$  rate for a given duration. The gas phase was trapped in a capillary glass tube (3 mm i.d.) containing ~100 mg of Tenax adsorbent. Before first use, these tubes were conditioned during 24 h with a  $\text{N}_2$  flow rate of 50  $\text{mL}\cdot\text{min}^{-1}$ . Thirty minutes before the purge step and until the end of this purge step, the samples were placed in a water bath at 25 °C. A new sample was used for each purge step (**Figure 1**).

The desorption and quantification of the aroma compound trapped on the Tenax adsorbent were done by a Varian GC 3380 equipped with a Chrompack TCT/PTI 4010 injector. The injector parameters were the following: precool of glass trap, -100 °C; preflush, 5 min at 25 °C with a  $\text{N}_2$  flow of 20  $\text{mL}\cdot\text{min}^{-1}$ ; desorption, 10 min at 250 °C with a  $\text{N}_2$  flow of 10  $\text{mL}\cdot\text{min}^{-1}$ , then injection of the gas samples. The gas chromatograph was equipped with a flame ionization detector (250 °C;  $\text{H}_2$ , 30  $\text{mL}\cdot\text{min}^{-1}$ ; air, 300  $\text{mL}\cdot\text{min}^{-1}$ ). It was equipped with a CP-Pora Plot U (Varian) column of 25  $\text{m} \times 0.32$  mm (i.d.). Nitrogen was used as carrier gas, at a rate of 1.6  $\text{mL}\cdot\text{min}^{-1}$  (makeup, 25  $\text{mL}\cdot\text{min}^{-1}$ ). The temperature of the oven was kept at 180 °C during 5 min and increased to 260 °C at a 5 °C $\cdot\text{min}^{-1}$  rate.

After each analysis, the Tenax adsorbent was reconditioned during 2 h in an oven (280 °C) with a nitrogen flow (50  $\text{mL}\cdot\text{min}^{-1}$ ).

Standardization of the chromatographic system was performed through the analysis of glass tubes filled with and containing various amounts of isoamyl acetate. Different dilutions of the aroma compound in pentane were directly put in the tube for that purpose. The Tenax tubes were then purged by  $\text{N}_2$  at a 10  $\text{mL}\cdot\text{min}^{-1}$  flow during 10 min before analysis to evaporate the solvent. In the case of long purge times, a second Tenax tube was placed after the first one to verify that no breakthrough occurred.

The release of isoamyl acetate was measured from water and from the four different matrices. No stirring was applied during these experiments to preserve the gelled structures of the matrix. This method leads to a cumulative quantity of isoamyl acetate released in the gas phase and trapped on the Tenax adsorbent as a function of time. The amount of aroma compound in the gas phase was compared with the total amount of this aroma compound available in the matrix.

**Statistical Analysis.** For the determined parameters, the confidence intervals at 95% were estimated and, when necessary, an analysis of variance procedure was applied. This was performed by means of Statgraphics Plus for Windows 3.1 (Manugistics, Inc., 1995). Confidence intervals and/or  $P$  values are reported in the tables.

## RESULTS

**Rheological Characterization of Starch Dispersions.** *Flow Behavior of Starch Pastes at 60 °C.* Viscosity measurements were performed at 60 °C to describe the differences between

**Table 2.** Flow Index and Apparent Viscosity (60 s<sup>-1</sup>) of Starch Pastes, from the Flow Curves (Measurements at 60 °C)<sup>a</sup>

starch paste	app viscosity (60 s <sup>-1</sup> ), mean ± CI <sup>b</sup> at 95%	flow index, mean ± CI at 95% <sup>c</sup>	<i>P</i> values for signif effect of stirring on flow index
NSP	1.312 ± 0.111	0.31 ± 0.08	0.0093
SNSP	0.685 ± 0.129	0.47 ± 0.14	
WSP	1.037 ± 0.129	0.43 ± 0.09	0.0142
SWSP	0.684 ± 0.129	0.58 ± 0.04	

<sup>a</sup> Flow index calculated from the Ostwald de Waele equation,  $\tau = K\dot{\gamma}^n$ , with  $\tau$  is stress (Pa),  $\dot{\gamma}$  shear strain rate (s<sup>-1</sup>),  $K$  is the consistency index (Pa·s<sup>*n*</sup>), and  $n$  is the flow index. <sup>b</sup> CI, confidence interval. <sup>c</sup> Three measurements.

starch pastes. Furthermore, this allowed indirect evaluation of how far swollen starch granules are broken down when high shear is applied. In fact, swollen starch granules can be mostly regarded as responsible of the viscosity increase during the thermal treatment as they absorb water and swell. At the end of the thermal treatment, the normal starch paste is mainly composed of swollen granules enriched with amylopectin suspended in an aqueous phase containing amylose (13). The waxy starch paste is composed of only amylopectin granules because it contains no amylose (<1%) (14). Then, the heated starch dispersion can merely be described as a suspension of highly deformable particles.

The flow index and the apparent viscosity at 60 s<sup>-1</sup> were extracted from these flow curves. As reported in **Table 2**, significant differences were observed for both parameters when extra shearing was applied and when the type of starch was varied. This is consistent with what is known of the behavior of corn starch. For normal cereal starches, it has been found that pasting conditions (heating rate, stirring rate) strongly determine the swelling–solubility behavior. However, for given pasting conditions, it is the maximum heating temperature that is the determining parameter (14). Furthermore, the swelling index was reached as soon as this maximum heating temperature was achieved. In the present case, we probably obtained equivalent swelling for starch granules in normal starch products (NSP and SNSP). The extra shearing that was applied once the maximal temperature was reached likely yielded a partial rupture of swollen starch granules. As foreseen, when extra shearing was applied, the apparent viscosity of both standard starch paste and waxy starch paste was decreased and the flow index was increased as a consequence of starch granule rupture (15).

In the case of waxy starch suspensions (WSP and SWSP), we obtained a higher flow index and a lower apparent viscosity than for normal starch pastes. Extra shearing led to a higher flow index and a lower apparent viscosity than for WSP, indicating that the mechanical treatment applied was efficient enough to produce significant differences in flow behavior.

**Rheological Characterization at 5 °C.** Viscoelastic measurements were performed after quenching from 60 to 5 °C. The structure of the paste after cooling was monitored during 9 h for the standard starch pastes and during 10 min for the waxy starch pastes.

The variations of  $G'$  and  $G''$  as a function of time are shown in **Figure 2a** for a normal starch dispersion with (SNSP) and without extra shearing (NSP). The corresponding mechanical spectra ( $G'$  and  $G''$  as a function of frequency) at the end of the aging period at 5 °C are shown in **Figure 2b**.

For the nonsheared starch dispersion (NSP),  $G'$  was much higher than  $G''$  from the very beginning of the aging period. This is consistent with the fact that as above-described the starch

**Table 3.** Storage Modulus ( $G'$ ) and Loss Modulus ( $G''$ ) Measured at 5 °C for Starch Dispersions (Angular Frequency = 1.26 rad·s<sup>-1</sup>)

	NSP	SNSP	WSP	SWSP
$G'$ (Pa)	357	54.1	5.42	2.71
$G''$ (Pa)	18.0	4.56	2.21	1.81
$\tan \delta = G''/G'$	0.051	0.084	0.407	0.669
structure	self-standing	self-standing	particulate	particulate
	gel (relatively rigid)	gel (relatively soft)	structured system	structured system: softer than WSP

paste at 60 °C is a suspension of swollen particles composed of amylopectin dispersed in a macromolecular solution composed of amylose. Actually, just after quenching amylose was still not gelled, and the fact that  $G' > G''$  reflects the major role of the dispersed phase (swollen starch granules) in the viscoelastic behavior of the system. It is clearly seen in **Figure 2a** that, rapidly after quenching, a sharp increase in  $G'$  was experienced for the first minutes; this was followed by a slower increase for several hours. Meanwhile,  $G''$  values remained low and stable. At the end of the aging experiment (9 h),  $G'$  was much higher than  $G''$ . These overall variations indicate that the structure of the system is setting. The  $G'$  increase as a function of time is therefore the result of amylose gelation within the continuous phase. The mechanical spectra (**Figure 2b**) were typical of highly structured systems, with  $G'$  almost independent of frequency and  $G' \gg G''$ . These overall features are consistent with the fact that such systems can be described as composites with swollen starch granules embedded in a continuous amylose network.

The same overall behavior was observed when high shear was applied (SNSP), although  $G'$  values were divided by 7. The aging curve (**Figure 2a**) also exhibited a rapid  $G'$  increase, which then leveled off. Moreover, the pattern of the mechanical spectrum was still typical of a highly structured system. These results suggest that SNSP systems can be also regarded as a composite. This is, however, much softer than the NSP gel, probably due to a partial rupture of swollen starch granules.

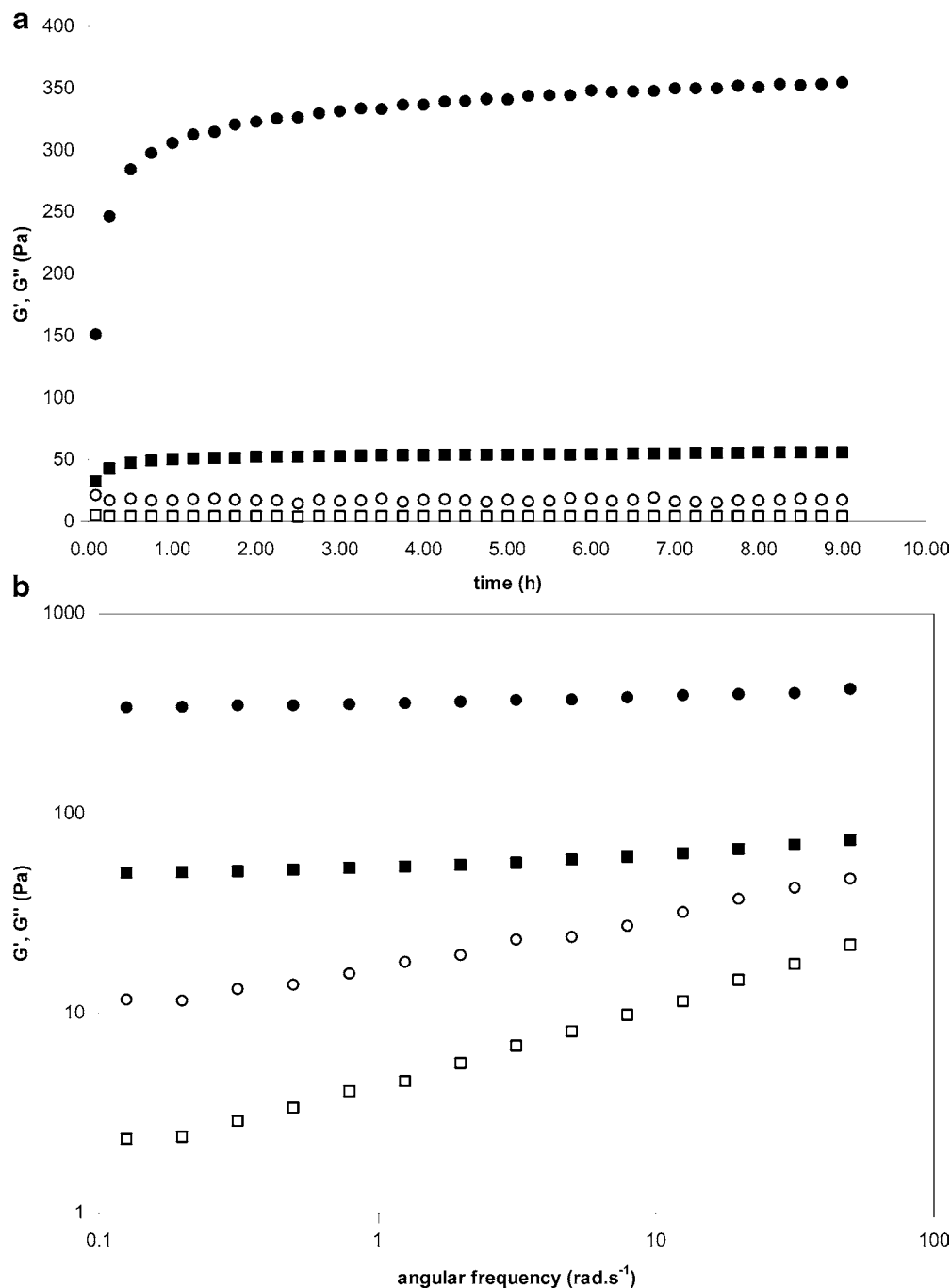
The variations of  $G'$  and  $G''$  as a function of time for a waxy starch paste with and without extra shearing are shown in **Figure 3a**. The corresponding mechanical spectra at 5 °C are displayed in **Figure 3b**.

Upon quenching,  $G'$  increased slowly and regularly while the  $G''$  values remained stable,  $G'$  being around twice as high as  $G''$ . The difference observed between  $G'$  and  $G''$  tended to slightly increase, suggesting some reinforcement of the system. For the sheared paste (SWSP) a similar trend was exhibited despite smaller  $G'$  values than for WSP were experienced.

The viscoelastic behavior of these two systems is illustrated in **Figure 3b**. A slight increase of  $G'$  and  $G''$  as a function of frequency was noticed,  $G'$  remaining higher than  $G''$  all along the frequency range. Moreover,  $G'$  tended to level off toward the low frequencies, indicating a solid-like behavior. All of these features are reminiscent of structured systems despite the storage modulus being low (few pascals). It can be inferred that these waxy corn starch dispersions can be described as particulate systems, the concentration of which is high enough to yield a solid-like behavior from a rheological point of view.

As far as SWSP systems are concerned, it is probable that the swollen starch granules have been partially ruptured, giving rise to a less structured system than nonsheared.

The overall characteristics ( $G'$ ,  $G''$ , and  $\tan \delta$  at 1.26 rad·s<sup>-1</sup>) of the different systems are given in **Table 3** with the



**Figure 2.** Rheological characterization of normal starch dispersions at 5 °C: (a) aging for 9 h after quenching from 60 to 5 °C (measurements at  $1.26 \text{ rad}\cdot\text{s}^{-1}$ ; deformation amplitude = 0.025;  $G'$ , solid symbols;  $G''$ , open symbols; NSP, circles; SNSP, squares); (b) mechanical spectra at the end of the aging experiment ( $G'$ , solid symbols;  $G''$ , open symbols; NSP, circles; SNSP, squares).

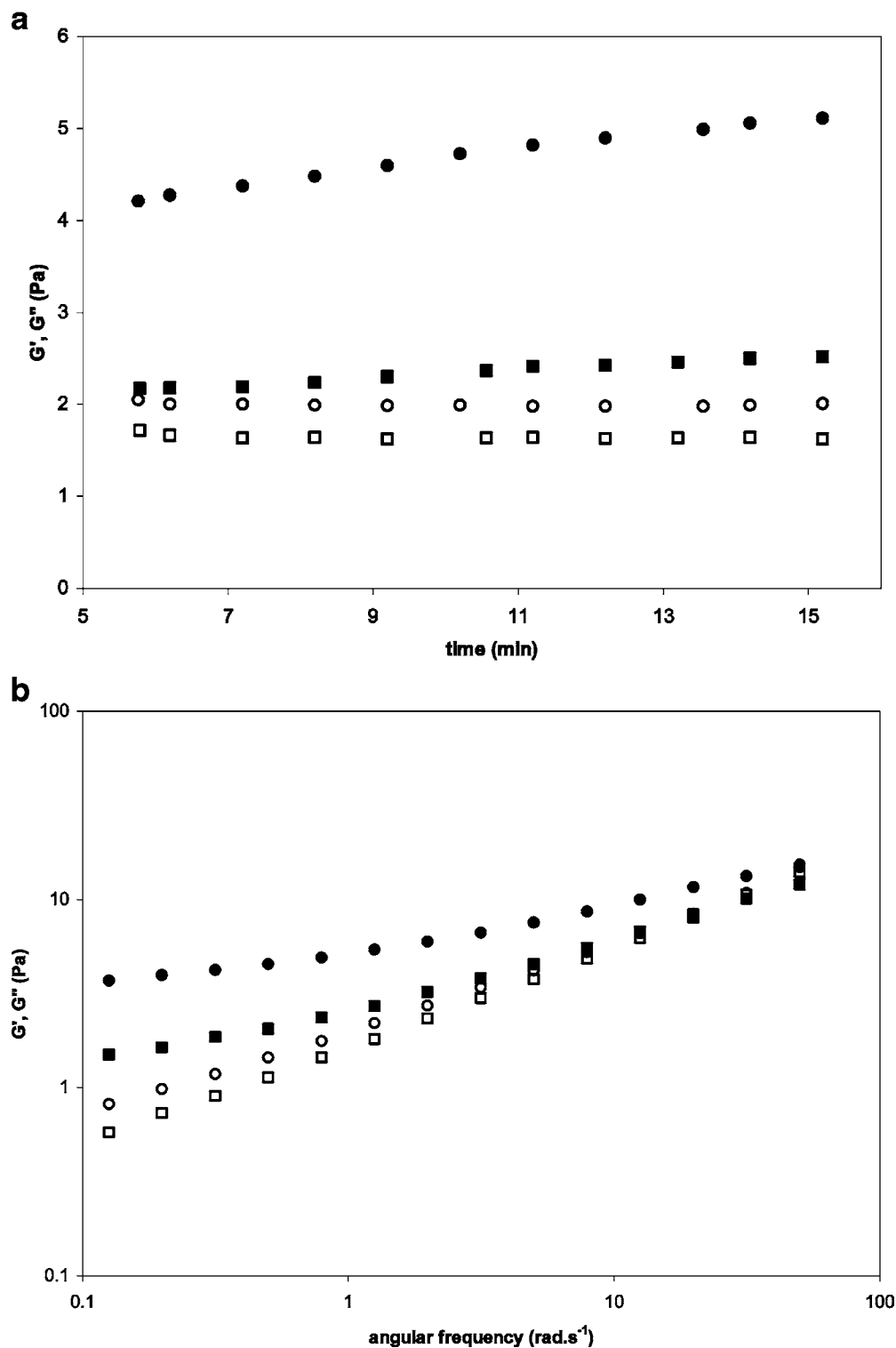
corresponding observed structure. We therefore obtained four matrices, all displaying a solid-like behavior but with different structures: self-standing gels with normal starch, the one with ruptured granules giving rise to a softer gel; soft particulate systems (not free-standing) with waxy corn starch, that with ruptured granules being the less structured one.

**Dynamic Release of Isoamyl Acetate.** The relative amount of aroma released was calculated as the ratio of the “quantity of released isoamyl acetate” to the “amount of isoamyl acetate measured in the matrix”. Its variations as a function of purging time are showed in **Figure 4** for the different matrices. Each point reported in this figure corresponds to the average of three

experimental values obtained from three different cooking batches for each matrix.

The same general pattern was found for the five curves. There was a rapid release of isoamyl acetate during the first 20 min. The rate of release then tended to level off until the depletion of the free aroma compound for which the cumulative quantities of isoamyl acetate trapped in the Tenax tube reached a plateau value.

To compare aroma release from the five different matrices, two parameters have been extracted from these curves: respectively, the initial slope and the plateau value at a 840 min purge time. The initial slope was estimated from the two first points



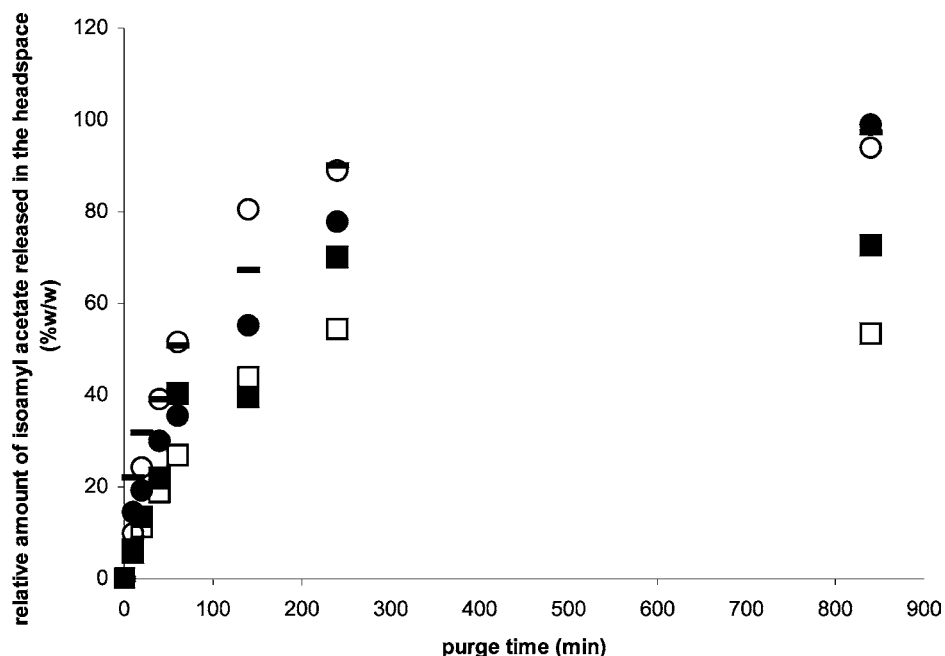
**Figure 3.** Rheological characterization of waxy starch pastes at 5 °C: (a) aging for 9 h after quenching from 60 to 5 °C (measurements at 1.26  $\text{rad}\cdot\text{s}^{-1}$ ; deformation amplitude = 0.025;  $G'$ , solid symbols;  $G''$ , open symbols; NSP, circles; SNSP, squares); (b) mechanical spectra at the end of the aging experiment ( $G'$ , solid symbols;  $G''$ , open symbols; NSP, circles; SNSP, squares).

of the curve. The plateau value could be expressed as the percent of the total amount of aroma remaining in the matrix after the cooking process. These parameters are reported in **Table 4**. Clearly, significant differences were observed for the various tested matrices.

Regarding the initial slope, this parameter was the highest when dealing with water only. In the case of the starchy systems, the lowest values were obtained for normal starch dispersions

with or without extra shearing. However, no significant differences were found between NSP and SNSP. The values obtained for waxy starch dispersions lay between normal starch gels and water. In that case, the initial slope was significantly modified in case of extra shearing.

Regarding the plateau value, three different behaviors were observed. More than 94% of the total available amount of isoamyl acetate was released from water only and from waxy



**Figure 4.** Time-dependent curves of aroma release obtained for different matrices flavored with isoamyl acetate (100% means that the total amount available in the starch dispersion has been released in the headspace): (■) NSP; (□) SNSP; (●) WSP; (○) SWSP; (—) water.

**Table 4.** Parameters Extracted from the Aroma Release Curves for Starch Pastes and for Water: Comparison with Thermodynamic and Kinetic Parameters<sup>a</sup>

structure: matrix:	water	gel NSP	gel SNSP	nongelled WSP	nongelled SQSP
initial slope ( $10^{-9}$ g·min <sup>-1</sup> ), mean $\pm$ CI at 95%	57.5 <sup>d</sup> $\pm$ 9.3	16.5 <sup>a</sup> $\pm$ 1.6	14.8 <sup>a</sup> $\pm$ 9.7	38.8 <sup>c</sup> $\pm$ 7.8	25.8 <sup>b</sup> $\pm$ 15.1
proportion of isoamyl acetate released for 840 min purge time (% of total amount determined in matrix)	98 <sup>c</sup>	73 <sup>b</sup>	53 <sup>a</sup>	99 <sup>c</sup>	94 <sup>c</sup>
flavoring rate measured after cooking (%)	nonheated sample	46 $\pm$ 5	65 $\pm$ 3	19 $\pm$ 4	34 $\pm$ 0
apparent air/matrix partition coefficients at 25 °C (15)	12.14	6.38	4.75	7.15	6.08

<sup>a</sup> Significant differences are indicated by different letters beside the values.

starch dispersions. In contrast, only 73% of the total amount of isoamyl acetate was released from the nonsheared normal starch gel, whereas this amount was lowered to 53% when extra shearing was applied.

It has to be noted that the flavoring rate we measured after cooking can also be used to evaluate the aroma release. As reported in **Table 4**, we observed that the amount of isoamyl acetate remaining in the matrices is higher for normal starch pastes than for waxy starch pastes. Moreover, the flavoring rate increased when extra shearing is applied.

## DISCUSSION

One of the aims of such studies is to propose models able to predict aroma release from food products. Linforth (16) reported that two main approaches can be used for the construction of such models. The first one is a theoretical approach, using the principles of physicochemistry; the second one is data driven. Different comprehensive theoretical models have already been developed (17). They were based either on gas phase dilution of equilibrium headspace (18) or on following up the return to equilibrium from initial condition with no volatile in the gas phase (19). Juteau and co-workers (20) proposed a comparison of models applied to aroma release from gels. For this comparison, they used part of the data reported in the present work. They emphasized that the present data are under both thermodynamic and kinetic dependency. As a consequence, such

experiments cannot provide a parameter that is directly linked to diffusion coefficients, which is a key problem when dealing with aroma release. However, the rate of release (initial slope of the curve as reported here) has been claimed to be a significant parameter to be taken into account for aroma release (21), and the method reported here can be considered as relevant to estimate such a parameter.

This type of experiment, with a gas renewal as is the case in the mouth, could then be an appropriate procedure to follow and model aroma release during the eating process. Of course, in the present case, the phenomena occurring during mastication were not taken into account and the time of analysis is far longer in such an experiment than the time spent to eat and swallow a food product. Nevertheless, the interest of such an experiment exists in the very beginning of the obtained curve. Moreover, it has to be noted that the end of the release curve can also be of interest because it can be deduced from it whether all of the aroma compound is released or if it is trapped within the starch matrix due to interactions with starch. Therefore, this method allows one to estimate the rate of aroma release (from the slope at the origin as reported in **Table 4**) and the amount of aroma irreversibly trapped in the matrix (the plateau value as reported in **Table 4**).

Even if the plateau value has been obtained in dynamic conditions, it could be interesting to compare it to thermodynamic parameters obtained by means of static measurements,

for example, apparent air/matrix partition coefficients as measured by Arvisenet (15) on similar starch pastes. These partition coefficients are also given in **Table 4**. This was higher in water than that for the starch dispersions. The partition coefficient obtained for the waxy starch paste was higher than the one obtained for the normal starch paste. This can be interpreted as an indication that aroma interaction with starch is more important in the case of the normal starch system, which actually can be regarded as a gel, than in the case of waxy starch, which is quite fluid, although structured, as shown by rheological measurements. Furthermore, these coefficients for both normal starch and waxy starch dispersions were lowered when extra shearing was applied. It can be assumed that extra shearing increased the availability of starch macromolecules to aroma compounds and as a consequence facilitated the physicochemical interactions between isoamyl acetate and the starch macromolecules.

On another hand, it can be noted that the lowest initial slope values were obtained when the matrices displayed the properties of strong gels (NSP and SNSP). However, although significant differences in gel strength were observed for the gels with normal starch (NSP, SNSP), no significant difference was observed for the rate of release of isoamyl acetate. In contrast, a significant difference was observed in this rate of release between the two waxy starch dispersions (WSP, SWSP). This parameter was found to be higher for the nonsheared waxy starch dispersion than for the waxy starch dispersion that underwent extra shearing. We may assume that in the case of the waxy starch dispersion without extra shearing, the continuous phase is composed essentially of water and the diffusion of the aroma compound might be as rapid as in water. In the case of the waxy starch dispersion with extra shearing, the continuous phase may contain some soluble amylopectin that might slow the diffusion of the aroma compound.

For the normal starch dispersions, the continuous phase is a network containing gelled amylose that has been solubilized upon pasting and then gelled upon cooling and aging. This gelled structure might explain why the slope is twice lower in the case of normal corn starch than for waxy corn starch.

#### ACKNOWLEDGMENT

Special thanks are expressed to Céline Lafarge for technical support.

#### LITERATURE CITED

- (1) Bakker, J. Flavor interactions with the food matrix and their effects on perception. In *Ingredients Interactions: Effects on Food Quality*; Gaonkar, A. G., Ed.; Dekker: New York, 1995; pp 411–439.
- (2) Roberts, D.; Elmore, J. S.; Langley, K. R.; Bakker, J. The effect of viscosity on dynamic flavour release. In *Bioflavour '95*; INRA: Paris, France, 1995; pp 14–17.
- (3) Carr, J.; Baloga, C.; Guinard, X.; Lawter, L.; Marty, C.; Squire, C. The effect of gelling agent type and concentration on flavor release in model systems. In *Flavor–Food Interactions*; McGorin, R. J., Leland, J. V., Eds.; ACS Symposium Series 33; American Chemical Society: Washington, DC, 1996; pp 98–108.
- (4) Guinard, J. X.; Marty, C. Time-intensity measurement of flavor release from a model gel system: effect of gelling agent type and concentration. *J. Food Sci.* **1995**, *60*, 727–730.
- (5) Yven, C.; Guichard, E.; Giboreau, A.; Roberts, A. D. Assessment of interactions between hydrocolloids and flavor compounds by sensory, headspace, and binding methodologies. *J. Agric. Food Chem.* **1998**, *46*, 1510–1514.
- (6) Kälviäinen, N.; Roininen, K.; Tuorila, H. Sensory characterization of texture and flavor of high viscosity gels made with different thickeners. *J. Texture Stud.* **2000**, *31*, 407–420.
- (7) Nuessli, J.; Sigg, B.; Condé-Petit, B.; Escher, F. Characterization of amylose-flavour complexes by DSC and X-ray diffraction. *Food Hydrocolloids* **1997**, *11*, 27–34.
- (8) Arvisenet, G.; Voilley, A.; Cayot, N. Retention of aroma compounds in starch matrices: competition between aroma compounds towards amylose and amylopectin. *J. Agric. Food Chem.* **2002**, *50*, 7345–7349.
- (9) Da Silva, J. A. L.; Castro, S. M.; Delgadillo, I. Effect of gelatinization and starch-emulsifier interactions on aroma release from starch-rich model systems. *J. Agric. Food Chem.* **2002**, *50*, 1976–1984.
- (10) Van Ruth, S.; King, C. Effect of starch and amylopectin concentrations on volatile flavour release from aqueous model food systems. *Flavour Fragrance J.* **2003**, *18* (5), 407–416.
- (11) Arvisenet, G.; Le Bail, P.; Voilley, A.; Cayot, N. Influence of physico-chemical interactions between amylose and aroma compounds on the retention of aroma in food-like matrices. *J. Agric. Food Chem.* **2002**, *50*, 7088–7093.
- (12) Likens, S. T.; Nickerson, G. B. Detection of certain hop oil constituents in brewing products. *Proc. Am. Soc. Brew. Chem.* **1964**, *5*, 5–12.
- (13) Doublier, J. L.; Llamas, G.; Le Meur, M. A rheological investigation of cereal starch pastes and gels. Effect of pasting procedures. *Carbohydr. Polym.* **1987**, *7* (4), 251–275.
- (14) Doublier, J.-L.; Llamas, G. A rheological description of amylose-amylopectin mixtures. In *Food Colloids and Polymers: Stability and Mechanical Properties*; Dickinson, E., Walstra, P., Eds.; The Royal Society of Chemistry: Cambridge, U.K., 1993; pp 138–146.
- (15) Arvisenet, G. Influence des interactions physico-chimiques entre amidons et composés d'arôme sur la libération des arômes et les propriétés rhéologiques dans des matrices aqueuses complexes. Thèse de doctorat, Université de Bourgogne, Dijon, France, 2001.
- (16) Linforth, R. Modelling flavour release. In *Food Flavour Technology*; Taylor, A. J., Ed.; Sheffield Academic Press: Sheffield, U.K., 2002; pp 185–209.
- (17) Taylor, A. J. Release and transport of flavors in vivo: physicochemical, physiological, and perceptual considerations. *Compr. Rev. Food Sci. Food Saf.* **2002**, *1*, 45–57.
- (18) Marin, M.; Baek, I.; Taylor, A. Volatile release from aqueous solutions under dynamic headspace dilution conditions. *J. Agric. Food Chem.* **1999**, *47*, 4750–4755.
- (19) Harrison, M.; Hills, B.; Bakker, J.; Clothier, T. Mathematical models of flavor release from liquid emulsions. *J. Food Sci.* **1997**, *62*, 653–658.
- (20) Juteau, A.; Cayot, N.; Chabanet, C.; Doublier, J. L.; Guichard, E. Flavour release from polysaccharide gels: different approaches for the determination of kinetic parameters. *Trends Food Sci. Technol.* **2004**, *15* (7–8), 394–402.
- (21) Taylor, A. J.; Besnard, S.; Puaud, M.; Linforth, R. S. T. In vivo measurement of flavour release from mixed phase gels. *Biomol. Eng.* **2001**, *17*, 143–150.

Received for review February 26, 2004. Revised manuscript received June 14, 2004. Accepted June 20, 2004.