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Massimiliano Rinaldi, Chiara Dall'asta, Maria Paciulli, Stefano Guizzetti, Davide Barbanti, Emma Chiavaro

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ORIGINAL PAPER

Innovation in the Italian ice cream production: effect of different phospholipid emulsifiers

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Abstract Artisanal Italian ice cream (called gelato) is one of the most appreciated Italian food specialties. Mono- and diglycerides of fatty acids represent the most used emulsifiers for gelato but the demand for "clean label" products containing lower amount or no additives or stabilizers is continuously increasing among consumers. In this work, the impact of three phospholipid emulsifiers (soy, milk and rice phospholipids) was evaluated on physicochemical, thermal and flavour characteristics of a basic Italian gelato formulation in comparison to those of mono- and diglycerides of fatty acids, used as control. Control sample showed the highest overrun and unfreezable water values but also the lowest fat destabilization percentages. On the contrary, gelato added with soy phospholipids exhibited the greatest resistance to melt and high fat destabilization ratio being also harder than the others. Sample with rice phospholipids revealed a richer volatile profile with herbal and green notes. The lowest performances were displayed from gelato where milk phospholipids were added as emulsifier as this sample showed higher mix viscosity, green colour notes, lower overrun, hardness and stickiness values. During a 4-week storage in a domestic freezer, all samples hardened and became more yellow, showing a decrease of volatiles except for samples with rice phospholipids added. These findings may encourage further research on the use of soy and rice phospholipids as emulsifiers to improve their performances in gelato making, by testing their use alone or in combination at different levels.

Keywords Italian gelato · Emulsifiers · Physical properties · Volatile compounds · Storage

M. Rinaldi · C. Dall'Asta (✉) · M. Paciulli · S. Guizzetti · D. Barbanti · E. Chiavaro (✉)
Dipartimento di Scienze degli Alimenti, Università degli Studi di Parma,
Parco Area delle Scienze 59/A, 43124 Parma, Italy
e-mail: chiara.dallasta@unipr.it
e-mail: emma.chiavaro@unipr.it

1 Introduction

Ice cream is defined by Goff et al. (1999) as *a complex food colloidal system*, *containing fat globules*, *air bubbles and ice crystals dispersed in a freeze-concentrated dispersion/solution* where *proteins*, *salts*, *polysaccharides and sugars* are dissolved.

All the steps of ice cream production contribute to the complexity of its structure: mixing creates a simple emulsion, where the discrete phase is made by a partially crystalline fat globules coated with a protein-emulsifier layer, while the continuous serum phase consists of unabsorbed casein micelles suspended in a concentrated solution of unabsorbed whey proteins, sugars, salts and high molecular weight polysaccharides (Marshall et al. 2003). Simultaneous freezing and foaming produce a dispersion of air bubbles and ice crystals. In addition, the partially crystalline fat phase undergoes partial coalescence resulting in a three-dimensional network of agglomerated fat, surrounding the air bubbles and leading to a solid like-structure (Marshall et al. 2003).

Stabilization of this complex structure is a very important goal to be achieved in formulating ice cream, and several factors contribute to obtain this objective. The addition of emulsifiers among them, mainly improves the whipping quality of the mix and promotes the fat destabilization through the lowering of fat/water interfacial tension in the mix and the consequent displacement of proteins from surface of fat globules, resulting in their partial coalescence. This process leads thus to a dry and stiff product, facilitating moulding and extrusion, and also providing a smooth body and texture as well as good shape retention properties and melt resistance (Goff 1997).

Artisanal Italian ice cream (commonly known as gelato) is one of the most appreciated Italian food specialties around the world. Italians are also among the highest consumers of gelato (about 6 kg annual per capita), with a global production of 360,000 tons in 2009 and a 10% increment of artisanal gelaterias in the last years to reach about 30,000 units (Italian gelato.info 2010). Gelato commonly shows lower overrun value (≤30%) than ice cream (50 to 100%), sometimes lower fat content (4–14%) and it is generally flavoured with raw ingredients and not flavourings (Marshall et al. 2003). In addition, handmade gelato or artisanal ice cream is not extruded but batch frozen and is not subjected to a hardening step after freezing. In fact, the lower overrun and the consistency allow to obtain a product that could be scooped (with a characteristic paddle-shaped scoop) at a softer state and served and stored at higher temperature (about −11 °C) than an ice cream (−18 °C) (Marshall et al. 2003).

Innovation demand is strongly perceived among Italian producers due to the increasing requests from consumers for new formulations of nutritional interest (Camino Feltes et al. 2013). At the same time, demand for “clean label” products containing lower amount or no additives or stabilizers is getting stronger (Le et al. 2011). Mono- and diglycerides of fatty acids, represent the most used emulsifier both in ice cream and gelato. They are actually recognized as additives as listed in Annex II of Regulation (EC) No 1333/2008 (Official Journal of the European Union 2008). Other sources of compounds with emulsifying ability received great attention in the last years as they could be listed as ingredients instead of additives.

In this context, the aim of this work was to investigate the impact of three emulsifiers (soy, milk and rice phospholipids) on the physicochemical, thermal and flavour characteristics of Italian gelato, in comparison with the most used emulsifiers.

2 Materials and methods

2.1 Materials and sample preparation

All samples were prepared according to Italian artisanal process and with the same recipe: 52.6% whole milk, 21% cream, 2.2% skim milk powder, 1.05% concentrated whey proteins, 0.78% sodium caseinate, 0.8% lactose, 10% sucrose, 8.38% dextrose, 2.6% glucose solids, 0.09% carob/locust bean gum, 0.11% guar gum, 0.04% xanthan gum and 0.35% emulsifier. No flavouring agent was added. The mixes used to prepare the gelato samples consisted of 25.7% sugars (8.2% monosaccharides, 15.6% disaccharides, 1.9% polysaccharides), 9.7% fats (6.6% saturated, 3.1% unsaturated), 10.6% milk solid-non-fat and 40.6% total solids.

Four different emulsifiers were added to the basic recipe to obtain four different formulations: mono- and diglycerides of saturated fatty acids (MDGc) as control (Reire, Reggio Emilia, Italy), soy phospholipids (LEC) (Lipoid GmbH, Ludwigshafen, Germany), milk phospholipids (MLK) (Arla Foods, Viby J, Denmark) and rice phospholipids (RCE) (Ribus, St. Louis, Missouri, USA). Phospholipids profiles of the tested emulsifiers were expected to be quite different on the basis of the literature data (Burling and Graverholt 2008). LEC presented the highest relative amount of phosphatidylcholine (44%) and phosphatidylinositol (23%) compared to RCE (30 and 12%, respectively) and MLK (27 and 8%, respectively). MLK presented a high percentage of phosphatidylserine (12%), which was very low in LEC (0.5%) and absent in RCE, as well as sphingomyelin (24%) from animal origin, which is not present in the other emulsifiers. Finally, the content of phosphatidylethanolamine was quite similar in all the tested emulsifiers with values of 19, 25 and 26% for LEC, MLK and RCE, respectively.

All ingredients were combined in water at room temperature, homogenized with a high-speed mixer (Fimar, Rimini, Italy) at 11,000 rpm for 1 min, heated at 65 °C and held for 30 min. The mix was then cooled and stored at 4 °C for 16 h for ageing. Batches of gelato mix (2.5 kg) were frozen in a horizontal freezer (Carpigiani, Anzola Emilia, Bologna, Italy) for 8 min at −6.0 °C as outlet temperature. Samples were rapidly cooled in −40 °C air to −25 °C (Carpigiani, Anzola Emilia, Bologna, Italy), stored at −25 °C for 24 h and up to 4 weeks from production at −18 °C in a domestic freezer. For each formulation, at least three different batches were prepared.

Samples were analysed at time 0 (after 24 h of storage) for all determinations and at time 4 (after 4 weeks of storage) for colour, texture and volatiles.

2.2 Physical analyses

Apparent viscosity of the mixes was evaluated after 24 h of ageing at 4 °C using a Brookfield (Brookfield Engineering Laboratories Inc., Middleboro, Massachusetts,

USA) viscometer equipped with spindle LV-1 at 10 rpm, equivalent to a shear rate of 2.25 s^{-1} and each analysis was replicated three times.

Overrun (%) was determined according to the method described by Marshall et al. (2003). A known volume of gelato mix and frozen gelato were weighted and percentage of overrun was calculated according to the equation:

$$overrun(\%) = \frac{m_{ice\ cream\ mix} - m_{ice\ cream}}{m_{icecreammix}}$$

where: $m_{\text{ice cream mix}}$ was the weight of mix and $m_{\text{ice cream}}$ the weight of ice cream after freezing, respectively.

Melting rate was evaluated according to Lee and White (1991). Briefly, gelato samples (100.0±2.0 g; at −18 °C) were placed on a mesh attached to a graduated cylinder and maintained in a controlled temperature chamber at 20 °C. The dripped volume was measured for 120 min every 5 min and the recorded data were expressed as percentage of melted volume relative to the initial one.

Fat destabilization ratio (%) was evaluated on gelato samples at time 0 as reported by Goff and Jordan (1989). Samples were diluted 1:500 with filtered water, centrifuged for 5 min at 1,000 rpm and absorbance was measured 10 min later at 540 nm by a spectrophotometer (Kontron Instruments, Milano, Italy) against water as blank. Each analysis was replicated three times. Fat destabilization was calculated as A mix−A frozen/A mix×100.

Instrumental hardness of gelato was measured immediately after removal of each sample from the freezer, making particular attention to standardize the time interval for the determination. A TA-XT 2i Texture Analyzer was used equipped with a 25 kg load cell (Stable Micro Systems, Godalming, UK) and Texture Expert for Windows software (version 1.22) for data analysis. Test was carried out using a cylindrical probe (6 mm diameter) with a crosshead speed of 120 $mm.min^{-1}$ and a penetration depth of 10 mm (Soukoulis et al. 2008). The probe was chilled in an untested sample before testing. Hardness was measured as the peak compression force (in newton) during the penetration, while stickiness as the negative peak force (in newton) during withdrawal (Guinard et al. 1997). The load cell calibration was daily performed according to the TA.XT2 manual (Stable Micro Systems). Triplicate analyses were carried out for each batch×sample×time of storage.

Gelato and emulsifier powder colour was determined using a Minolta Colorimeter (CM 2600d, Konica Minolta Sensing, Osaka, Japan) equipped with a standard illuminant D65 and Spectramagic software (Version 3.6) for data analysis. The instrument was calibrated before each analysis with white and black standard tiles. L^* (lightness, black=0, white = 100), a^* (redness >0, greenness <0), b^* (yellowness, b^*>0, blue<0), C (chroma, $C = \sqrt{\left(a^{*^2} + b^{*^2}\right)}$, 0 at the centre of the colour sphere), Hue° (Hue angle, red=0°, yellow=90°, 180°=green, 270°=blue) were quantified on each sample using a 10° position of the standard observer and measurements were carried out on 20 pre-selected locations for each batch×sample×time of storage.

2.3 Moisture content

Moisture content of all samples was determined by oven drying at 100 °C for 4 h (AOAC 1995). The initial and final weights of each sample were measured and moisture content (g_{water}/g_{sample}) calculated as:

$$\text{moisture content} = \frac{\text{initial weight} - \text{final weight}}{\text{initial weight}}$$

Triplicate analyses were carried out for each batch×sample×time of storage.

2.4 Thermal analysis

Gelato samples (8–10 mg) were weighed into aluminium pans, covers were sealed into place and the whole analysed with a DSC Q100 (TA Instruments, New Castle, DE). Indium (melting temperature 156.6 °C, ΔH_f=28.45 J.g^{-1}) and *n*-dodecane (melting temperature −9.65 °C, ΔH_f=216.73 J.g^{-1}) were used to calibrate the instrument and an empty pan was used as reference. Samples were equilibrated at −60 °C for 5 min and then heated from −60 °C to 40 °C at 5 °C.min^{-1}. Dry nitrogen was purged into the DSC cell at 50 cm^3.min^{-1}. DSC melting curves were analysed by Universal Analysis Software (Version 3.9A, TA Instruments) to obtain enthalpy (enthalpy$_w$, in joules per gram), onset (Ton$_w$, in degree Celsius), offset (Toff$_w$, in degree Celsius) and peak (Tp$_w$, in degree Celsius) temperatures of the endothermic peak around 0 °C identified as ice melting (Alvarez et al. 2005). Range of the ice melting transition (Trange$_w$, in degree Celsius) was calculated as temperature difference between T_{on} and T_{off}. The enthalpy of the ice melting transition was used to quantify freezable water (FW) according to previous work (Alvarez et al. 2005). Unfreezable water (UFW) values were also calculated from the difference between% moisture content and FW (Alvarez et al. 2005).

Triplicate analyses were carried out only at *t*=0 for each batch×sample.

2.5 Volatile compound analysis

The volatile fraction was extracted using headspace solid phase microextraction technique (HS-SPME), as recently described in Rinaldi et al. (2013). Besides gelato samples, also MDGc, RCE, MLK and LEC powders used as emulsifiers were analysed. A 2-g portion of gelato (or powder) was placed into a 30 ml glass vial, sealed with Black Viton septa (Supelco, Bellefonte, PA, USA) adding 1 g of NaCl (Prolabo, VWR, Leuven, Belgium). 3-Octanol (1 μg.g^{-1}) was used as internal standard for semi-quantification and calculation of the coefficients of response. Volatile compounds were then semi-quantified accordingly.

HS-SPME extraction was performed for 60 min at 30 °C (water bath) keeping the sample under continuous stirring, using a silica fibre coated with 50/30 μm of divinylbenzene-carboxen-polydimethylsiloxane (DVB/Carboxen/PDMS) (purchased from Supelco, Bellefonte, PA, USA). Before the analysis, the fibre was conditioned by insertion into the GC-MS injector at 220 °C for 2 min. GC-MS analyses were

performed using an Agilent Technologies 6890N gas-chromatograph coupled to an Agilent Technologies 5973 mass spectrometer. All samples were injected in splitless mode (the valve was closed for 2 min), with an injector temperature of 220 °C. Helium was used as carrier gas with a total flow of 18 ml.min^{-1}. Resolution of the mixtures was obtained by a SUPELCOWAX 10 capillary column (Supelco, 30 m×0.25 mm, f.t. 0.25 μm) (Supelco, Bellefonte, PA, USA). Analysis parameters were set according to Rinaldi et al. (2013).

Electron impact ionization was performed and the ion source temperature was maintained at 230 °C; the acquisition mode was full scan (from 40 to 500*m*/*z*). Each sample was analysed in triplicate.

Linear retention indexes (LRI) were calculated for compound identification and compared with those reported by NIST 08/NIST08/2008 database; in addition, mass spectra-based identification was also performed using reference mass spectra libraries (WILEY275, NBS75K). Compounds with LRI not present in the literature were tentatively identified by mass spectra matching with libraries: a match quality of 98% minimum was used as a criterion. For LRI calculation, a mixture of *n*-alkanes (C_8–C_{20}) dissolved in *n*-hexane was used (Supelco, Bellefonte, PA, USA). The LRI were calculated for components eluting under experimental conditions between *n*-octane and *n*-eicosane. For those components with elution after C_{20}, extrapolation using C_{18}–C_{20} alkanes was used.

Triplicate analyses were carried out for each batch×sample×time of storage.

2.6 Statistical analysis

SPSS statistical software (Version 19.0, SPSS Inc., Chicago, IL) was used to perform one-way analysis of variance among samples from different emulsifiers at the same time of storage. The least significant difference (LSD) at a 95% confidence level ($p \leq 0.05$) was performed to further identify differences among groups. A *t* test ($p \leq 0.05$) was also performed to analyse differences among samples at the two times of storage from the same emulsifier.

3 Results and discussion

3.1 Analytical results at time 0

3.1.1 Physical and thermal analyses

Apparent viscosity values of mixes measured for LEC and RCE (0.80 and 0.79 Pas, respectively) were not significantly different compared to the control (MDGc, 0.83 Pas). These values are in the literature range for ice cream with 40% of solids. Karaman and Kayacier (2012) reported a value of about 0.765 Pas for an ice cream with 38% of solids. Muse and Hartel (2004) reported apparent viscosity values ranging from 0.72 to 0.94 Pas obtained at a similar shear rate for an ice cream mix with similar solid content. On the contrary, MLK mix presented a significantly higher apparent viscosity (1.92 Pas) compared to the others, as previously found by Horn et al. (2012) for an oil-in-water, where the same phospholipid product from milk (MLK) was used to stabilize emulsions in comparison with soy lecithin.

The water affinity and the hydrophilic properties of MLK phospholipids could have influenced viscosity of the mix, too: sphingomyelin is neutral but slightly more polar than phosphatidylcholine and phosphatidylethanolamine, while phosphatidylserine, which was present at higher percentages in MLK and absent in LEC and RCE, is negatively charged. Abd El-Rahman et al. (1997) found that phospholipids of cream, which was added to ice cream mix, significantly increased mix apparent viscosity, thus acting as a better emulsifier than anhydrous milk fat.

Gelato samples showed fat destabilization values of 53.7, 8.9, 26.1 and 12.7% for LEC, MDGc, RCE and MLK, respectively. The destabilized fats were reported to stabilize the air cells and to trap the aqueous phase in ice cream, preventing drainage upon meltdown (Goff et al. 1999). LEC showed higher fat destabilization level than the other samples, probably in relation with its low hydrophilic/lipophilic balance value. Thus, it could be probably more effective in replacing proteins at the surface of the fat globules and in promoting fat destabilization, due to its lipophilic character (Hasenhuettl and Hartel 2008). Preliminary evaluations carried out by optical microscopy on melted gelatos (data not shown) showed that LEC exhibited the highest fat globules diameter confirming the occurrence of a high fat destabilization degree. No significant differences were observed among other emulsifiers, probably on account of the high variability in fat globule dimensions. MDGc showed the lowest value of fat destabilization, probably in relation with its degree of fatty acid saturation. Unsaturated fatty acids were indeed reported to promote greater fat destabilization compared to the saturated ones (Marshall et al. 2003).

Control samples (MDGc) presented the highest overrun value (31.8%), as expected. MDGc is recognized as a good foaming agent able to aid the formation of the initial foam prior to fat-droplet agglomeration at the air/water interface (Keeney 1982). The overrun was, on the contrary, the lowest for MLK (17.6%), probably on account of the high viscosity of the MLK mix, which did not favour the formation of foam, as reported by Stanley et al. (1996). In addition, milk phospholipids are reported to negatively affect foam formation and stability, as a considerable proportion of them is not associated with the milk fat globules, but it is present in the serum phase as fragments of the milk fat globule membrane (Huppertz 2010). These fragments are surface active and, as a result, associate on the foam bubble surfaces. Their inability to create a stable foam layer together with proteins leads to the general poor foaming properties (Huppertz 2010). LEC and RCE showed intermediate values (25.5 and 23.9%, respectively). An overrun decrease was already reported by Baer et al. (1997) in low fat ice cream, as consequence of soy lecithin used as emulsifier in comparison with mono- and diglycerides of fatty acids. Anyway, overruns of all samples were in the range of those found in literature for Italian artisanal gelato (Marshall et al. 2003).

Meltdown curves of ice cream samples were reported in Fig. 1. LEC presented the lowest melting behaviour while, on the contrary, MDGc was the fastest to melt down. MLK and REC presented similar trends. The great resistance to melt shown by LEC could be explained according to fat destabilization, as discussed above. LEC samples presented the highest level of fat destabilization and, thus, it could be expected that partially coalesced fat globules migrate towards air cell interface and stabilize the foam (Marshall et al. 2003). On the other hand, MDGc presented the lowest fat destabilization value and also the highest overrun percentage. It could be hypothesized that, if air

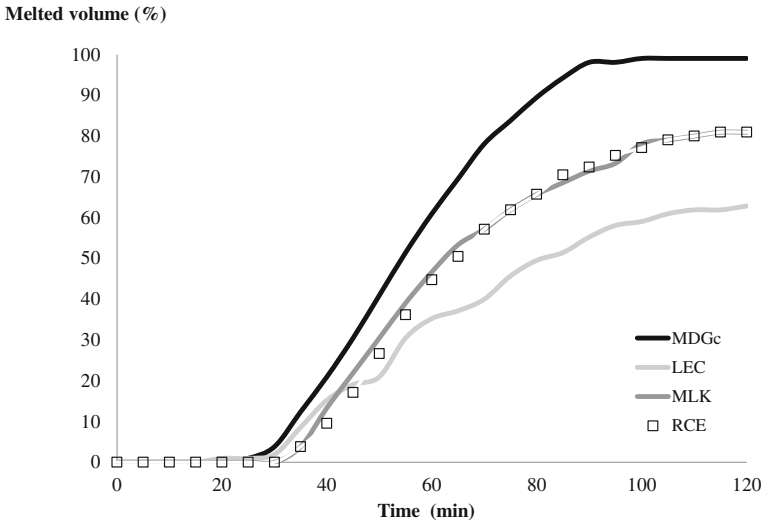

Fig. 1 Meltdown profiles of ice cream samples. Abbreviations: *MDGc emulsifier* mono- and diglycerides of fatty acids, control sample; *LEC emulsifier* soy phospholipids; *MLK emulsifier* milk phospholipids, *RCE emulsifier* rice phospholipids

bubbles are primarily stabilized by partially destabilized fat globules (Marshall et al. 2003), MDGc gelato may result as the less stable foam.

Ice cream hardness values at 0 week were reported in Table 1. The tested emulsifiers presented significant differences. MDGc showed a hardness value of about 10 N, which was consistent with Guinard et al. (1997). These authors reported values of about 12 N for ice creams with similar sugar and fat content but higher overrun (two-fold higher) than samples considered in the present study. Among the tested emulsifiers, LEC showed the highest value (12.2 N), MLK the lowest one (5.8 N) and RCE an intermediate value (7.4 N). LEC behaviour was in agreement with Baer et al. (1997), who reported lowest overall sensorial scores for body and texture in samples added with lecithin, probably because this emulsifier was less able in retarding ice crystallization and growth than other emulsifiers. On the other hand, MLK presented the lowest value of hardness (5.8 N) also exhibiting the highest mix viscosity value and the lowest overrun. Contradictory literature results have been observed relating air content and hardness in ice cream, as also stated by Sofjan and Hartel (2004), since many major and minor effects (air cell, fat cell and ice crystal size distributions) influenced ice cream hardness. Muse and Hartel (2004) also reported that the level of fat destabilization was positively correlated with ice cream hardness, as destabilized fat could provide a network between the air cells. This was in agreement with our results for samples with phospholipid emulsifiers as both fat destabilization and hardness of gelato samples decreased from LEC to MLK (Table 1). On the contrary, overrun values appeared to be not negatively correlated to hardness, as found by Muse and Hartel (2004), probably in view of the low values shown by Italian gelato.

Sample stickiness exhibited significant differences between emulsifiers at time 0 weeks (Table 1). LEC and MDGc presented the highest values similar to those reported by Guinard et al. (1997), while MLK showed the lowest stickiness. Guinard

Table 1 Colour (L^*, a^*, b^*, C, and Hue°) and textural parameters (Hd, St) of gelato samples

	MDGc	LEC	MLK	RCE
t=0 week				
L^*	92.3 ^{b}	92.2 ^{b}	93.6 ^{a}	91.4 ^{b}
a^*	−0.3 ^{ab}	−0.3 ^{b}	−0.9 ^{c}	−0.2 ^{a}
b^*	9.4 ^{bc}	9.8 ^{ab}	9.1 ^{c}	10.3 ^{a}
C	9.7 ^{bc}	10.1 ^{b}	9.5 ^{c}	10.6 ^{a}
$H°$	91.8 ^{b}	92.0 ^{b}	95.5 ^{a}	91.2 ^{c}
Hd (N)	10.0 ^{b}	12.2 ^{a}	5.8 ^{d}	7.4 ^{c}
St (N)	1.5 ^{a}	1.5 ^{a}	1.0 ^{b}	1.4 ^{a}
t=4 week				
L^*	91.8 ^{a}	90.4 ^{b}	91.3 ^{ab}	90.6 ^{b}
a^*	−0.3 ^{a}	−0.2 ^{a}	−0.9 ^{b}	−0.2 ^{a}
b^*	10.1 ^{c}	10.7 ^{ab}	10.8 ^{ab}	11.2 ^{a}
C	10.4 ^{b}	11.0 ^{ab}	11.1 ^{a}	11.5 ^{a}
$H°$	90.7 ^{b}	90.1 ^{b}	94.6 ^{a}	90.1 ^{b}
Hd (N)	13.2 ^{b}	14.3 ^{a}	8.8 ^{c}	9.2 ^{c}
St (N)	1.7 ^{b}	2.0 ^{a}	1.7 ^{b}	1.7 ^{b}

n=30 for colour and n=9 for texture RSD <5%. Means in rows followed by different letters at the same time are significantly different (p<0.05)

MDGc emulsifier: mono- and diglycerides of fatty acids, control sample; *LEC* emulsifier: soy phospholipids; *MLK* emulsifier: milk phospholipids; *RCE* emulsifier: rice phospholipids; *Hd* hardness; *St* stickiness

et al. (1997) reported that stickiness was dependent not only on fat and sugar content but also on water amount. Thus, MLK lowest stickiness may be related to the slightly lower MC values observed for this sample and the lowest UFW (bound water) (see below).

Colour data were also summarized in Table 1 and they were similar to those reported in literature for ice cream (Roland et al. 1999). At time 0, MLK appeared to be not only lighter (high L^*) but also greener (lower $-a^*$ and higher $H°$) than the other samples. This greenness may be probably related to the colour parameter of MLK powder (data not shown) that exhibited lowest a^* (negative value) than the others emulsifiers.

Calorimetric data obtained for ice melting transition (enthalpy, onset temperature and transition range, FW and UFW) were summarized in Table 2. No significant differences were found among samples at time 0 for enthalpy, onset and peak temperatures of ice melting, showing that these thermal properties were not influenced by the use of different emulsifiers. FW did not significantly differ among samples. On the other hand, significant differences were found for UFW (bound water) among MDGc, LEC and MLK samples, showing the highest for the former and the lowest values for the latter, respectively. This could be related not only to the different MC amounts (62 and 59% for MDGc and MLK, respectively) but also to the overrun value, which was higher for MDGc in comparison with the others samples.

Table 2 DSC data obtained from the ice melting curves of gelato samples at time 0[a]

	Enthalpy$_w$ (J/g)	Ton$_w$ (°C)	Trange$_w$ (°C)	Tp$_w$ (°C)	FW (%)	UFW (%)
MDGc	122.8 [a]	−28.6 [a]	31.3 [a]	−2.3[a]	36.8[a]	25.2 [a]
LEC	125.3 [a]	−28.9 [a]	31.7 [a]	−2.3 [a]	37.5 [a]	23.5 [b]
MLK	129.1 [a]	−27.9 [a]	30.2 [a]	−2.6 [a]	38.9 [a]	19.6 [c]
RCE	128.2 [a]	−29.3 [a]	32.1 [a]	−2.4 [a]	38.4 [a]	22.6 [abc]

n=9, RSD <3%. Means in column followed by different letters at the same time are significantly different (p<0.05)

MDGc emulsifier: mono- and diglycerides of fatty acids, control sample; *LEC* emulsifier: soy phospholipids; *MLK* emulsifier: milk phospholipids; *RCE* emulsifier: rice phospholipids; *Ton$_w$*, *Trange$_w$*, *Tp$_w$* onset, range and peak temperature of ice melting; *FW* freezable water, *UFW* MC-FW, unfreezable water

3.1.2 Volatile compound analysis

Although the use of different emulsifiers can significantly improve the physicochemical performances of artisanal gelato, different ingredients may differently affect the flavour of the final product by regulating the release of volatiles from gelato as well as by adding volatiles derived from the raw materials used for formulation. For this reason, information about volatile profile is important to better characterise the quality of modified Italian gelato formulations compared to control samples.

Very few data are reported in the literature so far and all of them are related to ice cream flavouring agents (Chung et al. 2004), whereas information about volatiles in Italian gelato are lacking.

In order to better identify the occurrence of volatiles derived from the emulsifiers, in this work a basic formulation was used and gelato samples were prepared without the addition of any flavouring agents. Thus, the expected volatiles were mainly those probably related to the milk fat fraction and processing (Irigoyen et al. 2012). A total of 24 gas-chromatographic signals, obtained by the triphasic fiber, were found within this study and reported in Table 3 along with the calculated retention indexes and the retention indexes from the literature, while semi-quantification data are reported in Table 4. Among them, 21 compounds were identified by LRI comparison and mass spectra matching with library data, while 3 volatiles were just tentatively identified on the basis of the mass spectra matching.

In order to verify the possible source of volatile compounds, the HS-SPME fingerprint of emulsifier powders has been also recorded and used for data comparison and discussion (data not shown).

By comparing data obtained in this study, 17 volatiles were found in all the considered gelato samples. Most of them are typical derivatives of fat milk lipolytic and oxidative phenomena, such as linear aldehydes, alkanes and alcohols, and may be ascribed to the milk used for gelato preparation. Other typical compounds from milk are those related to lactose degradation such as furfuryl alcohol and 2-furfural, those also found in all the considered samples.

Five compounds were present at significantly different levels in the considered formulations. RCE samples were characterised by higher content of linear aldehydes and alcohols, as commonly reported for rice (Tananuwong et al. 2010). In particular,

Table 3 Volatile compounds identified in gelato samples

Peak number	Identified compounds	Identification[a]	LRI calc[b]	LRI_{NIST}[c]
1	3-Octanone	MS+LRI	1,261	1,283
2	1-Octen-3-ol	MS+LRI	1,454	1,456
3	1-Heptanol	MS+LRI	1,459	1,460
4	Trisiloxane	MS	1,465	n.a.
5	Furfural	MS+LRI	1,476	1,472
6	Pentadecane	MS+LRI	1,494	1,500
7	Decanal	MS+LRI	1,496	1,497
8	Benzaldehyde	MS+LRI	1,535	1,539
9	2-Nonenal	MS+LRI	1,545	1,542
10	1-Octanol	MS+LRI	1,561	1,567
11	Ethyl-2 ,4-dimethyl-2-pentenoate	MS	1,581	n.a.
12	Hexadecane	MS+LRI	1,593	1,600
13	Carbitol	MS+LRI	1,628	1,589
14	γ-Butyrolactone	MS+LRI	1,648	1,647
15	Acetophenone	MS+LRI	1,668	1,660
16	2-Furfuryl alcohol	MS+LRI	1,675	1,669
17	2-Butyl-2-octenal	MS+LRI	1,678	1,659
18	Heptadecane	MS+LRI	1,699	1,700
19	Dodecanal	MS+LRI	1,722	1,700
20	Naphthalene	MS+LRI	1,724	1,718
21	Benzyl alcohol	MS+LRI	1,896	1,896
22	4-Ethyl guaiacol	MS+LRI	2,028	2,031
23	1-Phenoxypropan-2-ol	MS	2,061	n.a.
24	2-Phenoxyethanol	MS	2,151	n.a.

[a] *MS+LRI* Mass spectrum and LRI in agreement with the literature, *MS* tentative identification by mass spectrum matching with those reported in the library

[b] *LRI* linear retention index on a Supelcowax 10 capillary column

[c] LRI_{NIST} linear retention index reported in the NIST 08/NIST08/2008 database

n.a. data not available

2-butyl-2-octenal with a typical green and fruity note, was found only in RCE gelato; 1-heptanol, with the typical herbal note, was found in RCE and, in traces, in MDGc samples; 1-octen-3-ol, with an earthy note, was found at high levels in RCE and was completely absent in MLK. On the contrary, furfural, with a typical bready note, was found at higher levels in MLK gelato and MLK emulsifiers compared to other samples. Finally, ethyl-2,4-dimethyl-2-pentenoate, with a typical sour note, was found only in MLK and LEC, at a similar concentration.

For an easier comparison, the identified compounds have been classified into groups according to their chemical structure, as reported in Fig. 2. Alcohols are the most represented group, followed by alkanes, while aldehydes, ketones and esters are also present although at lower extent.

Table 4 Volatile compounds occurrence in different formulations. Data are given as mean and standard deviation (n=3)

Peak	*t*=0 week								*t*=4 week							
	MDGc (μg.g^{-1})		LEC (μg.g^{-1})		MLK (μg.g^{-1})		RCE (μg.g^{-1})		MDGc (μg.g^{-1})		LEC (μg.g^{-1})		MLK (μg.g^{-1})		RCE (μg.g^{-1})	
	Mean	std dev	Mean	std dev	Mean	std dev	Mean	std dev	Mean	std dev	Mean	std dev	Mean	std dev	Mean	std dev
1	5.68	0.18	15.19	3.63	11.16	1.43	23.48	0.42	13.08	0.65	14.57	1.01	15.15	1.31	17.24	0.10
2	0.09	0.02	0.09	0.01	n.d.	–	4.07	0.62	0.29	0.01	0.23	0.05	0.29	0.04	3.62	0.21
3	0.04	0.01	n.d.	–	n.d.	–	8.79	1.99	0.07	0.00	n.d.	–	0.19	0.02	7.27	0.80
4	1.62	0.01	3.02	2.03	1.04	0.07	0.89	0.03	n.d.	–	0.10	0.03	0.06	0.04	0.08	0.03
5	n.d.	–	n.d.	–	3.83	0.19	0.72	0.41	n.d.	–	0.49	0.03	0.39	0.23	0.22	0.01
6	5.98	0.10	6.50	0.41	5.74	0.47	5.19	0.24	0.76	0.04	0.80	0.23	0.53	0.31	0.59	0.12
7	3.22	0.44	4.05	0.11	2.40	0.10	3.06	1.05	2.97	0.15	2.51	0.61	2.07	0.02	1.90	0.07
8	7.28	0.14	8.32	0.57	7.37	0.04	5.75	0.33	3.51	0.18	1.60	0.88	2.65	0.21	2.54	0.20
9	0.07	0.08	0.33	0.30	0.79	0.39	2.41	0.18	0.46	0.02	0.17	0.08	0.26	0.17	1.28	0.02
10	1.69	0.65	1.84	0.08	2.06	0.09	9.55	1.54	0.36	0.02	0.32	0.25	0.64	0.12	8.43	0.46
11	n.d.	–	3.68	3.67	2.08	1.75	n.d.	–	0.93	0.05	0.33	0.20	0.25	0.00	n.d.	–
12	2.41	0.04	3.59	0.38	2.85	0.17	2.45	0.09	0.23	0.01	0.11	0.04	0.12	0.08	0.12	0.01
13	2.87	0.15	4.10	0.17	3.74	0.49	3.24	0.35	n.d.	–	n.d.	–	n.d.	–	0.07	0.01
14	4.16	0.12	5.18	0.43	4.55	0.20	3.99	0.29	n.d.	–	n.d.	–	n.d.	–	0.24	0.03
15	2.14	0.01	3.09	0.05	2.36	0.01	2.59	0.03	n.d.	–	0.09	0.01	0.13	0.02	0.32	0.00
16	1.05	0.12	1.07	0.28	0.44	0.23	1.31	0.29	0.66	0.03	0.79	0.38	0.74	0.25	1.40	0.09
17	n.d.	–	n.d.	–	n.d.	–	1.89	0.44	n.d.	–	n.d.	–	n.d.	–	2.10	0.04
18	1.28	0.02	1.75	0.16	1.28	0.03	1.20	0.05	n.d.	–	0.08	0.01	n.d.	–	0.10	0.02
19	3.02	0.07	3.44	0.29	2.95	0.51	3.42	0.16	0.28	0.01	0.22	0.13	0.35	0.13	0.32	0.03
20	2.07	0.03	1.85	0.42	1.15	0.04	1.05	0.07	n.d.	–	n.d.	–	n.d.	–	0.07	0.04

Table 4 (continued)

Peak	*t*=0 week								*t*=4 week							
	MDGc (μg.g^{-1})		LEC (μg.g^{-1})		MLK (μg.g^{-1})		RCE (μg.g^{-1})		MDGc (μg.g^{-1})		LEC (μg.g^{-1})		MLK (μg.g^{-1})		RCE (μg.g^{-1})	
	Mean	std dev	Mean	std dev	Mean	std dev	Mean	std dev	Mean	std dev	Mean	std dev	Mean	std dev	Mean	std dev
21	2.76	0.15	4.06	0.28	3.97	0.29	3.36	0.36	0.14	0.01	0.11	0.04	0.10	0.04	0.16	0.03
22	3.37	0.10	3.58	0.79	2.88	0.31	2.64	0.25	0.07	0.00	0.09	0.03	n.d.	–	0.07	0.01
23	8.69	0.09	11.36	1.38	9.82	0.04	9.05	0.21	1.06	0.05	0.51	0.22	0.63	0.08	0.90	0.02
24	11.57	0.26	14.82	1.58	11.55	0.67	9.92	0.61	0.47	0.02	0.68	0.32	0.64	0.25	0.69	0.19

[a] Numerical codices given for each volatile compound was reported in Table 3

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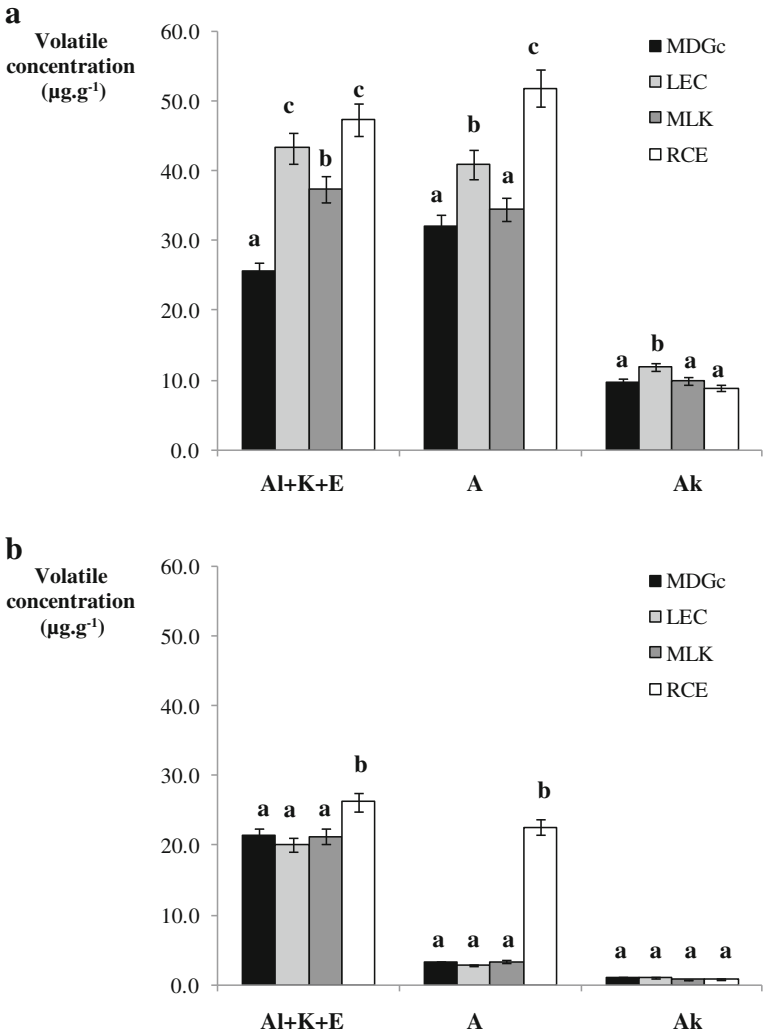

Fig. 2 Main classes of volatile compounds detected in different gelato formulations at **a** *t* 0; **b** *t* 4 weeks. *Bars of histograms with the same letters* are not significantly different (n=3; $p \leq 0.05$). Abbreviations: *MDGc emulsifier* mono- and diglycerides of fatty acids, control sample; *LEC emulsifier* soy phospholipids, *MLK emulsifier* milk phospholipids, *RCE emulsifier* rice phospholipids, *Al* aldehydes, *K* ketones, *E* esters, *A* alcohols, *Ak* alkanes

At time 0, the concentration of alcohols and carbonyl-containing compounds are higher in LEC, RCE and MLK compared to control, being the highest in RCE, as shown in Fig. 2a. Alkane content, on the contrary, is similar in all the considered samples.

3.2 Analytical results at time 4

The effect of prolonged frozen maintenance on properties dealing with organoleptic aspects (colour, texture and volatiles) was evaluated in this work as increases in

production and market for gelato have led to the tendency to extend commercial and domestic storage for longer period of time.

3.2.1 Physical analyses

Hardness of gelato samples increased during storage (Table 1), as values for all the samples were greater at 4 weeks compared to 0 weeks. These findings were in agreement with Soukoulis et al. (2008). These authors reported an increase in instrumental hardness with storage from 4 to 16 weeks, due to the increase of ice crystals size. Recrystallization commonly occurs, indeed, in frozen dessert during storage (Adapa et al. 2000). At 4 weeks, hardness values exhibited the same trend observed at 0 weeks, showing that all the tested emulsifiers exercised the same level of control in ice crystal growth. Regarding stickiness, after 4 weeks of storage, values slightly increased in all samples being LEC the stickiest among them (Table 1), as observed at time 0 week.

After 4 weeks of storage, all gelato samples became slightly brighter (lower L^*) and more yellow (higher b^* and lower $H°$) with an increased colour saturation (higher C) (Table 1), being these changes probably related to an initial fat oxidation phenomena (Ben-Yoseph and Hartel 1998). According to what observed at time 0, the MLK sample remained greener (lower $-a^*$ and higher H°) than the others also at the end of storage.

3.2.2 Volatile compound analysis

The same approach described above was used to evaluate the volatile profile of Italian gelato after 4 weeks of storage, as reported in Table 4. In general, the overall level of volatiles is significantly lower at time 4 weeks for all the considered samples, thus storage seems to result in a general loss of flavour. This is typical for artisanal gelato, which is usually supposed to be consumed in few days from the preparation. Nevertheless, RCE samples still maintain high levels of carbonyl-compounds and alcohols compared to other formulations (see Fig. 2b). Accordingly, while after 4 weeks MLK, LEC and MDGc samples are very closed, RCE still shows a characteristic volatile profile similar to that monitored at t 0.

4 Conclusions

This study represents one of the first literature attempts to characterise Italian gelato, showing the importance of a scientific background when elements of innovation were introduced on product formulation according to producer and consumer demands.

Among tested emulsifiers, LEC and RCE exhibited performances comparable to the control (MDGc) with lower overrun values but higher fat destabilization percentages, showing also stable colorimetric and textural properties during storage. In addition, RCE samples displayed a unique volatile profile, with typical green, fruity and herbal notes that could make this formulation more appreciable by the consumers. These flavour notes were maintained also during the long freezing storage, although most of volatiles was lost in all gelatos. On the contrary, MLK presented the

lowest performance with higher mix viscosity, green colour tones, and lower overrun and hardness values.

In conclusion, the use of LEC and RCE as emulsifiers, alone or in combination also at different levels from those tested in this study, could be of interest for the producers. This aspect deserves thus further study.

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