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Odour investigation of granular polyolefins for food flexible packaging by means of a sensory panel and an electronic nose

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Abstract

A study was carried out of the odour properties of polyolefins destined for food flexible packaging. A total of 25 homo- and copolymers of ethylene and 5 homo- and copolymers of polypropylene in pellet grade were analysed by means of a sensory panel. The principal component analysis performed on sensory data showed a perceptible and quantifiable difference between samples. Generally, polypropylene materials were judged less odorous than the majority of polyethylene pellets, especially less than ethylene vinyl acetate copolymers. The feasibility of using a commercial electronic nose, equipped with 10 metal oxide semiconductors, to discriminate between the odour of plastic materials was also explored. The instrumental results were satisfactory and correlated well with the panel answers, as showed by the statistical approach based upon partial least squares regression. Furthermore, the application of a cluster analysis made it possible to differentiate the samples into strongly, medium and weakly odorous polymers.

Keywords: odour, food packaging, polyolefin, electronic nose, sensory analysis, multivariate analysis.

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Introduction

The odour of a food product is an important quality perception attribute and its alteration could negatively influence consumer satisfaction. In fact, consumer complaints are often due to food taints, particularly related to interactions between products and packaging that can be detrimental to quality and safety (Hotchkiss 1995; Hotchkiss 1997). Therefore, off-odours in packaged foods represent a health and economical problem for industry, associated with a shattered brand image (Huber et al. 2002). Moreover, sensory contamination could also be the cause of legal cases between suppliers and end-users of packaging materials.

In order to safeguard consumer demands and reduce commercial disputes, European law requires that “materials and articles shall be manufactured in compliance with good manufacturing practice so that they do not transfer their constituents to food in quantities which could bring about a deterioration in the organoleptic characteristics thereof” (Reg. CE n. 1935/2004). Unfortunately, this is only a statement of principle that does not provide sensory or analytical threshold limits or specific methods of application. Usually, the evaluation of the contamination level is performed by voluntary rules and procedures.

The complexity of the problem is related to several factors that are peculiar to the odour perception phenomena and chemical nature of the packaging materials. In fact, the sensitivity of the human nose, capable of perceiving very low concentration of volatile compounds (even below 1 ng g⁻¹), imposes a high sensitivity level to analytical determination too. An off-odour can be caused by a single or by a mixture of substances. Odorous molecules are numerous and with few similar characteristics: low molecular weight (generally from 20 to 300 Dalton), polarity, number of atoms rarely higher than 20 and high volatility (Craven et al. 1996; Bartlett et al. 1997). The difficulties in off-flavour identification are also due to the presence of numerous molecules that have the same

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3 odour. But it is also true that the same substance can provide different odours depending on its
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5 concentration (Piringer and Rüter 2000; Ewender et al. 1995).
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10 The different composition of packaging materials involves many sources of contaminants. The most
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12 common volatile compounds that migrate from packaging to foods include residual monomers and
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14 oligomers, residual solvents from printing inks, adhesives, coatings, breakdown products of
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16 polymers and additives (Kim-Kang 1990; Robertson 1993). A great number of releasable
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18 compounds, especially from polyolefin, can be originated during different phases of the processing
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20 of plastic materials, for instance film extrusion, blow or injection moulding, thermoforming, sealing
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22 and corona treatment. In fact, heating the polymer induces a thermal oxidation that leads to the
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24 production of odorous volatile organic compounds (Hodgson et al., 2000). The presence and the
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26 effect of these migrating into packaged foods is commonly assessed by instrumental and sensory
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28 techniques. The latter methods are based upon the odour description of water, food and food
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30 simulants after exposure to packaging materials at accelerated conditions (Kim-Kang 1990) or on
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32 the direct evaluation of the volatile compounds emitted from packaging material. These procedures
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34 require a selected and trained sensory panel able to describe odour properties and to use rating
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36 scales for the quantification of the odour intensity. It is therefore not surprising that sensory
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38 analyses are generally expensive and time-consuming (Tice 1996).
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48 Whereas sensory techniques provide information about overall odour perception, olfactory
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50 thresholds and consumer acceptability, instrumental analyses identify and quantify the single
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52 volatile compounds that compose an odorous mixture. The most common technique used to
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54 evaluate the odour of packaging materials is gas chromatography coupled with mass spectrometry
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56 (Franz et al. 1990; Marin et al. 1992; Linssen et al. 1993; Linssen and Roozen 1994; Sanders et al.
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58 2005, Willoughby et al. 2003; Villberg and Veijanen 1998; Villberg and Veijanen 2001; Bravo et
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60 al. 1992; Hodgson et al. 1998; Pugh and Guthrie 2000; Ziegler 1998), sometimes preceded by

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solid-phase microextraction sampling (Ezquerro et al. 2002, 2003a, 2003b, 2003c, 2003d; Kusch and Knupp 2004;).

In recent years, a fast and reliable alternative has been the electronic nose. In accordance with the classical definition (Gardner and Bartlett 1994), an electronic nose is “an instrument which comprises an array of electronic chemical sensors with partial specificity and an appropriate pattern-recognition system, capable of recognising simple or complex odours”. In recent years, different kinds of multi-sensor systems have been introduced in the market and used for various applications in the food industry (Schaller et al. 1998). Many authors have in fact demonstrated the effectiveness of the e-nose in odour evaluation of packaging materials such as paper (Holmberg et al. 1995), paperboard (Ljungberg Willing et al. 1998) and plastic films (Frank et al. 2001; Van Deventer and Mallikarjunan 2002) and in the determination of sensory contamination of packaged foodstuffs (Heiniö and Ahvenainen 2002). Nevertheless, only few studies that have appeared in literature have focussed on the odour of polymers in pellet form (Hodgson et al. 2000). However, a study performed on plastic resin could provide useful information for defining the material sensory requirements in the supply contract in order to reduce possible litigation between producers and converters. Moreover, it could represent the first step for understanding the influence of the raw material odour on the sensory quality of the film product and therefore the role of the resin in the sensory contamination of packaged food.

The work aimed to investigate the odour of granular polyolefin for food packaging via sensory and instrumental analyses. In particular, the possibility of using a commercial portable electronic nose to discriminate between different plastic materials was explored. The main interest was to evaluate the relationship between the responses from a trained sensory panel and the sensor signals.

Materials and methods

Samples

The chosen polymers were polyolefins commonly used in the manufacturing of packaging films intended to come in contact with foodstuffs, in mono- and multilayer systems as well as in lined cardboard and aluminium packages (Linssen and Roozen 1994). Twenty-five homo- and copolymers of ethylene and five homo- and copolymer of propylene were selected and kindly provided by the Italian Association of producers of printed flexible packaging (GIFLEX).

According to the provider's opinion, polypropylene copolymers with high percentages of ethylene and terpolymers were not considered because they are already known as very odorous. Lots with the most recent production date were chosen. The form of the materials was always pellet grade. Samples were packaged in aluminium foil and kept at room temperature in a dark and dry place until analysis. The sampling procedure was aimed to give representative samples, even if of small size. The provider picked up few kilos of the product from the silos, in a randomised way. Afterwards, in the lab, we took the samples after mixing the pellet for about 2 min. The description of the 30 samples is detailed in Table I. The materials used were of standard processing grades, with different density and melt flow indices (MFI), characterized by the presence/absence of slip or anti-blocking additives.

“[Insert Table I about here]”

Sensory evaluation

The recruitment of the panelists took place within the Faculty of Agriculture of the State University of Milan. The 24 candidates who applied for the study were given a questionnaire to fill in. On the basis of the answers received, 20 volunteers were judged suitable for availability of time, reliability, powers of concentration, verbal skills and motivation. The members of a sensory panel need an ability to detect and describe differences of intensities of a certain odours (Huber et al. 2002; ASTM 1981; Meilgaard 1999). In order to test their capacity in discriminating plastic materials, the

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candidates were submitted to three triangular tests carried out with odorous pellets of polyolefin. Assessors who failed two of these basic tests were excluded from the selection. The final sensory panel consisted of 16 judges: 10 males and 6 females, aged between 19-40 years (19-23: 31%; 24-29: 50%; 30-40: 19%), 20% of which were smokers. The proportion of smokers in the panel is quite similar to the percentage of smokers in the Italian population (22% of citizens more than 14 years old, according to the National Institute of Statistics, ISTAT) and little lower than in Europe (27%). Our main goal was to have a response well representative of reality.

In sensory profile testing, samples are assessed using an agreed-upon list of sensory descriptor terms (Tice 1996). In two sessions, each of 45 min duration, a trained panel leader guided the panelists in the generation of a sensory vocabulary useful for describing the odour of plastic materials. In order to train the panel, 7 materials (PE7, PE9, PE10, PE11, PE14, PE20, PP4) were chosen for their different odorous properties on the basis of the suppliers' declaration. Initially 21 descriptors were generated by the panel. In a second step, all attributes were submitted to the judges who assigned them a score according to their importance in the evaluation of the sample odour (1 not important, 10 very important). Based upon the results obtained, a limited number of descriptors were selected for use in the subsequent descriptive tests. In the sensory profile method only the terms that received an average score ≥ 5 were considered: global intensity, global persistence, solvent, paste, vinyl, paint, acetic acid, alcohol, adhesive, pungent, acrid. The remaining 10 attributes (spicy, benzine, lemon, metal, deterative, vegetable resin, fruity, burnt, acrylic, mothball like) that received a score less than 5 were excluded. The scorecard included the 11 selected attributes and a short description for every score of the nine point evaluation scale: 0 absent, 1 trace, 2 barely perceptible, 3 weak, 4 determinate, 5 pronounced, 6 intense, 7 strong, 8 very strong. All 30 samples were evaluated by 16 assessors in two replicates. During each sensory session, only 4 samples were tested in order to avoid the physiologic weariness of the sense of smell. It is a well known fact that when more than 5-6 samples are submitted to evaluation consecutively, the risk of

loss in the panellist's discrimination capability is high (Pagliarini 2002). Every sample was randomly presented to the panel (to avoid the so-called order effect) with a three digit random code. Test samples included 2 g of polyolefin pellets in 20 ml glass vials covered and closed with aluminium foil, and presented to the sensory panel after 24 hours of storage at room temperature. At the same temperature, the headspace of the vials was smelt by the assessors through a drinking straw.

Instrumental analysis

A commercial portable electronic nose (PEN 2, WMA Airsense Analytics Inc.) was used to analyse the olfactory quality of different plastic polymers. The instrument was equipped with an array of 10 metal oxide semiconductors (MOS) positioned in a small chamber (volume of 1.8 ml). The sensors were different in thickness and chemical composition in order to provide selectivity towards volatile compounds as shown in Table II. These devices, also called oxide or ceramic gas sensors, rely on changes of conductivity induced by the adsorption of odour molecules. The high operating temperature (200-500°C) allowed no interference from water and fast responses and recovery times (Kohl 1992). The detection limit of hot sensors was in the range of 1 mg kg⁻¹.

“[Insert Table II about here]”

The effects of the sample quantity and measurement temperature on instrumental response were studied in order to identify the suitable analytical conditions to be applied during the experimental phase.. Preliminary analyses with increasing sample quantity (1, 2.5 and 5 g) were carried out at 25°C, 50°C and 90°C on three different polypropylene pellets (PP1, PP2 and PP3) that, according to suppliers' expertise, were characterized by a low emission in volatile compounds. We assumed that if the electronic nose was able to discriminate between similar samples, then it would also be able to discriminate between different materials. Preliminary results showed that at the lowest temperature

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it was easier to discriminate different samples and different quantities. For this reason, 5 g of each of the 30 samples were placed in air tight 45 ml glass vials, sealed with a PTFE/silicone septum and a screw cap, stored at 25°C for 1 hour to equilibrate, and analysed at the same temperature. The measurement device sucked the gaseous compounds from the headspace of the sample through the sensor array at 400 ml/min for 360 sec. The sampling flow rate and time of sucking were established through preliminary trials with several samples and offered good discriminating ability. The long time, particularly, permitted to obtain a steady state in the sensor responses. Then a second pump transported the filtered reference air to the sensor array (the flow rate was 600 ml/min) for 780 sec to rinse the system between the two following samples. Ten replicates were taken using separate repeat samples for each kind of plastic specimen.

Multivariate analysis of data

For the sensory and instrumental data, the one-way analysis of variance (ANOVA) was used to determine whether there were any significant differences between the means of each attribute or metal oxide sensor evaluated for all the samples ($P < 0.05$). To identify which polyolefin samples were significantly different, the Fisher's least significant difference (LSD) at the 95% confidence level was calculated (software Statgraphics® Plus version 4.0, 1999).

The principal component analysis (PCA) was used to separately examine the data obtained from the panel sensory and the electronic nose (software XLStat version 4.0, 1999). The instrumental response was also analysed by the cluster analysis (CA) applying an Euclidean distance metric and a complete method of linkage (software Minitab® Release 14, 2004). To execute the CA, according to the broken stick criteria (Todeschini 1998), the first 5 principal components (PCs) were selected (98% of explained variance) in order to limit the overloaded information and noise implied in components with low variance. In order to relate the sensory data to the instrumental data, the

means of all 21 variables (10 sensors and 11 descriptors) were processed using Partial least squares analysis techniques (PLS). This was performed by The Unscrambler® software version 9.2, 2005.

Results and discussion

Sensory analysis

The ANOVA performed on the data obtained from sensory evaluation showed that there is a statistical significant difference ($P < 0.05$) between all the samples and for every descriptor used to describe the plastic materials. As an example, a typical table of one-way analysis of variance for three sensory descriptors is shown (Table III). The results of the applied multiple range test (LSD) to determine which attribute discriminated the samples are reported in Table III. It is evident that all the descriptors contributed to the differentiation between odorous plastic materials, but some attributes such as acrid and paint were less important in discrimination process than the others.

“[Insert Tables III and IV about here]”

As is common in food sensory analysis, the average values were also used to build the sensory profiles of all samples. In Figure 1, the olfactory impact of two very different samples is depicted.

“[Insert Figure 1 about here]”

The polypropylene sample (coded PP1) was almost always assessed with scores lower than 1. On the contrary, the plastic pellets containing ethylene vinyl acetate (code PE19) had high sensory scores, especially for global intensity and persistence, vinyl and acetic acid attributes. Generally, for most samples, attributes such as global intensity and persistence received scores higher than solvent, paste, vinyl, paint, acetic acid, alcohol, adhesive, pungent and acrid (Table IV).

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Nevertheless, the radar plot does not compare the quality odour of a broad number of samples, so a multivariate approach was preferred.

A PCA of the average responses of the sensory panel was performed to detect relationships between all samples. The main components were analysed for their variance percentage to determine their significance. The two first PCs accounted for 91% of the total variability (83% and 8% respectively) (Figure 2).

“[Insert Figure 2 about here]”

The samples were distributed along the PC1 according to their increasing odour intensity. In fact, on the right side are present the samples that produced a strong olfactory impact on sensory panel. To this group belong the copolymers that contain an acetic component (Ethylene Vinyl Acetate, codes PE9, PE19 and PE20) or acrylic acid (Ethylene Acrylic Acid, code PE25). The position of these samples in the biplot (a scatter plot for scores and factor loadings that illustrates mutual relationships between samples and attributes) is explained by the high scores obtained for most descriptors as demonstrated by the same direction of variable vectors. On the contrary, the samples characterized by a poorly perceptible odour and average scores below 2 were grouped on the opposite side. The polymer polypropylene (coded PP1, PP2, PP3, PP4 and PP5) and in particular the least smelling sample (the Ethylene Vinyl Alcohol, coded PE10) resulted belonging to this group. In other words, the positioning on the left side is determined by weakness in most descriptors.

Electronic nose analysis

Figure 3 shows a PCA of the response of the array of 10 sensors to the head space of 30 different granular plastics examined. Each sample is represented by a cluster in order to evaluate the

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3 repeatability of ten replicates. For some materials (PE5, PE6, PE10, PE18, PE19, PE21, PP1, PP3,
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5 PP4, PP5) the repeatability was better than others (PE7, PE12, PE9), characterised by a higher
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7 dispersion in two-dimensional space. As can be seen, it is possible to distinctively separate few
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9 granular plastic (PE5, PE10, PE11, PE18) from the other materials, because large overlaps among
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11 the clusters are evident.
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22 The average values and the standard deviations obtained from the ten replicates are summarised in
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24 Table V. The one-way analysis of variance applied to instrumental data has shown a statistical
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26 significant difference ($P < 0.05$) between all the samples and for every MOS (as an example, a
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28 typical table of ANOVA for the W1C, W5S and W2W sensors is presented in Table VI). In order to
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30 understand which polyolefin pellets were significantly different, the results of the LSD test were
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32 also added in Table V. It is noticeable that the W5S sensor provided the highest response for all
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34 plastic materials and contributed a lot in discrimination of samples. At the contrary, the lowest
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36 responses were provided by W1C, W3C and W5C sensors that, nevertheless have shown a good
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38 ability in differentiation of sample odour.
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46 “[Insert Tables V and VI about here]”
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51 A PCA performed using the average values of the ten replicates was proposed in order to facilitate
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53 the graphical comparison between the 30 samples (Figure 4).
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58 “[Insert Figure 4 about here]”
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Two main PCs were responsible for 78% of total variation. PC1 (54%) describes the odour intensity of the samples, as similarly observed previously by the sensory PCA. In fact, to negative values of PC1 correspond samples with high emission of volatile compounds (PE9, PE19 and PE20) which are particularly reactive with semiconductors W1S, W2S and W5S. These sensors were in inverse relationship to W1C, W3C and W5C that provide lower responses. The electronic nose analysis confirmed that polypropylene and EVOH samples give out a low odour, as previously indicated by the sensory analysis. PC2 (24%) seems to describe the odour quality of samples. In fact, as shown in the biplot of Figure 5, four MOS sensors (W1W, W2W, W3S and W6S) made it possible to separate five samples (PE11, PE12, PE13, PE23 and PE24) from others in function of their chemical nature, since they are all ethylene-metacrylic ionomers. The important contribution of W1W and W2W in ionomeric sample discrimination was also evident observing the LSD results in Table V.

A cluster analysis was performed to investigate the possible similarities between the different samples. Two main branches corresponding to the main groups of samples are shown by the unbroken line cut in figure 5. In the left group, we observed those samples characterized by a weak odour, because they were located in the positive side of the PCA score plot (Figure 4). Likewise, highly smelling granular polyolefins that were positioned on the negative side of PCA score plot were assembled in the right-hand group. Furthermore, two subclasses could be distinguished in the right cluster, as indicated by the broken cut line; the one exclusively composed of ionomeric polymers and the second with a prevalence of EVA copolymers. These pellets were distributed along the first principal component at more negative values than the five ethylene-methacrylic samples (Figure 4). The broken cut line identifies two subclasses also in the left main cluster, nevertheless is not easy to explain this result. In fact, all five polypropylene samples were grouped in the same subclass together with the two EAA copolymer but LDPE and LLDPE granules were separately distributed in different subclasses. Although the broken line suggests the formation of

four groups, examining the chemical nature of the materials, we assume a classification of the 30 samples in three clusters defined as weakly, medially and strongly odorous polymers (Figure 5).

“[Insert Figure 5 about here]”

Correlation of sensory and instrumental results

Partial least squares (PLS) regression is a multivariate technique used to compare two blocks of variables. In this paper, PLS was used to investigate the relationships between the instrumental and sensory variables (respectively X- and Y-variables). In the results from the PLS analysis for all 21 variables and 30 objects, two principal components were found describing in total 32% of the variance of the descriptor results (Table VII). The loading plot obtained from the PLS analysis (Figure 6) performed with all the samples data showed that the sensory descriptors were positively correlated with the W1S, W2S and W5S sensors and negatively correlated with the W1C, W3C and W5C sensors. As expected, the last three variables, which are MOS sensor specific for similar volatile compounds, were located in the same direction in the biplot.

“[Insert Table VII and Figure 6 about here]”

An examination of the estimated regression coefficients (data not shown) revealed that six sensors (marked one by one with a circle in Figure 6) were the most important X-variables in explaining the link between changes in the predictors (e-nose sensors) and variability in the sensory response (Y-variables). Nonetheless, the correlation (r) calculated for each sensory descriptor based on 10 instrumental variable PLS models was rather low, not higher than 0.66 in the best case (Table VIII).

“[Insert Table VIII about here]”

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Since four remaining sensors that poorly correlated with the sensory data (W1W, W2W, W3S and W6S, unmarked with a circle in Figure 6) corresponded to an MOS able to discriminate a particular chemical nature of polymers (Figure 4), the PLS analysis was repeated excluding the data relative to the ionomeric samples (PE11, PE12, PE13, PE23 and PE24). This was carried out in order to obtain a more comprehensive and higher predictive PLS model (Table VII). The last obtained correlation coefficients (Table VIII) clearly showed that the predictability for sensor descriptors was increased in the PLS model considering only the 25 non-ionomeric samples. All r values were comprised from 0.85 to 0.92 (except 0.54 for adhesive) to indicate the high relationships between every sensory attribute and the global instrumental response. Finally, it was possible to conclude that the electronic nose tested in this work was able to provide good correlated results with the sensory data even if not for all kinds of chemical polymers. The only partial correspondence with the sensory results could be explained remembering that the sensor array system measures all volatile compounds, not only the odorous volatile substances which are perceived by the human olfactory sensors (Willing et al. 1998).

Conclusions

The investigation carried out by the sensory profile method revealed that the polymers in pellet form were characterized by a perceptible odour, qualitatively and quantitatively different in function of their plastic composition. The feasibility of using a commercial portable electronic nose was verified. Satisfactory results were obtained because the e-nose showed a notable ability in discriminating between samples releasing different amount of odorous volatiles. Furthermore, the sensor array system also made it possible to distinguish a particular group of materials from others for its chemical nature. On the basis of e-nose data, the cluster analysis identified three sample groups defined as strongly, medially and weakly odorous polymers. Finally a good correlation

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3 appeared from the comparison between the instrumental and sensory results, performed by partial
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5 least squares regression.
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10 These results, however, have been obtained analysing a single production lot for each sample and,
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12 therefore must be confirmed considering several production lots and evaluating a possible age effect
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14 on the odour released by the polyolefin. Works are in progress to investigate these points as well as
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16 to study the effects of the extrusion processes on the production and release of volatile organic
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18 compounds in polyolefin films.
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22 23 24 **Acknowledgements** 25

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Table I: Experimental codes, commercial initials and properties of 30 plastic materials.

Code sample	Sample description	Density (g/cm ³)	MFI (g/10')	Additives
PE1	LDPE	0.925	2.0	no
PE2	LDPE	0.925	2.0	yes
PE3	LLDPE C4 comonomer	0.918	1.0	no
PE4	LLDPE C6 comonomer	0.917	1.0	yes
PE5	LLDPE C8 comonomer	0.919	1.1	no
PE6	LLDPE C8 comonomer	0.919	1.1	yes
PE7	mVLDPE C8 comonomer	0.902	1.0	no
PE8	mVLDPE C8 comonomer	0.902	1.0	yes
PE9	EVA copolymer (4% vinyl acetate)	0.925	2.0	yes
PE10	EVOH	1.190	1.6	no
PE11	Ethylene/methacrylic ionomer (Zn partially salified)	0.950	5.5	no
PE12	Ethylene/methacrylic ionomer (Zn partially salified)	0.940	4.5	no
PE13	Ethylene/methacrylic ionomer (Na partially salified)	0.940	1.3	no
PE14	EAA copolymer (6% acrylic acid)	0.932	9.0	no
PE15	LDPE	0.920	7.5	no
PE16	LDPE	0.921	4.0	no
PE17	LDPE	0.918	7.7	no
PE18	LDPE	0.915	8.0	no
PE19	EVA copolymer (9% vinyl acetate)	0.928	3.0	no
PE20	EVA copolymer (grafted with maleic anhydride)	0.943	3.2	no
PE21	VLDPE C8 comonomer	0.910	2.2	no
PE22	LLDPE C8 comonomer	0.919	1.1	yes
PE23	Ethylene/methacrylic ionomer (Zn partially salified)	0.940	5.4	no
PE24	Ethylene/methacrylic ionomer (Zn partially salified)	0.940	5.4	yes
PE25	EAA copolymer (6% acrylic acid)	0.931	8.0	no
PP1	PP homopolymer	0.900	9.0	yes
PP2	propylene/ethylene random copolymer	0.900	8.0	yes
PP3	propylene/ethylene random copolymer	0.900	8.0	no
PP4	propylene/ethylene heterophasic block copolymer	0.900	0.8	no
PP5	propylene/ethylene block copolymer	0.900	1.2	no

Table II: Codes of sensor arrays of the portable electronic nose.

Sensor code	Compound class
W1C	Aromatic
W5S	Broadrange
W3C	Aromatic
W6S	Hydrogen
W5C	Arom-aliph
W1S	Broad-methane
W1W	Sulphur-organic
W2S	Broad-alcohol
W2W	Sulp-chlor
W3S	Methane-aliph

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Table III. One-way analysis of variance for some sensory descriptors.

Sensory descriptors	Source of variation	Sum of Squares (SS)	Degrees of Freedom (DF)	Mean Square (MS)	F-ratio	p-value
Global Intensity	between groups	858.85	29	29.6155	17.28	<0.05
	within groups	1593.81	930	1.71378		
Solvent	between groups	183.234	29	6.31843	4.63	<0.05
	within groups	1269.66	930	1.36522		
Acrid	between groups	90.7958	29	3.13083	2.83	<0.05
	within groups	1029.5	930	1.10699		

Table IV. Mean and standard deviation of the 11 sensory descriptors for the 30 plastic materials (means with the same letter are not significantly different at the 95% confidence level).

Sample	Global intensity		Global persistence		Solvent	Paste	Vinyl	Paint	Acetic acid	Alcohol	Adhesive	Pungent	Acrid									
PE1	3.3±1.5	ilmn	2.4±1.3	ghi	1.4±1.2	fghi	1.1±1.2	cdefghi	1.2±1.3	defg	1.5±1.5	fghil	1.0±1.3	defg	1.1±1.5	defg	1.5±1.6	ef	1.2±1.5	efg	0.8±1.3	defghilm
PE2	3.1±1.2	hil	2.3±1.3	fgh	1.2±1.1	defgh	0.9±1.3	bdefgh	1.6±1.6	fghi	1.4±1.3	defghil	0.8±1.3	cdef	1.3±1.4	efgh	1.2±1.4	cde	0.8±1.3	bcd	0.5±0.9	abcdefg
PE3	3.4±1.4	lmn	2.5±1.4	hi	0.9±1.2	bdefg	0.8±1.2	bcd	1.0±1.1	bcde	1.4±1.4	defghil	0.8±1.2	cdef	0.8±1.1	abcde	1.5±1.6	ef	0.9±1.3	cdefg	0.9±1.4	fghilm
PE4	2.5±1.5	defg	2.0±1.4	efgh	1.1±1.5	cdefgh	0.8±1.2	bcde	0.4±0.8	ab	1.0±1.3	abcdefg	0.7±0.9	abcde	0.8±1.1	abcdef	0.7±1.1	abcd	0.8±1.1	abcdef	0.6±1.0	abcdefgh
PE5	2.3±1.5	cdef	1.7±1.4	bcd	0.8±1.2	abcde	0.7±1.1	abcd	0.8±1.2	abcde	0.9±1.2	abcdef	0.4±0.8	abcd	0.8±1.2	abcde	0.6±1.0	abc	0.5±0.9	abc	0.4±0.9	abcdefg
PE6	2.0±1.3	abcd	1.5±1.2	abcde	0.7±0.9	abcd	0.5±0.8	abc	0.8±1.0	abcde	0.7±1.0	abc	0.5±1.0	abcd	0.7±1.2	abcde	0.7±1.0	abc	0.4±0.9	abc	0.4±0.9	abcdef
PE7	3.8±1.6	mno	3.3±1.8	lm	1.8±1.8	i	1.5±1.9	hil	1.8±1.9	ghi	1.5±1.7	efghil	1.2±1.6	efg	1.6±2.1	ghi	1.5±1.8	ef	1.9±1.7	il	1.2±1.4	lm
PE8	2.4±1.3	cdefg	1.9±1.3	defgh	0.6±0.7	abc	0.6±1.0	abc	0.4±0.7	ab	0.8±1.1	abcd	0.6±1.0	abcde	0.8±1.2	abcdef	0.9±1.1	bcde	0.5±0.8	abc	0.5±0.9	abcdefg
PE9	4.5±1.2	pq	3.6±1.6	lmn	1.8±1.6	i	1.5±1.8	ghil	2.1±2.1	hi	1.7±1.9	hil	2.1±1.9	hi	2.1±2.1	i	0.8±1.2	abcd	1.8±1.8	hil	1.0±1.4	hilm
PE10	1.4±1.1	ab	1.0±1.1	a	0.4±0.7	ab	0.3±0.8	ab	0.2±0.6	a	0.5±0.8	a	0.1±0.5	a	0.3±0.7	a	0.8±1.1	abcd	0.3±0.7	ab	0.3±0.7	abcd
PE11	4.4±1.1	opq	3.8±1.2	mn	1.5±1.4	ghi	1.8±1.9	l	1.7±2.0	fghi	1.7±1.9	il	2.0±1.9	hi	1.5±1.5	fgh	0.7±0.9	abc	1.5±1.4	ghi	0.9±1.2	ghilm
PE12	2.5±1.4	defgh	1.8±1.4	cdef	0.8±1.2	abcde	0.9±1.3	bcd	0.7±1.2	aobcd	1.1±1.1	abcdefgh	0.5±0.9	abcd	0.8±1.4	abcde	1.0±1.3	bcde	0.6±1.0	abcd	0.6±0.9	abcdefghi
PE13	2.9±1.2	ghil	2.3±1.3	fgh	1.1±1.2	cdefgh	0.8±1.1	abcde	1.0±1.4	bcde	1.4±1.2	defghil	0.8±1.1	bcdef	1.2±1.4	defg	0.9±1.1	abcd	0.6±0.9	abcde	0.5±0.9	abcdefgh
PE14	2.7±1.3	efghi	2.0±1.4	efgh	1.3±1.4	efgh	0.7±1.0	abcd	0.5±1.0	ab	1.6±1.8	ghil	1.2±1.9	efg	1.1±1.5	cdefg	0.9±1.1	bcde	0.7±1.1	abcde	0.8±1.2	cdefghil
PE15	4.2±1.0	opq	3.1±1.2	il	1.5±1.1	hi	1.4±1.7	fghil	1.4±1.8	efgh	1.2±1.4	bcd	0.8±1.2	bcdef	0.9±1.3	abcdefg	2.1±1.7	f	1.3±1.2	fgh	0.9±1.2	efghilm
PE16	2.0±1.1	abcd	1.5±1.1	abcde	0.6±1.0	abc	0.7±1.2	abcd	0.7±1.1	abcd	0.9±1.1	abcdefg	0.3±0.5	abc	0.3±0.7	ab	0.7±0.9	abcd	0.2±0.5	a	0.2±0.5	a
PE17	2.2±1.2	cde	1.5±1.2	abcde	0.5±0.7	ab	0.8±1.0	abcde	1.0±1.4	bcde	0.8±1.1	abcd	0.3±0.8	abc	0.8±1.3	abcde	1.0±1.4	bcde	0.3±0.7	ab	0.3±0.8	abc
PE18	2.5±1.1	defgh	1.9±1.1	efgh	0.9±1.1	abcdef	0.8±1.1	bcd	1.2±1.4	cdef	0.8±1.1	abcde	0.8±1.1	bcdef	0.8±1.1	abcde	0.8±0.9	abcd	0.7±1.1	abcde	0.4±0.8	abcde
PE19	4.8±1.0	q	4.0±1.3	n	1.6±1.7	hi	2.6±1.9	m	2.8±2.2	l	2.0±1.8	l	2.2±2.0	i	1.9±1.8	hi	1.0±1.4	bcde	2.3±1.9	l	1.3±1.6	m
PE20	3.3±1.9	ilm	3.0±1.9	il	1.4±1.7	fghi	1.3±1.7	efghil	1.2±1.8	defg	1.3±1.5	cdefghil	1.3±1.8	fg	1.1±1.5	defg	1.3±1.7	de	1.2±2.0	efg	1.1±1.7	ilm
PE21	2.2±1.3	cde	1.5±1.0	abcde	0.6±0.9	abcd	0.7±1.1	abcd	0.9±1.3	bcde	0.8±1.0	abcd	0.3±0.7	abc	0.6±0.9	abcd	0.7±1.1	abc	0.3±0.7	ab	0.4±0.9	abcdef
PE22	2.2±1.6	cde	1.6±1.5	abcde	0.8±1.0	abcdef	0.5±0.8	abc	0.6±0.9	abcd	1.1±1.3	abcdefghi	0.6±1.1	abcde	1.0±1.4	bcdefg	0.8±1.1	abcd	0.7±1.2	abcde	0.5±1.0	abcdefg
PE23	2.9±1.4	fghil	2.1±1.4	efgh	0.8±1.0	abcd	1.2±1.2	defghil	0.8±1.1	abcde	1.0±1.1	abcdefg	0.8±1.2	cdef	0.8±1.3	abcdef	1.2±1.5	cde	1.1±1.5	defgh	0.7±1.2	abcdefghi
PE24	2.2±1.5	cde	1.8±1.4	cdefg	0.5±1.0	abc	0.6±1.1	abc	0.4±0.7	ab	1.2±1.3	bcd	0.5±1.0	abcd	0.9±1.2	abcdef	1.2±1.3	cde	0.3±0.9	ab	0.4±0.6	abcde
PE25	4.0±1.2	nop	3.1±1.1	l	1.4±1.2	fghi	1.6±1.6	il	2.1±1.8	i	1.7±1.6	il	1.5±1.7	gh	1.6±1.5	ghi	0.9±1.3	bcde	1.3±1.4	fgh	0.7±1.1	bcd
PP1	1.4±1.2	a	1.0±1.0	a	0.3±0.7	a	0.2±0.5	a	0.4±0.8	ab	0.8±1.1	abcd	0.5±0.8	abcd	0.4±0.8	ab	0.3±0.7	a	0.5±0.9	abc	0.3±0.6	abc
PP2	1.5±1.1	ab	1.1±1.0	ab	0.5±0.8	ab	0.4±0.9	ab	0.3±0.8	a	0.7±1.1	ab	0.5±0.9	abcd	0.3±0.9	ab	0.8±1.0	abcd	0.3±0.7	ab	0.2±0.6	a
PP3	1.5±1.2	ab	1.2±1.2	abc	0.4±0.8	ab	0.5±0.9	abc	0.6±0.9	abc	0.5±0.9	a	0.2±0.7	ab	0.5±1.0	ab	0.5±0.8	ab	0.2±0.7	a	0.4±1.0	abcde
PP4	1.8±1.2	abc	1.3±1.1	abcd	0.8±0.9	abcde	0.5±0.9	abc	0.4±0.8	ab	0.8±1.0	abcde	0.3±0.7	abc	0.8±1.1	abcde	0.5±0.8	ab	0.4±0.9	abc	0.2±0.5	ab
PP5	2.1±1.3	bcd	1.5±1.1	abcde	0.6±0.9	abc	0.8±1.1	abcde	0.7±1.1	abcd	0.9±1.1	abcdef	0.5±1.0	abcd	1.1±1.2	cdefg	0.8±1.1	abcd	0.4±0.9	abc	0.4±0.9	abcdef

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Table V. Mean and standard deviation of MOS response values for the 30 plastic materials (means with the same letter are not significantly different at the 95% confidence level).

Sample	W1C	W5S	W3C	W6S	W5C	W1S	W1W	W2S	W2W	W3S
PE1	0.84±0.02 ^{mn}	6.17±0.35 ^{hi}	0.95±0.02 ^l	0.98±0.06 ^{abc}	0.94±0.02 ^o	0.94±0.04 ^{abc}	1.12±0.02 ^a	0.90±0.05 ^{ab}	1.12±0.01 ^{abc}	0.98±0.00 ^{cd}
PE2	0.74±0.02 ^{hi}	6.37±0.62 ^{hi}	0.84±0.02 ^{gh}	1.01±0.06 ^{cdefghi}	0.85±0.02 ^{il}	1.04±0.04 ^{fgh}	1.06±0.01 ^a	1.03±0.05 ^{efg}	1.09±0.01 ^{abc}	1.03±0.01 ^{mno}
PE3	0.81±0.01 ^{lm}	3.40±0.35 ^d	0.88±0.01 ⁱ	1.00±0.01 ^{cdefgh}	0.89±0.01 ^m	1.12±0.01 ^{il}	1.05±0.01 ^a	1.05±0.02 ^{efgh}	1.05±0.01 ^{ab}	1.00±0.00 ^{efg}
PE4	0.77±0.02 ⁱ	4.78±0.48 ^{fg}	0.83±0.02 ^g	1.00±0.07 ^{bcdefg}	0.84±0.01 ^{hi}	1.07±0.05 ^{ghi}	1.08±0.01 ^a	1.07±0.05 ^{ghilm}	1.02±0.01 ^{ab}	0.99±0.01 ^{de}
PE5	0.69±0.01 ^f	11.14±0.75 ^{mn}	0.73±0.01 ^e	0.96±0.02 ^{ab}	0.75±0.01 ^g	1.10±0.04 ^{hil}	1.13±0.01 ^a	0.97±0.02 ^{cd}	1.09±0.01 ^{abc}	0.97±0.00 ^{ab}
PE6	0.76±0.01 ⁱ	4.37±0.25 ^{ef}	0.82±0.01 ^g	1.01±0.01 ^{cdefgh}	0.84±0.01 ^{hi}	1.13±0.02 ^{il}	1.07±0.02 ^a	1.06±0.03 ^{fghil}	1.08±0.00 ^{abc}	1.02±0.00 ^{hilm}
PE7	0.40±0.02 ^a	18.16±2.11 ^r	0.43±0.02 ^a	1.07±0.03 ^{lm}	0.47±0.02 ^a	1.81±0.12 ^v	1.52±0.05 ^{cd}	1.39±0.10 ^r	1.59±0.08 ^f	1.04±0.02 ^{no}
PE8	0.95±0.05 ^p	3.47±0.46 ^{de}	1.03±0.03 ⁿ	0.98±0.05 ^{abcdef}	1.01±0.03 ^{pq}	0.91±0.03 ^{ab}	1.47±0.16 ^{bcd}	0.86±0.04 ^a	1.20±0.06 ^{cde}	0.98±0.01 ^{cd}
PE9	0.51±0.04 ^c	15.39±3.18 ^q	0.53±0.06 ^b	1.00±0.01 ^{cdefgh}	0.54±0.06 ^b	1.73±0.33 ^u	1.15±0.11 ^a	1.49±0.22 ^s	1.28±0.05 ^{de}	1.01±0.00 ^{fgh}
PE10	1.15±0.03 ^s	1.20±0.07 ^a	1.16±0.02 ^p	1.01±0.04 ^{cdefgh}	1.13±0.02 ^t	0.89±0.03 ^a	1.02±0.00 ^a	0.87±0.03 ^a	0.98±0.01 ^a	0.96±0.01 ^a
PE11	0.61±0.03 ^e	5.98±1.34 ^h	0.62±0.06 ^c	1.01±0.01 ^{cdefghi}	0.75±0.01 ^g	1.52±0.06 ^t	3.31±0.33 ^f	1.31±0.06 ^q	6.01±0.45 ^m	1.07±0.02 ^p
PE12	0.81±0.04 ^{lm}	3.49±0.77 ^{de}	0.87±0.04 ^{hi}	1.07±0.03 ^m	0.94±0.03 ^o	1.25±0.08 ^{opq}	2.57±0.37 ^e	1.36±0.15 ^{qr}	1.85±0.32 ^g	1.13±0.06 ^q
PE13	0.72±0.07 ^{gh}	8.07±2.26 ^l	0.73±0.05 ^e	0.99±0.01 ^{bcdefg}	0.83±0.02 ^h	1.35±0.06 ^r	2.78±0.42 ^e	1.13±0.04 ^{mno}	4.80±0.42 ^l	1.00±0.01 ^{def}
PE14	1.03±0.02 ^r	1.55±0.05 ^{ab}	1.06±0.02 ^o	1.06±0.14 ^{lm}	1.05±0.02 ^{rs}	0.96±0.07 ^{bcde}	1.02±0.02 ^a	0.95±0.10 ^{bcd}	0.98±0.01 ^a	0.96±0.02 ^{ab}
PE15	0.71±0.05 ^{fg}	5.94±0.46 ^h	0.73±0.05 ^e	0.99±0.02 ^{abcdef}	0.75±0.05 ^g	1.21±0.11 ^{mno}	1.08±0.03 ^a	1.15±0.10 ^{nop}	1.06±0.01 ^{abc}	0.99±0.02 ^{de}
PE16	0.47±0.01 ^b	12.68±0.98 ^o	0.55±0.01 ^b	1.05±0.04 ^{ilm}	0.58±0.01 ^c	1.31±0.04 ^{qr}	1.11±0.02 ^a	1.18±0.03 ^{op}	1.08±0.04 ^{abc}	1.03±0.01 ^{ilmn}
PE17	0.61±0.02 ^e	11.81±0.76 ^{no}	0.67±0.01 ^d	0.95±0.04 ^a	0.70±0.01 ^f	1.16±0.04 ^{lmn}	1.07±0.01 ^a	1.05±0.04 ^{efghi}	1.02±0.01 ^{ab}	0.97±0.01 ^{bc}
PE18	0.54±0.01 ^d	13.63±0.72 ^p	0.61±0.01 ^c	0.98±0.04 ^{abcd}	0.64±0.01 ^e	1.29±0.04 ^{pqr}	1.08±0.01 ^a	1.11±0.03 ^{hilmn}	1.04±0.00 ^{ab}	0.99±0.00 ^{cd}
PE19	0.48±0.02 ^{bc}	12.17±0.74 ^o	0.54±0.02 ^b	1.02±0.02 ^{defghi}	0.55±0.02 ^b	1.15±0.02 ^{lmn}	1.44±0.09 ^{bc}	1.12±0.02 ^{ilmn}	1.33±0.04 ^e	1.03±0.01 ^{lmn}
PE20	0.55±0.03 ^b	10.71±0.95 ^m	0.60±0.03 ^c	1.01±0.03 ^{cdefghi}	0.61±0.02 ^d	1.44±0.07 ^s	1.45±0.11 ^{bcd}	1.30±0.07 ^q	1.29±0.04 ^{de}	1.01±0.02 ^{ghi}
PE21	0.60±0.01 ^e	12.11±0.57 ^d	0.65±0.01 ^d	1.01±0.02 ^{cdefgh}	0.68±0.01 ^f	1.24±0.01 ^{op}	1.21±0.03 ^{ab}	1.01±0.03 ^{defg}	1.16±0.01 ^{bcd}	0.96±0.01 ^{ab}
PE22	0.88±0.03 ^o	7.00±0.48 ⁱ	0.94±0.02 ^l	1.03±0.08 ^{ghilm}	0.95±0.02 ^o	1.00±0.03 ^{cdefg}	1.09±0.02 ^a	1.00±0.05 ^{cde}	1.08±0.01 ^{abc}	1.02±0.01 ^{hil}
PE23	0.76±0.06 ⁱ	6.17±2.32 ^{hi}	0.77±0.05 ^f	1.01±0.01 ^{cdefghi}	0.86±0.03 ^l	1.22±0.07 ^{nop}	2.69±1.56 ^e	1.15±0.06 ^{nop}	3.25±0.58 ⁱ	1.05±0.03 ^o
PE24	0.86±0.05 ^{no}	5.66±0.38 ^{gh}	0.88±0.04 ⁱ	1.03±0.01 ^{hilm}	0.91±0.03 ⁿ	1.16±0.07 ^{lmn}	1.72±0.07 ^d	1.21±0.06 ^p	2.12±0.12 ^h	1.08±0.02 ^p
PE25	0.77±0.03 ⁱ	6.50±0.59 ^{hi}	0.83±0.03 ^g	1.03±0.06 ^{ghil}	0.85±0.02 ^{hil}	1.10±0.06 ^{hil}	1.03±0.01 ^a	1.10±0.07 ^{hilmn}	1.04±0.02 ^{ab}	1.02±0.02 ^{hilm}
PP1	0.97±0.04 ^p	1.71±0.09 ^{ab}	0.99±0.03 ^m	0.98±0.03 ^{abcde}	0.99±0.04 ^p	1.01±0.02 ^{defg}	1.05±0.03 ^a	1.01±0.03 ^{defg}	1.05±0.02 ^{ab}	1.03±0.02 ^{hilmn}
PP2	0.95±0.05 ^p	2.14±0.41 ^{abc}	0.99±0.04 ^m	1.00±0.01 ^{cdefgh}	0.99±0.04 ^p	1.02±0.05 ^{efg}	1.02±0.00 ^a	1.00±0.05 ^{def}	1.04±0.02 ^{ab}	1.02±0.02 ^{ghil}
PP3	1.01±0.02 ^{qr}	1.54±0.10 ^{ab}	1.04±0.02 ⁿ	1.02±0.01 ^{efghi}	1.03±0.02 ^{qr}	1.00±0.02 ^{cdef}	1.04±0.01 ^a	1.03±0.03 ^{efg}	1.06±0.01 ^{abc}	1.05±0.01 ^o
PP4	0.80±0.02 ^l	2.20±0.12 ^{bc}	0.84±0.02 ^g	1.02±0.02 ^{efghi}	0.85±0.02 ^{il}	1.14±0.03 ^{ilm}	1.03±0.01 ^a	1.12±0.04 ^{lmno}	1.06±0.01 ^{abc}	1.04±0.01 ^{no}
PP5	1.00±0.03 ^q	2.73±0.35 ^{cd}	1.06±0.02 ^o	1.02±0.05 ^{fghi}	1.05±0.02 ^s	0.94±0.03 ^{abcd}	1.02±0.00 ^a	0.94±0.04 ^{bc}	1.02±0.01 ^{ab}	0.98±0.00 ^{cd}

Table VI. One-way analysis of variance for some e-nose sensors.

e-nose sensors	Source of variation	Sum of Squares (SS)	Degrees of Freedom (DF)	Mean Square (MS)	F-ratio	p-value
W1C	between groups	10.2955	29	0.355017	335.91	<0.05
	within groups	0.28536	270	0.00105689		
W5S	between groups	6207.54	29	214.053	187.59	<0.05
	within groups	308.085	270	1.14106		
W2W	between groups	389.392	29	13.4273	470.74	<0.05
	within groups	7.70136	270	0.0285236		

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Table VII. The results from the PLS analysis.

PC	All samples				Without ionomeric samples			
	Explained X-variance	Explained X-variance (cumulative)	Explained Y-variance	Explained Y-variance (cumulative)	Explained X-variance	Explained X-variance (cumulative)	Explained Y-variance	Explained Y-variance (cumulative)
1	54	54	31	31	64	64	34	34
2	23	78	1	32	12	76	4	38
3	5	83	3	35	12	88	2	40

Table VIII. Contributing proportions in PLS models calculated from all samples and excluding ionomeric polymers.

Sensory attributes	Correlation (r)	
	All samples	Without ionomeric samples
Global intensity	0.61	0.87
Global persistence	0.66	0.90
Solvent	0.57	0.89
Paste	0.64	0.92
Vinyl	0.63	0.87
Paint	0.49	0.85
Acetic acid	0.53	0.87
Alcohol	0.55	0.89
Adhesive	0.20	0.54
Pungent	0.60	0.92
Acrid	0.53	0.91

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Figure 1. Sensory profiles of PE19 e PP1 samples.

Figure 2. Factor loadings and principal component score plot extracted from description sensory data.

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Figure 3. Principal component score plot extracted from e-nose data (ten replicates).

A PCA plot showing the relationship between 24% of the variance (PC 2) on the y-axis and 54% of the variance (PC 1) on the x-axis. The plot includes 24 sampling points (PE 1 to PE 25) and 10 environmental variables (W1S, W2S, W3S, W5S, W6S, W1W, W2W, W3C, W5C, W6C). The sampling points are represented by black dots, and the environmental variables are represented by black lines. The plot shows a clear separation between the sampling points and the environmental variables, with the sampling points clustered in the lower right quadrant and the environmental variables clustered in the upper left quadrant.

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Figure 5. Dendrogram that describes the three clusters of samples: (a) weakly, (b) medially and (c) strongly odorous polymers.

Figure 6. Loading plot from PLS analysis.

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15 Table IV. Mean scores of the 11 sensory descriptors for the 30 plastic materials (Means with the
16 same letter are not significantly different at the 95% confidence level).
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18 Table V. Mean and standard deviation of MOS response values for the 30 plastic materials (means
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42 Figure 4. Factor loadings and principal component score plot extracted from e-nose data (average
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45 Figure 5. Dendrogram that describes the three clusters of samples: (a) weakly, (b) medially and (c)
46 strongly odorous polymers.
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48 Figure 6. Loading plot from PLS analysis.
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