Volatile Compounds Extracted from Polypropylene Sheets by Hot Water: Influence of the Temperature of Sheets Injection

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SYNOPSIS

The influence of the formulation of polypropylene (PP) on the organoleptic properties of the foodstuff in contact is of great importance for the quality of the product. A study was made on PP pellets degraded and not degraded and pointed out the presence and olfactive importance of volatile components extracted from PP pellets by hot water. Plastic packaging materials correspond to a further step of manufacturing: the injection step, and this is often conducted at high temperature. PP (not degraded) and PP-CR (degraded) were transformed into sheets at several temperatures; Lickens–Nickerson extracts were made and allowed the quantification of volatile compounds already identified. A statistical analysis showed that temperature was a very significant parameter. An increasing injection temperature (275 or 300°C) creates increasing quantities of volatiles. This was well correlated with the sensory analysis made on the organic extracts of the sheets and also directly on molded cups. © 1993 John Wiley & Sons, Inc.

INTRODUCTION

Optimization of plastic food packaging is a main concern for plastic manufacturers. Beside the essential optimization of their mechanical properties and the necessary minimization of the migration of gases, additives, and monomers from or through the material to the food, occasional organoleptic contaminations demonstrated the importance of fundamental studies on the migration of trace contaminants susceptible to modify the organoleptic quality of food.[1-19]

A recent study led us to identify a series of minor volatiles with strong odors that could be extracted from polypropylene (PP) pellets by hot water and that are, therefore, susceptible to alter the flavor of food heated in contact with such materials.[20] These include aliphatic aldehydes, 2-methylketones, quinones, and some disubstituted phenols found in a dichloromethane fraction and some aliphatic alcohols and acids found in an ether fraction, both fractions obtained by high-performance liquid chromatography (HPLC) of a Likens–Nickerson flavor extract.

Since the influence of the injection molding of the pellets was not considered in this former study, our aim was to point out the chemical origin of the odor of PP items (cups, tablets) injection molded at high temperatures. Even though the presence of a peroxide agent did not significantly modify the volatile composition of the PP pellets,[20] the two types of pellets were used to observe if some differences could be revealed by the heating step of the injection.

MATERIALS AND METHODS

Materials

As described earlier, two types of PP pellets (Hostalen PP, Société Française Hoechst) differing in their peroxide contents were used for injection

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molding: the PP type did not contain any peroxide, whereas PP-CR contained 0.22% of peroxide. Pellets were transformed into sheets or cups using a Battenfeld (BAT 800) press heated at several temperatures (from 220 to 320°C every 10°C for the cups and at 250, 275, and 300°C for the sheets). Before analysis, the sheets and the cups were ground to small pieces using a blade grinder. The sheets were made and analyzed in duplicate. Solvent purities and purification techniques were obtained and realized as previously reported.[20]

Analysis of Volatiles

The general procedure used for analyzing volatiles is schematized in Figure 1. Extractions were performed on ground sheets using a Likens and Nickerson system;[20] the organic extracts thus obtained were separated by HPLC into three fractions of different polarity using, respectively, pure pentane, dichloromethane, and ether as eluents. Although quantitatively major, the first fraction was discarded as odorless. After concentration, the two last fractions were analyzed since they were previously shown to contain all the constituents responsible for the odor of the extract. The odorous components of the fractions were selected from gas chromatographic effluent sniffing as described by Etiévant et al.[13] These compounds were identified by GC–MS and quantified with the internal standard method.[20]

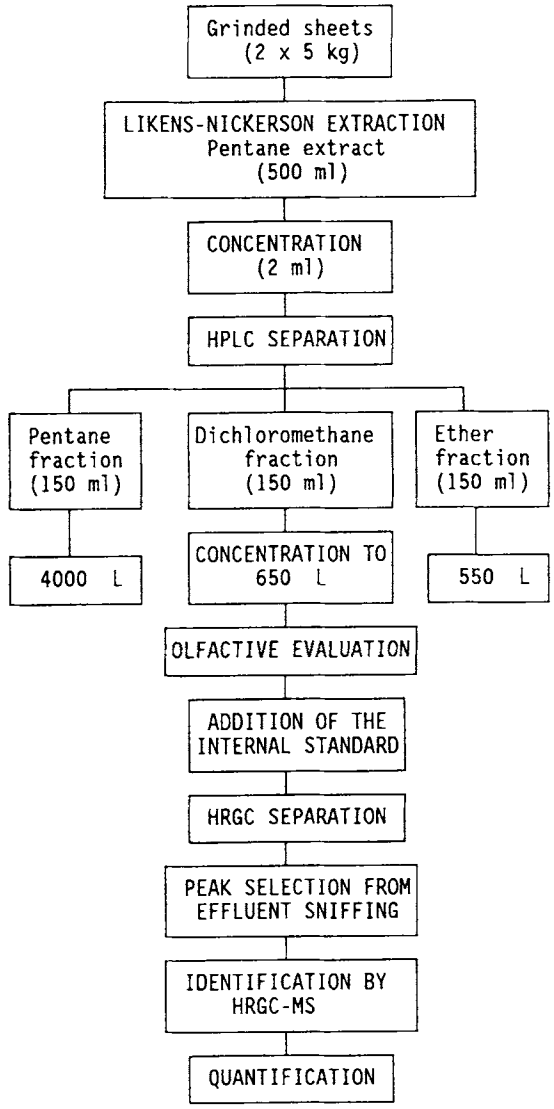

Figure 1 Procedure used to analyze volatiles extracted from plastic sheets.

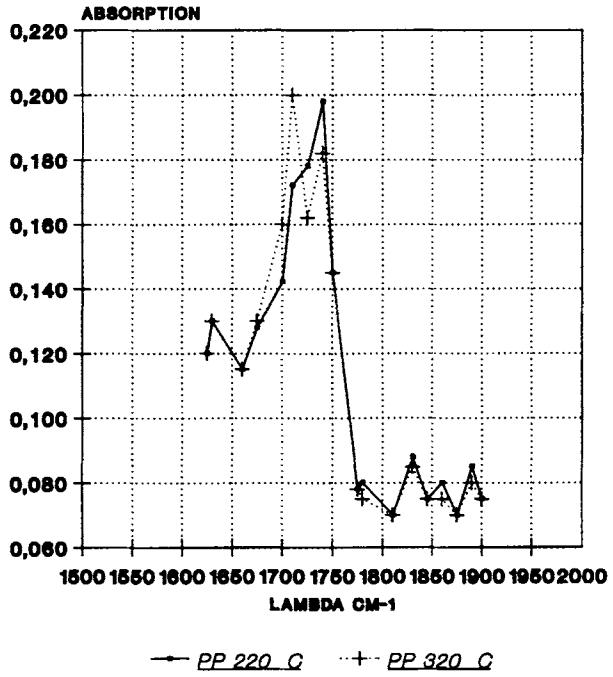

Figure 2 Infrared spectra of films obtained from PP-molded cups.

A simple analysis of variance was used to make an estimation of the significance of the difference of concentration for each compound in the sheets made at three different temperatures. When necessary, a Duncan test was applied to visualize the difference within the three samples.

Infrared Spectroscopy

Plastic cups ground to pieces were pressed with a Carver press (5T) at 180°C into 150 μm-thick films. Infrared spectra of the films were recorded using a Perkin-Elmer spectrometer (IRFT 1710) at a 2 cm^{-1} resolution.

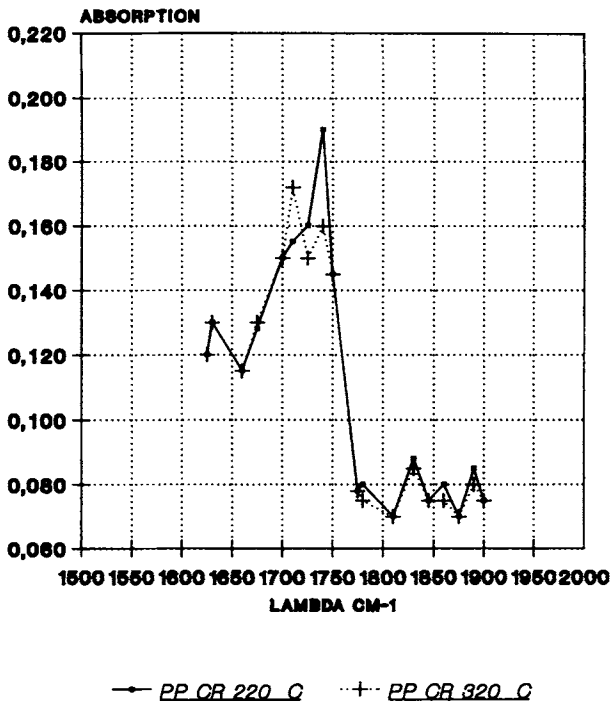

Figure 3 Infrared spectra of films obtained from PP-CR-molded cups.

Sensory Analyses

Odor quality and intensity of the cups were given directly from the production by three people in the plant. The same parameters were evaluated in the laboratory by three trained people smelling the organic extracts obtained from the sheets. The extracts were given in random order in small coded vials.

RESULTS AND DISCUSSION

The sensory evaluation of the cups gave no difference at a particular temperature between those made from PP or from PP-CR pellets (Table III). This result reinforces our previous statement concerning the small influence of the chemical degradation of the polymer upon the composition of volatiles extractable by hot water. However, at temperatures higher than 290°C, the cups were described as more odorous with pungent odors reminding one of overheated caramel and burning plastic.

The infrared spectra of the films made from PP and PP-CR cups injected at 220 and 320°C are given in Figures 2 and 3. They show a decrease of the 1750 cm^{-1} band that is explained by a decrease of the

Table I Mean Concentrations (g/kg PP) of Volatile Components Extracted by Steam from PP-CR Sheets

Name of the Constituent	Concentration in Sheets Made at 250°C	275°C	300°C	Significance of the Difference
Heptanal (C)	4.95	4.27	5.04	NS*
4-Methyl-2-heptanone (C)	46.70	52.50	68.80	NS*
Methyl ketone (C)	25.30	23.10	31.20	NS*
Octanal (C)	6.57	7.18	10.80	NS*
Nonanal (C)	9.04	7.94	11.40	250, 275 = 300
Decanal (C)	6.57	5.91	12.30	250, 275 = 300
Undecanal (C)	5.67	4.97	8.46	250, 275 = 300
Dodecanal (C)	5.76	7.80	12.70	250, 275 = 300
2,6-di-*t*-Butylquinone (C)	237.00	235.00	397.00	250, 275 = 300
2,6-di-*t*-Butylphenol (C)	398.00	409.50	440.10	NS*
Tetradecanal (C)	5.85	6.46	13.80	250, 275 = 300
2,6-di-*t*-Butyl-4-ethylphenol (C)	19.80	26.60	41.50	250, 275 = 300
2,6-di-*t*-Butyl-4-propylphenol (C)	26.60	10.04	39.80	250, 275 = 300
Decanol (e)	10.35	3.60	12.56	275 = 250 = 300
Dodecanol (e)	19.60	8.37	32.31	275 = 250 = 300
Tetradecanol (e)	7.02	2.52	5.76	275 = 250 = 300
Tetradecanoid acid (e)	56.70	94.41	136.90	250 = 275 = 300
Hexadecanol (e)	11.97	7.29	15.93	275 = 250 = 300
Hexadecanoid acid (e)	208.80	197.10	228.60	NS*
Octadecanol (e)	202.20	84.60	316.80	275 = 250 = 300
Sum	1314.45	1199.16	1841.76	

NS*: not significantly different; =: significantly different ($P < .05$); (C): compound quantified in the dichloromethane HPLC fraction; (e): compound quantified in the ether HPLC fraction.

concentration of a phenolic antioxidant and by a parallel increase of the concentration of some carbonyl constituents that could be responsible for the burned odor of the cups. This technique was previously used by Frostling et al.[21] to test the performance of different antioxidants in PP. At 250°C, they observed a similar absorption band corresponding to carbonyl substances only in a sample in which no antioxidant was added. According to our own results, this band occurred in all samples when the temperature of the injection press was raised over 280°C.

To obtain more precise information on the chemical origin of undesirable odor of the cups, aromatic extracts were made from sheets, similarly prepared, using an extraction technique involving a steam distillation associated with a codistillation of pentane. The steam distillation was chosen because it simulates a number of drastic interactions between food and plastic material, as met when making coffee in an electric coffee machine, rehydrating lyophilized food in a plastic bowl, or heating food in its package in a microwave oven.

The sensory analysis of the organic extracts made from the six types of sheets (three temperatures for PP and PP-CR pellets) showed that the intensity of their odors increased with the temperature of the press (Table I). It can be noticed that some people used the descriptor "burned" to describe only the samples made at 300°C. This result is in agreement with the sensory description of the cups, thus showing that the odor of the extracts were representative of that of the plastic material.

A quantitative analysis of constituents selected for their odors was made in the two odorous fractions obtained from the extracts by HPLC.[20] The results are given in Tables I and II. For a particular formulation (PP or PP-CR), an increase of most compounds is observed for the sum of the concentrations between 275 and 300°C. Looking at the individual compounds, the increase is generally more significant over 275°C than below it. This correlates well with the increase of the odor of the extracts with the highest temperature of the injection press, indicating the validity of the selection that we made.

In the samples without the peroxide (PP sheets),

Table II Mean Concentrations (g/kg PP) of Volatile Components Extracted by Steam from PP Sheets

Name of the Constituent	Concentration Sheets Made at 250°C	275°C	300°C	Significance of the Difference
Heptanal (C)	3.15	6.10	11.70	NS*
4-Methyl-2-heptanone (C)	18.50	53.10	97.20	250 = 275
Methyl ketone (C)	15.80	28.35	39.80	250 = 275
Octanal (C)	5.40	8.73	11.25	NS*
Nonanal (C)	12.20	12.51	19.98	NS*
Decanal (C)	10.28	11.16	15.57	NS*
Undecanal (C)	10.20	6.39	15.66	NS*
Dodecanal (C)	12.51	7.92	17.73	NS*
2,6-di-*t*-Butylquinone (C)	142.20	84.80	144.90	NS*
2,6-di-*t*-Butylphenol (C)	446.40	422.10	531.90	250, 275 = 300
Tetradecanal (C)	9.27	9.99	25.47	250, 275 = 300
2,6-di-*t*-Butyl-4-ethylphenol (C)	47.34	60.60	76.95	NS*
2,6-di-*t*-Butyl-4-propylphenol (C)	7.47	13.68	21.51	NS*
Decanol (e)	11.97	13.05	13.77	NS*
Dodecanol (e)	14.40	14.49	13.68	NS*
Tetradecanol (e)	2.52	2.34	1.74	NS*
Tetradecanoic acid (e)	69.50	109.50	160.90	250 = 275 = 300
Hexadecanol (e)	9.72	9.54	10.98	NS*
Hexadecanoic acid (e)	245.70	287.10	424.80	250 = 275 = 300
Octadecanol (e)	199.98	194.40	174.60	NS*
Sum	1294.51	1355.85	1830.09	

NS*: not significantly different; =: significantly different ($P < .05$); (C): compound quantified in the dichloromethane HPLC fraction; (e): compound quantified in the ether HPLC fraction.

Table III Odors Intensity and Description of the Organic Extracts of Sheets of PP

Injection-Molding Temperature	Formulation PP		Formulation PP-CR	
	Intensity (0–5)	Description	Intensity (0–5)	Description
250°C	1–2	Hot plastic, gaz	1–2	Hot plastic, gaz
275°C	2+	Plastic	2+	Plastic
300°C	3–4	Unpleasant, burnt	3–4	Caramel, burnt

the concentration of most volatiles selected was not significantly affected by the temperature of the press (nine among thirteen in the dichloromethane fraction and five among seven in the more polar ether fraction). This effect is more important in the samples containing initially 0.2% of the peroxide agent since eight substances among thirteen selected increased significantly in the dichloromethane fraction and five of seven in the ether fraction.

These results confirm the conclusion given by Fernandes et al.[19] indicating a degradation of the polymer into aldehydes and ketones when the temperature of the press was raised from 280 to 320°C. Nevertheless, it is likely that the compounds we quantified are not responsible for the modification of the IR spectrum because 1710 cm^{-1} corresponds to a carbonyl absorption of ketones, which are minor constituents in the polymer (< 100 ppb), and not of quinones or aliphatic aldehydes, which are much more abundant. Other volatiles, not selected in this study as odorless, or nonvolatile compounds must be responsible for it.

Even though a new descriptor "burned" was only used in the samples made at 300°C, no qualitative differences could be noted in the corresponding chromatograms. This odor cannot be explained by the presence or the increase of the concentration of one particular volatile component; that is why the analysis of the results is not so easy. The "burning plastic" odor might come from the different percentages of volatile components in the fractions corresponding to the sheets injection molded at increasing temperatures. The only way to reduce it is, in fact, to reduce the injection temperature itself.

CONCLUSIONS

This study showed that a very important parameter in the organoleptic properties of injection-molded PP is the temperature of this processing step. It was necessary to point out this fact since the food is directly in contact with the molded plastic packaging.

PP could be considered as "organoleptic packaging" when it is processed at a low temperature. The plastic processers must be aware of this problem and of the consequences of processing in high temperatures.

The increasing demand for single-serving meals requires the upgrading of the quality of the food and also of the packaging material. The recommendation showed in this article could be one step for accomplishing this.

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