FOOD PACKAGING

Food Packaging Compendium

PerkinElmer®
For the Better

FOOD PACKAGING

Table of Contents

Food Packaging

APPLICATION NOTE

Thermal Analysis

Importance of DSC Rapid Cooling for the Analysis of Plastic Microwave Food Trays

DSC 8500

Introduction

Differential scanning calorimetry (DSC) is widely used to characterize the thermophysical properties of polymers. DSC can measure important thermoplastic properties including:

- Melting temperature
- Heat of melting
- Percent crystallinity
- Tg or softening
- Crystallization
- Presence of recyclates/regrinds
- Nucleating agents
- Plasticizers
- Polymer blends (presence, composition and compatibility)

Most DSC experiments on polymers are conducted by heating from ambient conditions to above the melting temperature. But, for some thermoplastics, which do exhibit differences during processing, standard heating DSC may not show any significant differences. A more sensitive test, for detecting subtle, but important differences between different batches of a given thermoplastic, is the DSC isothermal crystallization test.

During the manufacture of plastic products, such as bottles, fibers, films, containers, housings, pipes and trays, the thermoplastic is melted, cooled, thermoformed and crystallized. The complete

PerkinElmer®
For the Better

study of the behavior of plastics, which are melt-processed, requires having a DSC instrument that is capable of rapid cooling to simulate and fully explore the properties of these materials.

To study the melt-crystallization properties of polymers, several informative DSC tests can be conducted:

- Isothermal crystallization (at a single or multiple temperatures)
- Cooling (at different rates from very fast to normal)
- Reheating after cooling (at different rates)

The successful measurement of these particular tests requires a DSC instrument with a very fast response time. This is because many thermoplastics can crystallize rapidly when cooling from the melt. It is important that the DSC be able to cool and equilibrate as fast as possible in order to detect the complete crystallization exothermic peak. The DSC with the fastest response time is the Pyris™ Power Compensated DSC from PerkinElmer.

Power Compensated DSC

The Pyris Diamond DSC from PerkinElmer uses the Power Compensated approach. This DSC uses two independently controlled, low mass (1 g) sample and reference furnaces. The low mass of the Power Compensated furnaces yields a DSC with low thermal inertia and the fastest response time of any DSC instrument available.

The Power Compensated DSC allows samples to be linearly heated and/or cooled at rates as fast as 500 °C/min. This is important when measuring isothermal crystallization times and behaviors of polymers.

In contrast, heat flux DSC instruments employ a large mass furnace. Some DSC devices use a silver block with a mass of 100 g or more. This provides a much higher thermal inertia and a slower inherent DSC response time. The heat flux DSC instruments cannot achieve the very fast cooling and heating provided by the Power Compensated DSC.

Need for Fast Cooling for Microwave Food Trays

The thermophysical properties of plastic microwave food trays were studied using Power Compensated DSC. The microwave food trays must be capable of withstanding large and rapid extremes in temperatures. The trays are generally thermoformed from polyethylene terephthalate (PET) since this polymer is semicrystalline and exhibits the desired end-use properties such as stability, ease of processing and impact resistance. However, to further enhance the thermal stability of the PET polymer for use as microwave food trays, the crystallinity of the polymer is increased by adding nucleating agents. These agents induce a higher level of crystallization of the PET resin during cooling from the melt. Higher concentrations of a given nucleating agent will result in a higher level of crystallinity of the plastic during processing.

DSC cooling experiments are important for the assessment of the effects of these nucleating agents on the crystallization properties of the PET resin. Standard DSC may not reveal obvious differences between two different nucleated resins, whereas these differences will become evident during DSC cooling experiments. For the highly nucleated and fast crystallizing PET microwave food trays, the Power Compensated DSC is necessary for the best in-depth study of the rapid crystallization of the resin.

Experimental

The heat flow properties of two different PET microwave food trays (Tray 1 and Tray 2) were studied, along with the non-nucleated PET precursor resin. The experiment conditions presented in the table were used to study the cooling properties of the PET resins.

The outstanding rapid response of the Power Compensated DSC may be seen in Figure 1. This plot shows the heating and cooling performance of the Power Compensated DSC at heating and cooling rates of 400 and 200 °C/min between 200 and 0 °C. The DSC was equipped with the refrigerated cooling system, Intracooler II and a helium purge was applied. The actual sample temperature (red) and program temperature (blue) are displayed as a function of time. The sample temperature tracks the program temperature very well even at the ballistic cooling rate of 400 °C/min and the use of a refrigerated cooling system, rather than liquid nitrogen. No other DSC instrument can match this level of performance.

Experimental Conditions	
Instrument	Pyris 1 DSC
Cooling system	Intracooler II
Sample pan	Crimped aluminum standard pan
Sample mass	Approximately 10 mg
Purge gas	Helium
Cooling rate (isothermal crystallization studies)	500 °C/min from 300 °C
Cooling rates for cool-reheat experiments	400, 300, 100 and 50 °C/min between 300 and 0 °C
Heating rate for heating experiments	20 °C/min

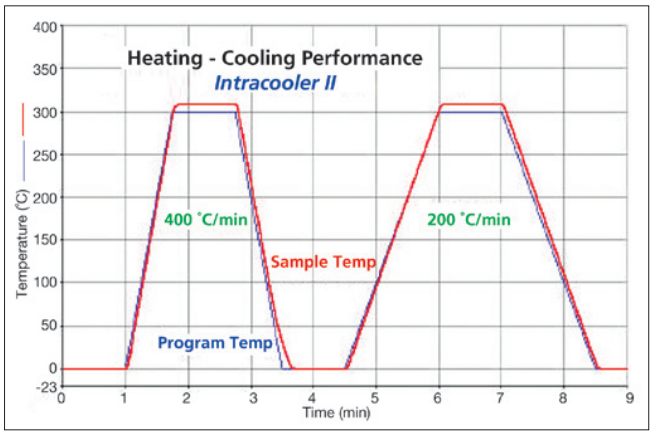


Figure 1. Fast heating and cooling performance of the Power Compensated DSC.

Results

Displayed in Figure 2 are the DSC results obtained on the PET precursor polymer before the nucleating agents are added. The plot shows the first and second heating results. The PET resin was rapidly cooled at a rate of 200 °C/min between the first and second heats. During the first heating, no crystallization exothermic peak is observed reflecting the fact that the polymer has a high level of crystallinity in its as received state. The resin undergoes melting at 261 °C with a heat of melting of 66.7 J/g.

When the PET sample is rapidly cooled down to room temperature and then reheated, a well-defined cold crystallization peak is obtained at 173 °C, which is typical for this polymer. The heat of crystallization is found to be 30.1 J/g. During the second heating segment, the PET undergoes melting at 257 °C with a heat of melting of 33.0 J/g. The net heat of crystallization (melting – cold crystallization) is 2.9 J/g, which is reflective of a nearly amorphous polymer. This demonstrates the ability of the Power Compensated DSC to yield an amorphous polymer directly in the DSC with the application of a fast cooling rate. In comparison, many heat flux DSC instruments require that the sample be physically removed from the hot cell in order to generate an amorphous state by manual quench cooling.

To make the PET resin suitable for the manufacture of the microwave food trays, nucleating agents are added to the polymer. The presence of these nucleating additives drastically changes the morphology of the polymer allowing it to crystallize much more rapidly. Displayed in Figure 3 are the DSC results obtained from the PET sample extracted from a microwave food tray (Tray 1). The sample was heated through its melt temperature and then cooled at a rate of 200 °C/min back to room temperature.

When the cooled food tray is reheated, the cold crystallization exothermic peak occurs at a much lower temperature (134 °C) and is much smaller than that of the PET chip. These major differences are reflective of the changes caused by the presence of the nucleating agents.

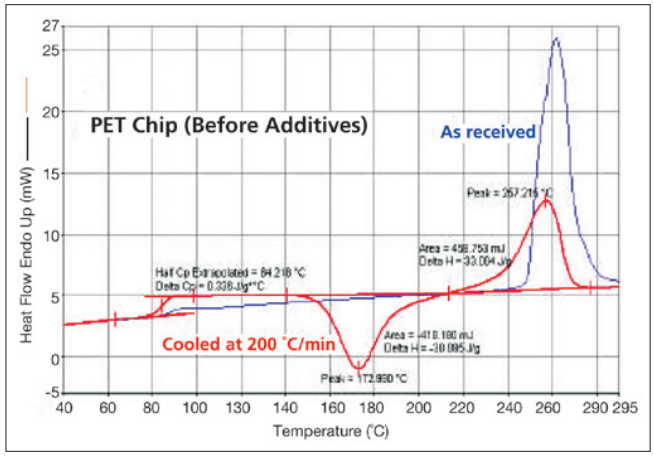


Figure 2. DSC results for PET chip (before additives) showing as received resin and resin after being melted and cooled at 200 °C/min.

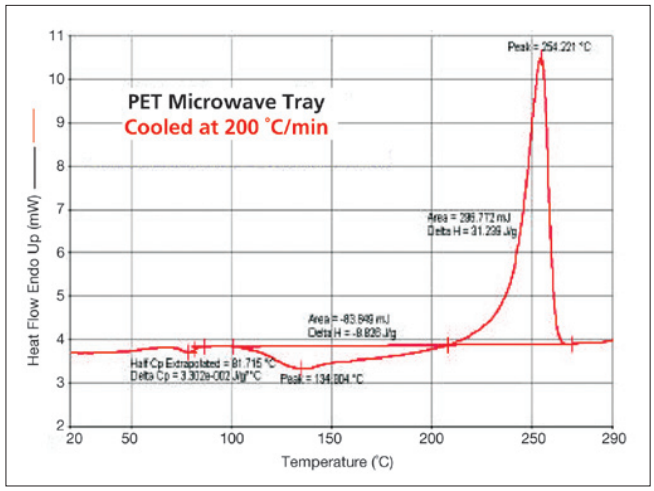


Figure 3. DSC heating results for PET microwave tray resin after cooling from the melt at 200 °C/min.

For quality assurance purposes, the manufacturers of the plastic microwave food trays like to induce a more well-defined cold crystallization peak for the nucleating resin. This provides a sensitive indicator as to the effectiveness of the nucleating agents based on the peak shape, magnitude and temperature. However, this requires ballistically cooling the PET resin from the melt to develop an amorphous material. Displayed in Figure 4 are the DSC results obtained on the food tray PET resin when cooled at the very fast rate of 400 °C/min. It may be seen that a well-defined cold crystallization peak is observed at 131 °C. This is possible only with the cooling capability provided by the Power Compensated DSC for such heavily nucleated polymers.

In contrast, most heat flux DSC units can heat at a maximum rate of only 100 ˚C/min. This is not fast enough to avoid crystallization for fast crystallizing polymers such as nylon or nucleated PET. Shown in Figure 5 are the DSC results generated for the PET tray resin when cooled from the melt at a rate of 100 ˚C/min. The cold crystallization peak is just barely observed, as these results demonstrate. Much valuable characterization information on the effects of the nucleating agents is lost when required to use the slower heating rates necessitated with heat flux DSC. The Pyris Power Compensated DSC provides the ability to cool over an extremely wide range of rates for the most comprehensive characterization information.

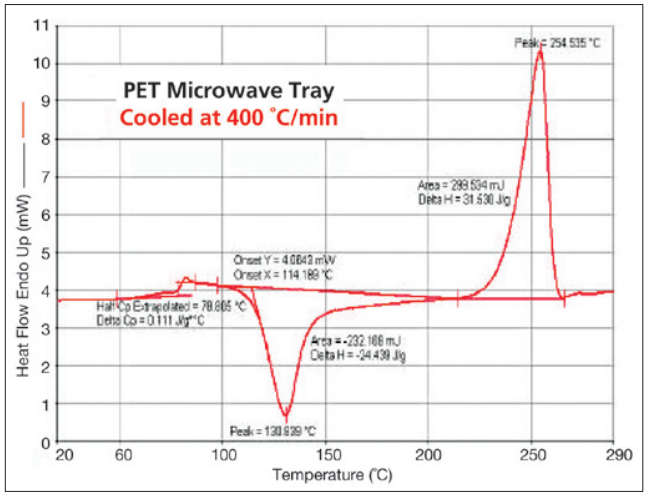


Figure 4. DSC results for PET tray resin after cooling at 400 ˚C/min.

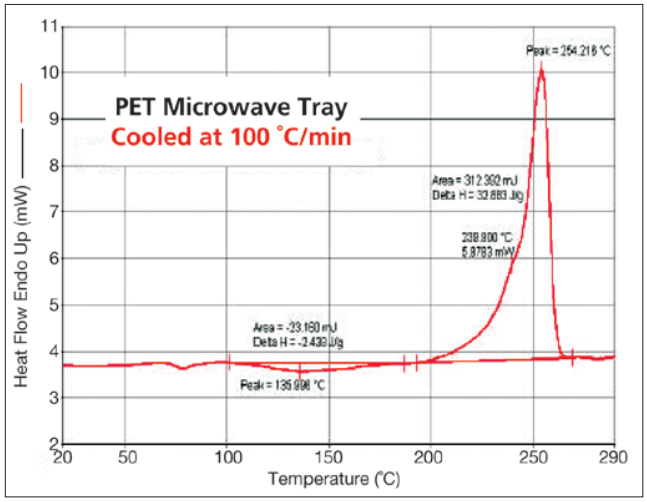


Figure 5. DSC results for PET tray resin after cooling at 100 ˚C/min.

The effects of the applied cooling rate for the PET tray resins may be seen in Figure 6. This shows a direct overlay of the heating curves obtained after cooling from the melt at 400, 200, 100 and 50 ˚C/min. Due to the heavy nucleation of the PET resin, there is a major change in the results when the cooling is slowed from the very fast 400 ˚C/min to 200 ˚C/min.

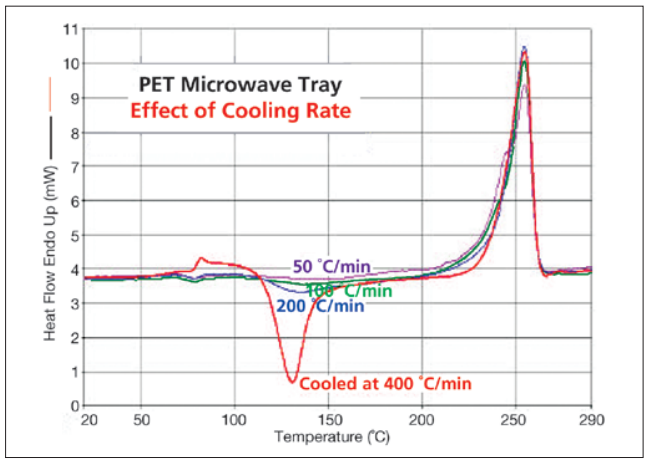


Figure 6. Overlay of DSC results on PET tray after cooling at rates of 400, 200, 100 and 50 ˚C/min.

This demonstrates the great importance of the need for the very fast cooling to get a complete picture of the crystallizable nature of this PET resin material.

Additional supplementary characterization information can be obtained by performing isothermal crystallization measurements on the nucleated PET resins. With this test, a sample of polymer is heated up through its melt and held under isothermal conditions for several minutes to destroy the existing crystalline structure. The sample is then ballistically cooled to a temperature below the melting temperature to allow the polymer to crystallize under tightly controlled conditions. DSC monitors the resulting crystallization exothermic peak as a function of time.

The isothermal crystallization test provides valuable information on polymers including:

- Average molecular weight
- Molecular weight distribution
- Presence of recyclates/regrinds
- Plasticizers
- Nucleating agents, pigments or other additives
- Copolymers
- Injection molding lubricants or flow enhancers

Because of its very fast response time and ability to cool quickly, the Power Compensated is ideally suited for the measurement of the isothermal crystallization of polymers.

Displayed in Figure 7 are the isothermal crystallization results generated for Tray 1. The sample was cooled from 300 ˚C to the target isothermal temperatures at a cooling rate of 500 ˚C/min. The crystallization behavior was monitored at temperatures of 230, 225, 220, 215 and 210 ˚C. At the temperature of 210 ˚C, the resin reached its maximum rate of crystallization in about 30 seconds. This demonstrates the ultra fast responsiveness of the Power Compensated DSC.

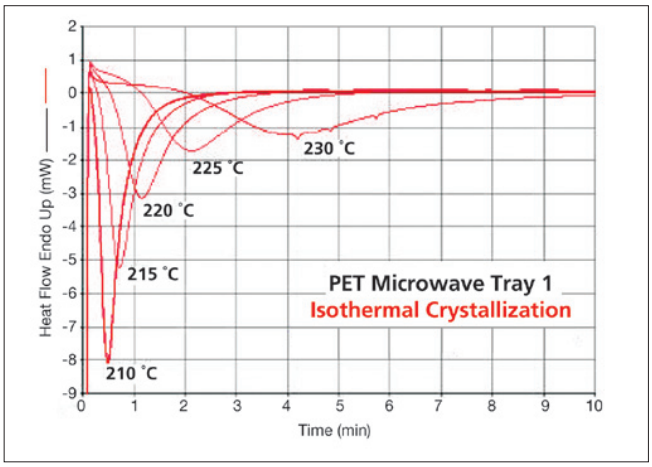


Figure 7. Isothermal crystallization results for PET Tray 1.

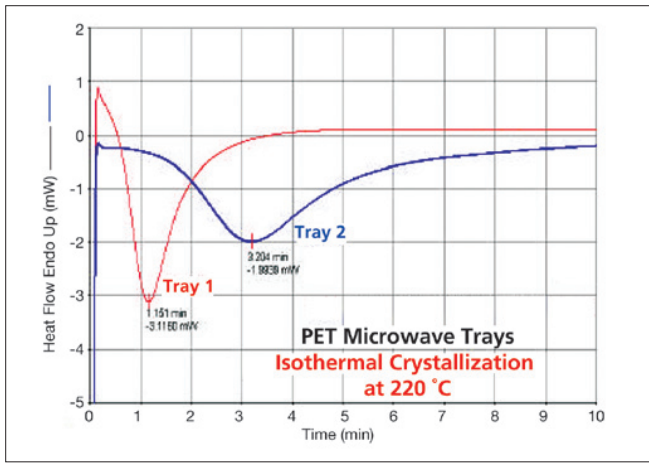


Figure 9. Overlay of DSC isothermal crystallization results at 220 °C for PET microwave trays 1 and 2.

Another PET microwave tray (Tray 2) was analyzed using the DSC isothermal crystallization test and these results are displayed in Figure 8. This resin was clearly different in its resulting crystallization behavior as compared to the Tray 1 sample in that it took longer for it to crystallize under identical conditions. This indicates that the Tray 1 resin was more heavily loaded with nucleating agents as compared to Tray 2.

The differences between the crystallization behaviors of the Tray 1 and Tray 2 PET resins is more evident in an overlay (Figure 9) of the isothermal crystallization behaviors at 220 °C. Tray 1 clearly crystallizes more rapidly as compared to Tray 2.

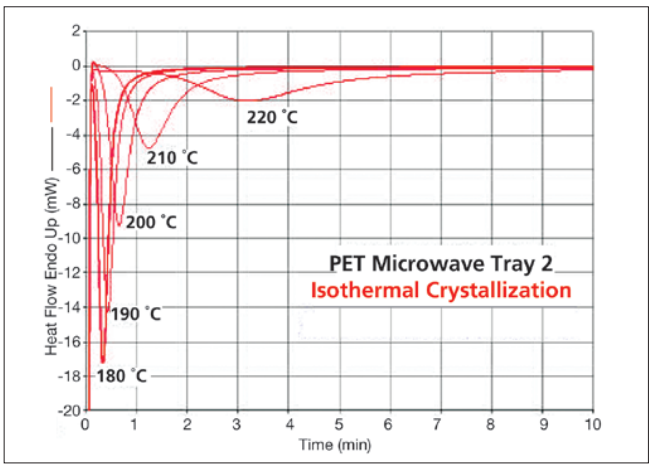


Figure 8. Isothermal crystallization results for PET Tray 2.

These differences would not be apparent with standard heating DSC, but are very noticeable with the DSC isothermal crystallization measurements. The measurement of the very fast crystallization responses of these nucleated resins requires a DSC with an ultra-fast response time, and this is the Power Compensated DSC.

Summary

Most plastic processes require that the polymer be melted and cooled during the thermoforming stage. The most comprehensive characterization of plastics undergoing melt processing necessitates that the material be studied under both heating and cooling conditions. The cooling analysis allows the effects of nucleating and plasticizing agents to be more fully quantified. Oftentimes thermoplastics may not exhibit any significant differences by standard heating DSC. However, when cooling studies are performed, significant differences, due to the presence of nucleating agents or flow enhancers, may become apparent. Such DSC data is extremely valuable for quality assurance or for process control purposes. The successful performance of cooling studies requires a DSC with a fast response time so that the sample can be analyzed at ballistic cooling rates. The DSC instrument with the fastest response time and the ability to heat and cool ballistically (up to 500 °C/min) is the Diamond Power Compensated DSC from PerkinElmer.

PerkinElmer, Inc.
940 Winter Street
Waltham, MA 02451 USA
P: (800) 762-4000 or
(+1) 203-925-4602
www.perkinelmer.com

PerkinElmer

010009_01

APPLICATION NOTE

Mass Spectrometry

Author:

Sharanya Reddy

PerkinElmer, Inc.
Shelton, CT USA

Quantitation of BADGE: An Epoxyphenol-based Food Can Coating in Canned Tuna Extracts Using UHPLC-TOF

Introduction

Metal cans are often coated with a resin barrier to prevent contact between food and the can. Components from these coatings can migrate into the food affecting its safety and quality. Polyepoxyphenol coatings on the inside of cans based on bisphenol A epoxy resins can release the epoxy monomer bisphenol A diglycidyl ether (BADGE) into food (1,2). Bisphenol A and its derivatives are considered as endocrine disruptors (3). Both Europe and the U.S. have set regulations on the limit of BADGE migration into food at 1 mg/Kg. Using the quantitative capability of the AxION® 2 Time-of-Flight (TOF) mass spectrometer, we were able to set up a calibration curve and quantitate BADGE in a tuna extract. In addition, the high mass accuracy capability of the TOF along with the proprietary AxION EC ID software, allowed us to identify an unknown impurity cyclo-di-BADGE without having an authentic standard of this compound.

PerkinElmer®
For the Better

Experimental

Sample preparation:

10 g of tuna was transferred into a 50 mL tube and spiked with BADGE standard (200 ng). To this, 10 mL of acetonitrile was added and shaken. Salts (1 g sodium chloride, 4 g magnesium sulfate, 1 g trisodium citrate, 0.5 g disodium hydrogen citrate) were added to the sample, which was shaken and centrifuged (3700 rpm) for 5 min. The supernatant (1 mL) was transferred to a dispersive SPE micro-centrifuge tube containing primary and secondary amine (PSA, 25 mg) and magnesium sulfate (150 mg) and C18 (25 mg). Sample was vortexed and centrifuged at 3000 rpm for 5 min. The supernatant was carefully removed, pH adjusted with 5 µL of 5% formic acid and used for analysis.

LC conditions:

Pump: PerkinElmer® Flexar™ FX-15 pump
Flow: 0.4 mL/min
Mobile phase A: Water containing 0.1% formic acid
Mobile phase B: Acetonitrile containing 0.1% formic acid
Gradient conditions: 70% A/30% B to 10%A/90%B in 5 mins in a linear gradient
Injection volume: 5 µL in partial fill mode.
Column used: PerkinElmer Brownlee™ SPP C-18, 2x50 mm, 2.7 µm, 25 °C

MS conditions:

Mass spectrometer: PerkinElmer AxION 2 TOF MS
Ionization source: PerkinElmer Ultraspray™ 2 (Dual ESI source)
Ionization mode: Positive
m/z range: 90-700
Capillary exit voltage: 100 V
Internal calibration was performed using *m/z* 118.08625 and 622.02896 as lock mass ions.

Results

The mass spectrum showed BADGE was predominantly observed as the [M+NH4+] ion (Figure1). We were easily able to detect as low as 2 ppb concentration of BADGE (S/N = 52) standard. Excellent linearity (r^2 > 0.995) was observed for the calibration curve generated between 2 to 500 ng/mL (Figure 2) of BADGE standard. The intra assay %RSD for triplicate injections at the 2 ppb concentration was <10%. Tuna extracts spiked with 20 ng/mL of BADGE standard were easily detected by UHPLC-TOF (Figure 3). A 94% recovery of BADGE was observed in the spiked tuna extracts suggesting little or no ion suppression of the analyte in the extracts.

We tried to identify two unknown peaks with same exact masses eluting between 2.5 to 3 mins (Figure 4) using the exact mass capability of the AxION 2 TOF. The accurate mass and isotope profile was entered into the AxION EC ID calculator of the software. The software uses this

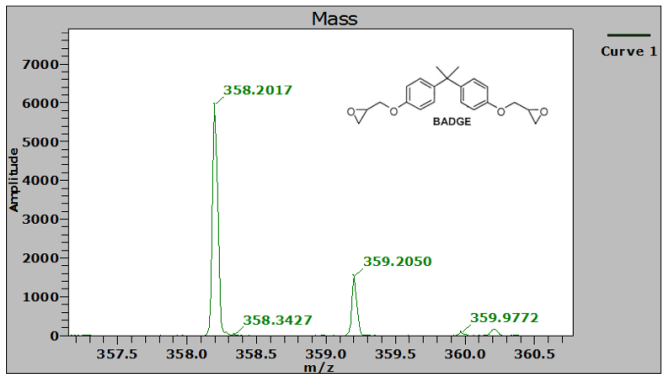


Figure 1. Mass spectrum shows [M+NH4]+ as the predominant peak for BADGE. Expected accurate mass of BADGE is 358.2013 (mass error < 2 ppm).

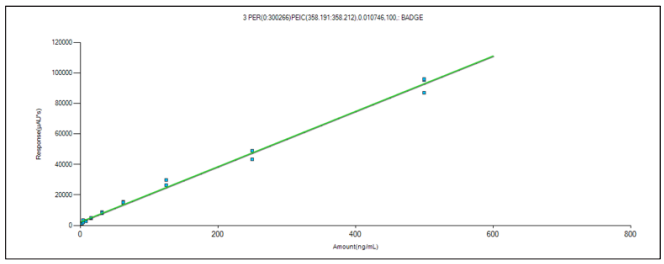


Figure 2. Shows calibration curve for BADGE analysis (r2 0.995).

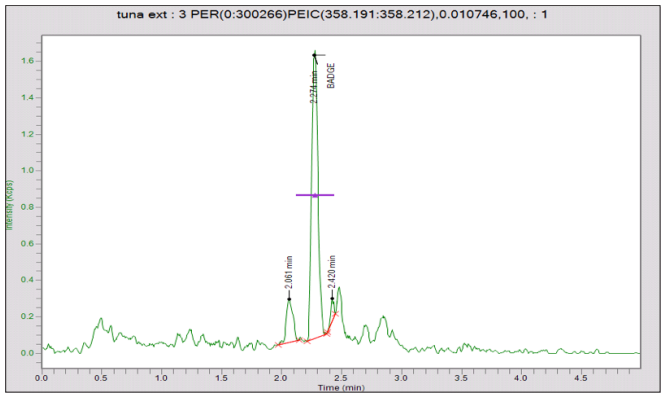


Figure 3. Analysis of BADGE by UHPLC-TOF in tuna extracts spiked at 0.2 mg/Kg .

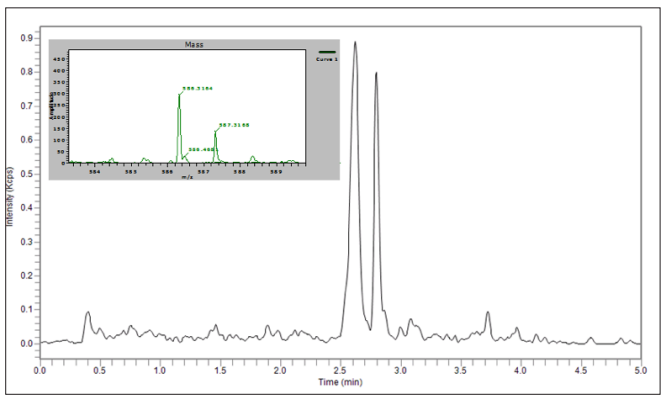


Figure 4. Unknown peaks in tuna extracts with the same *m/z* 586.3164 eluting at 2.6 and 2.8 min. Inset shows mass spectrum.

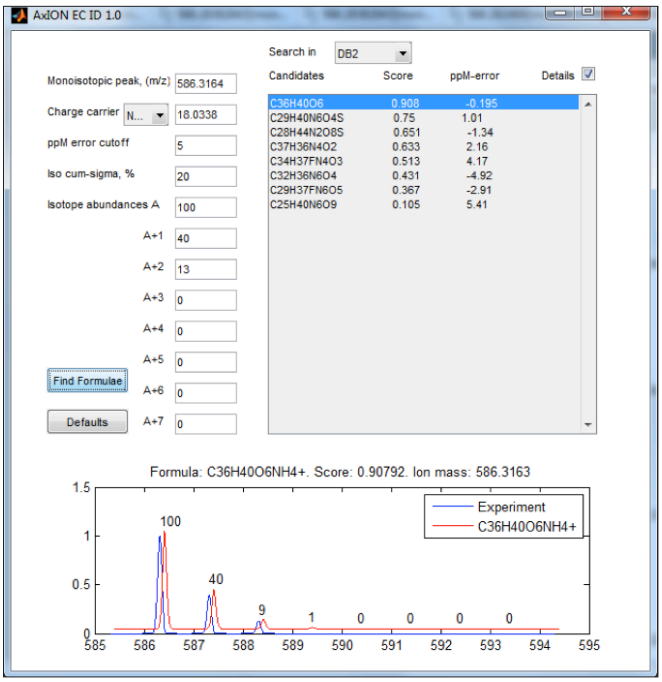


Figure 5. AxION EC ID software gave the elemental composition C36H40O6 as the top choice for the unknown mass 586.3164.

information and searches against the PubChem database and identifies potential molecular formulae matches. The first potential match with the highest score was identified with the elemental composition $C_{36}H_{40}O_6$ within a mass error of < 1 ppm (Figure 5). The software also provides a list of possible structures for the given elemental composition and one of the listed structures that related to bisphenol family of compounds was the BADGE.BPA linear structure (Figure 6a). However, an isomeric structure cyclo-di-BADGE compound described in the literature could also be possible (Figure 6b). Based on the fragmentation pattern and the retention time matching with an authentic standard, the presence of linear versus cyclo structure could be further confirmed.

Conclusion

Using the high sensitivity AxION 2 TOF, we were able to detect 0.2 mg/Kg of BADGE in tuna extract well below the regulation limits set at 1 mg/Kg. Using the high mass accuracy capability of AxION 2 TOF along with the AxION EC ID software, we were able to detect unknown peaks and match them to the isomers BADGE.BPA linear structure/cyclo-di-BADGE structures without the use of authentic standards.

References

1. Cao XL, Dufresne G, Clement G, Bélisle S, Robichaud A, Beraldin F. JAOAC Int 92 (2009) 1780.
2. Míguez J, Herrero C, Quintás I, Rodríguez C, Gigosos PG, Mariz OC. Food Chem. 135 (2012) 1310.
3. Schug T, Janesick A, Blumberg B, Heindel J Steroid Biochem Mol Biol. 127 (2011) 204.

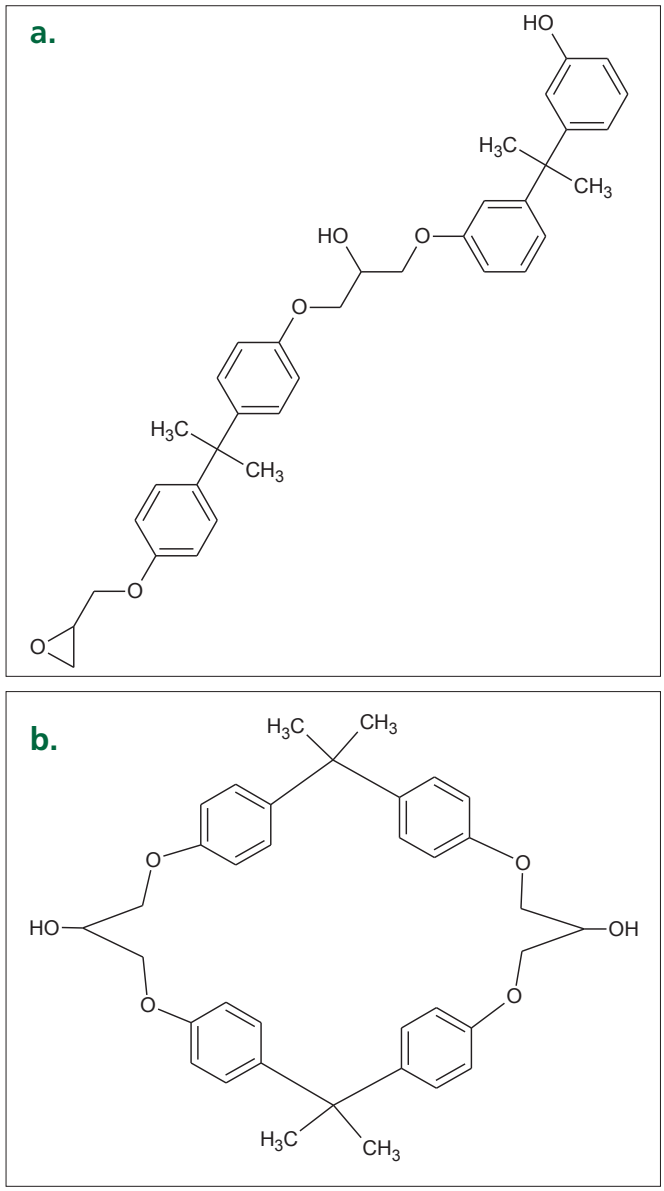


Figure 6 a and b. Structures that fit the elemental composition C36H40O6.
a. Linear BADGE.BPA
b. Cyclo-di-BADGE

Acknowledgements: We would like to thank Ariovaldo Bisi and Lucca Piatti, PerkinElmer Inc, Italy for the BADGE standard and tuna samples.

PerkinElmer, Inc.
940 Winter Street
Waltham, MA 02451 USA
P: (800) 762-4000 or
(+1) 203-925-4602
www.perkinelmer.com

For a complete listing of our global offices, visit www.perkinelmer.com/ContactUs

011006_01

APPLICATION NOTE

Gas Chromatography/
Mass Spectrometry

Authors

Miles Snow

Heidi Grecsek

PerkinElmer, Inc.
Shelton, CT 06484 USA

Analysis of Food-Packaging Film by Headspace-GC/MS

Introduction

Food-packaging material is typically manufactured as a thin film and coated with inks which usually contain multiple, harmful, volatile organics. Therefore, they must be carefully monitored and quantitated to ensure that the amounts are limited.

Traditionally, the test for solvent materials in food-packaging film was performed using a technique of heating a square meter of the film material inside a mason jar. This jar is then opened and tested (by smell) for volatile organic compounds. Later, this test was expanded to extract a headspace sample out of the mason jar by syringe and then injected into a gas chromatograph (GC) for quantitative analysis. This produced significantly better results and provided laboratories with a quantitative number. This process is still very time-consuming and labor intensive as a result of the number of manual steps involved. The manual process of cutting food packaging, placing it in a mason jar, heating the jar, and manually collecting a sample for GC analysis dramatically limits the number of samples that can be analyzed each day. The technique demonstrated here will greatly improve the efficiency and throughput of this analysis.

PerkinElmer®
For the Better

This analysis can be completely automated using a PerkinElmer® TurboMatrix™ Headspace (HS) sampler with the Clarus® Gas Chromatograph/Mass Spectrometer (GC/MS). This system passed all the requirements for food-packaging analysis.

Experimental

The first food packaging film used for this experiment was from a typical package of cookies. This film was cut into squares: 325 cm^2 pieces. The typical volume used in a mason jar is a square meter but this volume is not required for the headspace sampler. The desired sensitivity can be reached with significantly lower quantities. The second packaging material tested was obtained from a shopping bag that you would typically find at a department store.

The 325 cm^2 pieces of film were added directly to a 22-mL headspace vial. The vial was then sealed with silicone/PTFE septa (PerkinElmer Part No. B0104241). In addition, a calibration standard was prepared to get an estimate of the expected concentration of the typical solvents. This standard was prepared by adding 4.7 µg of each solvent in a 22-mL headspace vial (Table 2).

The instrument used for this analysis was a TurboMatrix HS 40 Headspace Trap sampler run in headspace-only mode. This bypassed the trapping capability. If extra sensitivity is required, the trap option could be used for up to 100 times lower detection levels. The shaker option on the headspace was utilized for a faster equilibration of the solid film material. The headspace was controlled using the TurboMatrix remote control software and was coupled to the Clarus GC/MS. The Clarus GC was equipped with a programmable split/splitless (PSS) injector and programmable pneumatic control (PPC). Deactivated fused silica (0.32 mm) transfer line connects the TurboMatrix HS 40 Trap to the Clarus GC. The GC column was directly connected to this transfer line using a universal union (PerkinElmer Part No. N9302149). The Clarus MS was controlled via TurboMass™ 5.1 GC/MS software and operated in electron ionization (EI) mode.

Results

The TurboMatrix HS 40 Headspace sampler was successful in analyzing the solvents in food packaging. Six solvents were identified: 1 – MIBK (Methyl Isobutyl Ketone), 2 – NPAC (n-Propyl Acetate), 3 – ETAC (Ethyl Acetate), 4 – Propanol, 5 – ETOH (Ethanol) and 6 – Heptane (Figures 2 and 3). Ethanol and Propanol were the largest responders and over-loaded the system. However, the requirements of the testing were to only get semi-quantitative information. Therefore, the overloading was accepted. All components were positively identified using a NIST® library database.

The cookie package/wrapper had approximately 0.22 mg/m^2 of solvents found. However, Propanol was very significant, making up the large majority of the total solvents identified. The cookie wrapper also had a lower level of interferences from outside sources (Figure 1). The shopping bag (purple) had approximately 0.32 mg/m^2 of total solvent material (of the six solvents tested) – Table 2. This represented a very good response of all six solvents. In addition, there is a significant amount of other materials found in the food film. This is evident in the chromatogram shown on Figure 2. Because of the ability of the MS to extract only the required ion from the component of interest, this interference was not an issue.

The headspace system enabled the method to be set up and run unattended with no sample preparation. This eliminated the need for mason jars and operator attention. In addition, the system showed a significant amount of sensitivity for the required components, demonstrating the ease of setup methodologies of many types of food packaging at many different levels.

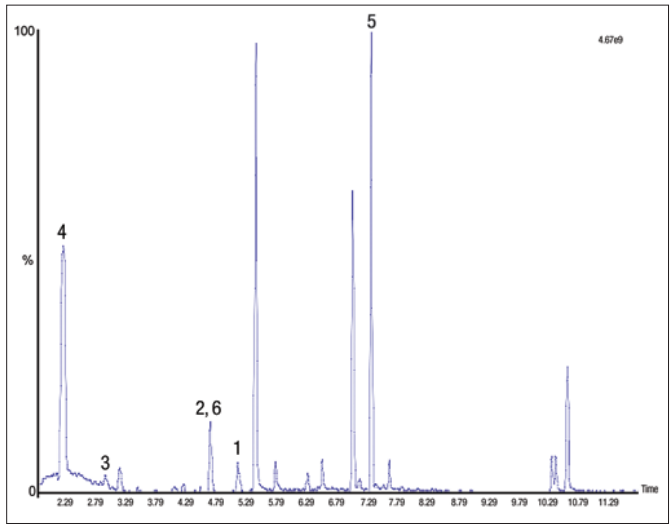


Figure 1. Chromatogram of cookie wrapper.

The significant response of the volatile solvent material by this heated headspace technique would allow for a flame ionization detector (FID) to be used as a substitute for the MS detector. While the MS gives a positive identification as well as selectivity, the FID can be used in a majority of standard QA/QC environments.

Conclusions

The PerkinElmer TurboMatrix Headspace Trap with the Clarus GC/MS meets all the requirements for food-packaging analysis. The main requirement for this application is fast, easy and quantitative solvent determination. Using the setup demonstrated here, the sample is placed into a vial and placed in the autosampler tray of the headspace. Then the automated analysis is completed without operator attention. In addition, the headspace's overlapping thermostatting allows up to 12 samples to be processed simultaneously, thus allowing 50-75 analyses per day.

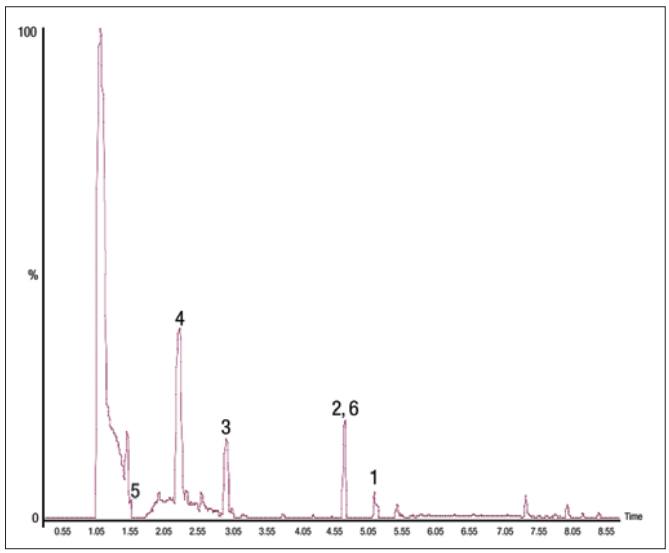


Figure 2. Chromatogram of shopping-bag film – with expanded ethanol chromatogram.

Table 1. **Instrument Parameters.**

GC		**Headspace Trap**	
Injector Temp:	120 ˚C	Needle Temp:	85 ˚C
Oven Program – Initial Temp:	35 ˚C	Transfer-Line Temp:	85 ˚C
Initial Time:	Hold 2 mins	Oven Temp:	80 ˚C
Ramp:	10 ˚C/min	Shaker:	On
Final Temp:	200 ˚C	High-Pressure Injection:	On
Final Time:	Hold 5 mins	Trap Option:	Off
Column:	Elite 200*	Constant Mode:	On
MS	**SIFI Conditions EI**	Thermostatting Time:	30 min
Mass Range:	30-300 amu	Pressurization Time:	1 min
Scan Time:	0.41 sec	Withdrawal Time:	1 min
InterScan Delay:	0.01 sec	Injection Pressure:	20 psi
Transfer-Line Temp:	200 ˚C	Column Pressure:	25 psi
Electron Energy:	70 eV	Injection Time:	0.08 min
Detector Voltage:	400 V	GC Cycle Time:	35 min
Threshold:	0	Carrier Gas:	Helium at 99.999%
*PerkinElmer Part No. – N9316630 (30 m, 0.32 mm, 1 µ).			

Table 2. **Semi-Quantitative Results.**

Sample: Standard

Peak #	Solvent Name	RT (min)	Area	µg in Vial
1	MIBK	5.104	15165890	4.7
2	NPAC	4.663	19381950	4.7
3	ETAC	2.932	14047220	4.7
4	Propanol	2.256	16693610	4.7
5	ETOH	1.518	31902978	4.7
6	Heptane	4.69	12375010	4.7

Sample: Purple Shopping Bag 300 cm²

Peak #	Solvent Name	RT (min)	Area	µg in Vial	mg/m²
1	MIBK	5.12	162823	0.05	0.00
2	NPAC	4.665	4010297	0.97	0.03
3	ETAC	2.927	4236236	1.42	0.04
4	Propanol	2.244	19894030	5.6	0.17
5	ETOH	1.526	15599010	2.3	0.07
6	Heptane	4.686	14941	0.01	0.00
Total					**0.32**

Sample: Cookie Wrapper 325 cm²

Peak #	Solvent Name	RT (min)	Area	µg in Vial	mg/m²
1	MIBK	5.112	30410	0.01	0.00
2	NPAC	4.664	2320430	0.56	0.02
3	ETAC	2.947	472144	0.16	0.00
4	Propanol	2.243	21689300	6.11	0.19
5	ETOH	1.533	2630198	0.39	0.01
6	Heptane	4.692	211345	0.08	0.00
Total					**0.22**

PerkinElmer, Inc.
940 Winter Street
Waltham, MA 02451 USA
P: (800) 762-4000 or
(+1) 203-925-4602
www.perkinelmer.com

PerkinElmer®

007553A_01

APPLICATION NOTE

Gas Chromatography

Author:

Mariacarola Salvi

PerkinElmer, Inc.
Monza, Italy

Determination of Residual Solvents in Flexible Packaging According to EN 13628-2:2004

Introduction

The reference standards for food contact materials are rapidly evolving in favor of increasing consumer protection.

The Commission Regulation (EC) No. 1935/2004 is the main reference legislation in the European community. This regulation establishes that any materials that come into contact with food must not release chemicals in quantities which could:

- Pose a danger to the health of consumers
- Result in an unacceptable change in the composition of food
- Change the organoleptic properties

Part 2 of the regulation focuses the attention of food contact material producers on the need to operate in terms of quality assurance. The Commission Regulation (EC No. 2023/2006) has made it mandatory to adopt a system of Good Manufacturing Practice (GMP); with GMP referring to the set of actions to ensure a consistently high quality both in production and control process. This requires not only a deep knowledge of the materials used but also of the entire production and control process.

PerkinElmer®
For the Better

Flexible Packaging

In case of printed flexible packaging, Commission Regulation (EC) No. 2023/2006 Annex I prohibits the printed side of the materials to come into contact with food. Verification by GMP is also required in order to prevent any "Set-off" (process transfer of substances, from the printed side of a film to the non-printed side, due to the fact that these materials are normally produced in coils) that could ultimately transfer these chemicals onto foods.

The solvents in the inks used to print flexible packaging may represent a possible source of food contamination and therefore must be controlled.

For the determination of residual solvents from printed materials, it is highly recommended that an analytical method such as the official UNI EN 13628-2:2004[1] is followed. If the application of a non-official method is adopted, it requires validation by the laboratory; a task that is often long, complex and expensive.

Experimental Instrumentation

The analysis was performed using a PerkinElmer Clarus® 580 gas chromatograph equipped with a capillary column injector and an FID detector coupled to an automatic TurboMatrix™ 40 Headspace sampler. The capillary column used was a PerkinElmer Velocity-1 (30 m, 0.32 mm, 3 um – P/N N9306329).

Figure 1. Clarus 580 GC and TurboMatrix 40 Headspace sampler.

Analytical Conditions

The instrument conditions are given below:

Table 1. Instrument Conditions.

HS Conditions:	
Thermostatting Temperature	110 °C
Needle Temperature	130 °C
Transfer line Temperature	150 °C
Thermostatting Time	20 min
Pressurization Time	3 min
Injection Time	0.06 min
Pressure	21 psi
Mode	Constant
GC Conditions:	
Carrier Gas	He 1.7 ml/min
Split Ratio	1:20
Injector Temperature	230 °C
Detector Temperature FID	280 °C
Ramp	50 °C for 5 min, ramp to 100 °C @ 5 °C/min, ramp to 250 °C @ 10 °C/min

Standard Preparation

Standards are prepared together as a stock mixture. Using the Total Vaporization Technique[2], different levels of the calibration curves were obtained analyzing increasing amounts of the standard mixture added to the vial prior to analysis.

Table 2. Calibration Amounts.

Solvent	Level 1 mg	Level 2 mg	Level 3 mg	Level 4 mg
Ethanol	0.0065	0.0130	0.0260	0.0390
Isopropanol	0.0064	0.0128	0.0256	0.0384
MEK	0.0066	0.0132	0.2640	0.0396
Ethyl Acetate	0.0074	0.0148	0.0296	0.0444
Isobutanol	0.0065	0.0130	0.0260	0.0390
Methoxy Propanol	0.0075	0.0150	0.0300	0.0450
Ethoxy Propanol	0.0073	0.0146	0.0292	0.0438
Toluene	0.0058	0.0116	0.0232	0.0348
Butyl Acetate	0.0073	0.0146	0.0292	0.0438
m-Xylene	0.0071	0.0142	0.0284	0.0426
o-Xylene	0.0073	0.0146	0.0292	0.0438

Analytical Results

The software runs the standards/sample, calibrates the instrument and automatically produces the report. In the real world, samples can widely vary in concentration, therefore it is paramount that a high level sample does not carryover and contaminate the following samples and give false high results. The inert flow path and post sampling needle purge ensures the lowest possible carryover, producing quality results day after day. Another important area to consider is that the instrument's natural background levels are as low as possible, thus enabling ultra-low level detection when needed for those difficult analyses.

The chromatogram in Fig. 2 was obtained from the standard mixture Level 3 (blue) as compared with a blank (red) that was obtained by the analysis of an empty vial. The blank is clean and void of extraneous peaks, thus simplifying the reporting of data.

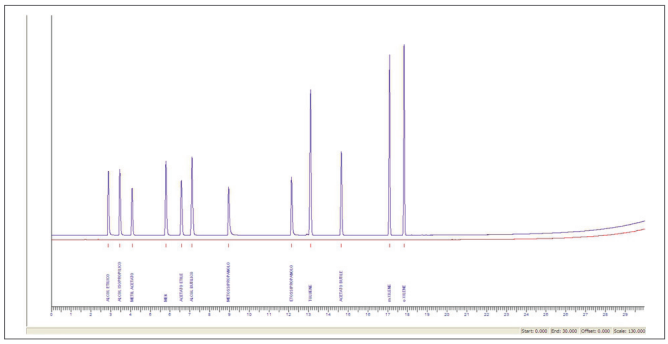


Figure 2. Chromatogram of Level 3 Standard.

Figures 3 and 4 represent the calibration curves for two example analytes: methyl acetate and toluene, both showing excellent linearity of the four calibration levels, thus enabling easy operation for the end user and improved accuracy of the results.

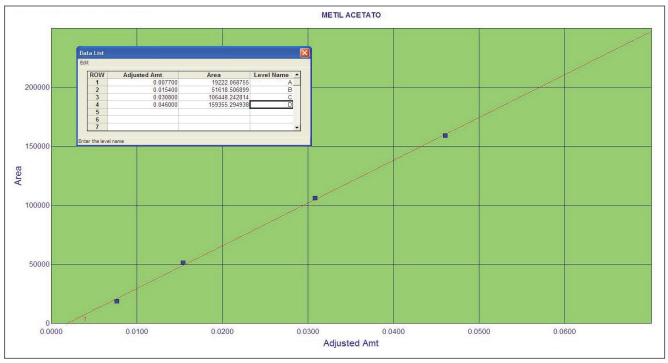


Figure 3. Methyl Acetate Calibration Curve.

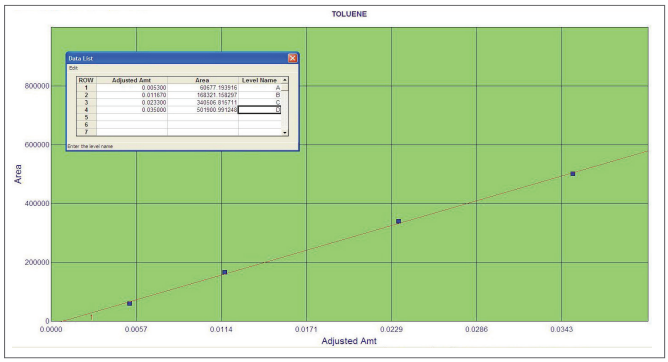


Figure 4. Toluene Calibration Curve

Example of a Real Sample

A known Area (1 dm2) of the unknown sample is introduced into the vial and analyzed using the same analytical conditions as the standards above. The quantitative result obtained is then reported as the overall amount of solvents per m2 of material.

Figure 5 below shows the analysis of a real sample. For this sample the total content of solvent is found to be equal to 7.20 mg / m2.

Figure 5 also shows there is the presence of several unknown peaks, the one in the center is labeled "incognito." This is investigated further in the next section.

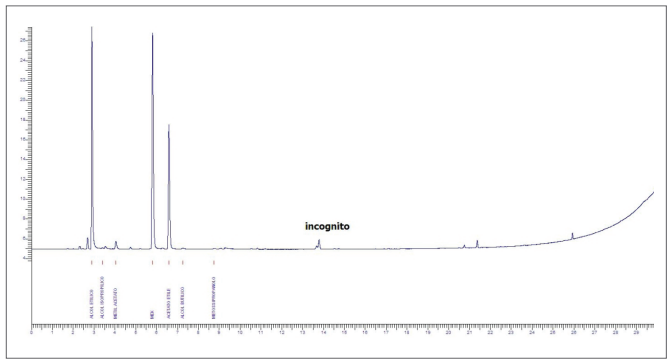


Figure 5. Chromatogram of Real Sample Showing Unknown Peak.

GC/MS

Although the standard UNI EN 13628-2:2004 requires the use of an FID detector, at times it may be necessary to identify an unknown solvent in a real sample, i.e. a solvent not included in the standard mixture. A mass spectrometer (MS) is a powerful detector for the determination of unknowns. We will use the same chromatographic system, vide supra, but coupled to a Clarus 560S MS. Figure 6 shows our target compound labeled as "incognito" at approximately five minutes into the chromatogram.

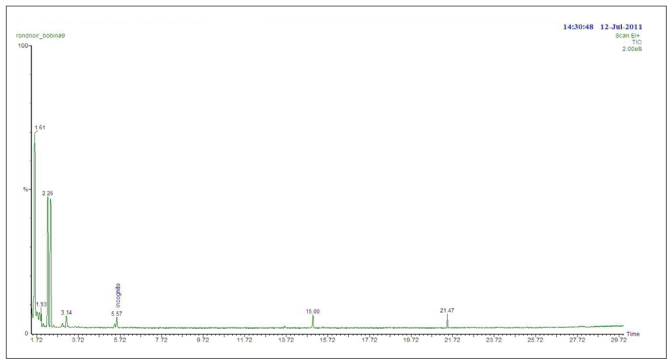


Figure 6. GC/MS Chromatogram of Sample Shown in Figure 5.

A mass spectrum of the unknown peak can easily be obtained by clicking on the peak. To assist in the identification of this unknown, the resulting mass spectrum was searched against a NIST mass spectra library that contains over 200,000 compounds. The NIST library software has selected the following solvent, 3-methyl heptane, as a possiblibility in Figure 7.

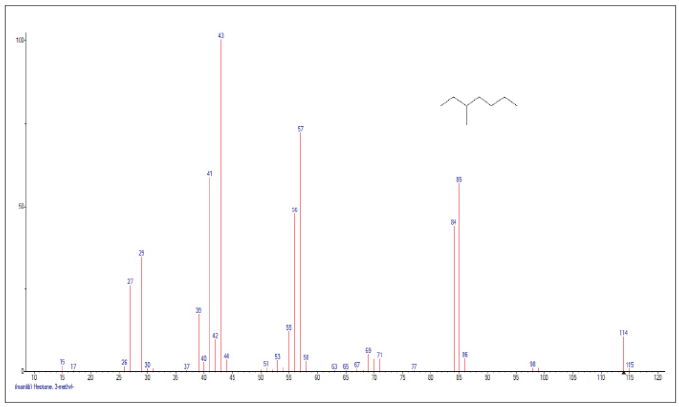


Figure 7. NIST Library Search Match of Peak Labeled "Incognito."

In order to verify and quantify this new solvent, it will be sufficient to have a small quantity of it added to the calibration mixture. Alternatively, in order to have a semi-quantitative result, you can compare the response factor to one of the other solvents inside the standard mixture.

Conclusion

The Clarus 580 GC and TurboMatrix HS system can easily and accurately quantify the amount of residual solvents according to the official method EN13628-2:2004.

References:

1. Uni En 13628-2:2004 Packaging - Flexible Packaging Material - Determination Of Residual Solvents By Static Headspace Gas Chromatography - Part 2: Industrial Methods.
2. Static Headspace-Gas Chromatography Theory and Practice by B. Kolb, L. Ettre, 1997 p. 142 Wiley-VCH.

PerkinElmer, Inc.
940 Winter Street
Waltham, MA 02451 USA
P: (800) 762-4000 or
(+1) 203-925-4602
www.perkinelmer.com

PerkinElmer®

009812_03 PKI

APPLICATION NOTE

Infrared, IR Microscopy

Author:

Ian Robertson

PerkinElmer, Inc.
Seer Green, UK

Characterizing Polymer Laminates Using IR Microscopy

Introduction

Multilayer polymer films, or laminates, are used in a wide variety of industries. A major use of these materials is for packaging of foods and consumer products. The composition of multilayer films can often be quite complex as they may have to satisfy a variety of requirements to preserve the contents. A package must collate and contain the product, requiring strength and the ability to seal the packaging. It must be machineable at a reasonable cost. In the case of food products, it must be able to preserve the contents and protect it from external influences that would affect the product quality or safety, ultimately leading to increased shelf-life. Each of the layers in the laminate will perform a different barrier function, protecting the product from different external factors, such as moisture, light, oxygen, microbial materials and other chemicals or flavors.

Generally, traditional polymer materials, such as polyethylene terephthalate (PET), polyethylene (PE), polystyrene (PS), and polypropylene (PP), have been used for packaging materials. These packaging materials account for a significant proportion of materials ending up at landfill sites or recycling plants. Some of these materials biodegrade slowly or do not biodegrade at all and are environmentally unfriendly. Consequently, there is increasing focus on the use of biodegradable or compostable polymers that can be used as packaging materials. Bio-based materials are partly or entirely made of renewable raw materials, such as cellulose, starch or polylactic acid (PLA). These bio-based plastics can be biodegradable, but are not always. Compostable plastics can be completely biodegraded by microorganisms leaving only water, carbon dioxide, and biomass. These materials are more environmentally friendly and are expected to be used increasingly in the future.

PerkinElmer®
For the Better

Infrared microscopy has long been the most important technique for characterizing multilayer polymer films. Infrared spectroscopy has the ability to identify materials and the addition of an infrared microscope allows for small samples (down to <10 microns) to be analyzed, including the determination of the identities of the different layers of laminates. This Application Note describes the use of infrared microscopy applied to "traditional" multilayer polymer films as well as the newer compostable materials.

Infrared Microscopy of Multilayer Polymers

Infrared microscopy of polymer films can be performed using transmission or Attenuated Total Reflectance (ATR) techniques. Infrared transmission measurements require the sample to be optically thin, generally not thicker than 20 to 30 microns. This requires the sample to be prepared as a thin film by the use of a microtome. The sample can then be placed on an infrared-transmitting window material, such as potassium bromide (KBr), for measurement of transmission spectra. ATR measurements can be performed on optically thick materials as ATR is a surface technique. The sample needs to be physically supported, either in an embedding resin or in a sample clamp specially designed for use in infrared microscopes. ATR measurements have the additional benefit of generating spectra at a significantly better spatial resolution than transmission measurements.[1]

Transmission of Laminate

A polymer laminate sample was cut to a thickness of 25 microns using a microtome and taped flat onto a 7 mm diameter KBr window. This sample was then placed in a standard microscope sample holder on the microscope stage of the PerkinElmer Spotlight™ 200i. A visible image of the sample is shown as Figure 1. The laminate is approximately 350 micrometers across (top to bottom).

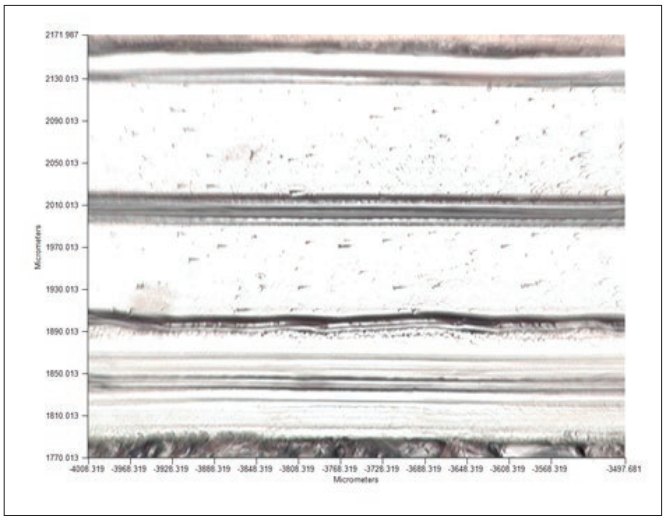


Figure 1: Visible image of polymer laminate measured in transmission.

If detailed information is required about all of the layers in the laminate then it is possible to setup a linescan, collecting spectra at very small intervals across the laminate. Such an experiment was set up to collect spectra at 3 micrometer steps across the laminate, using an aperture size of 5 micrometers with a total of 140 spectra collected. The linescan data is shown as Figure 2.

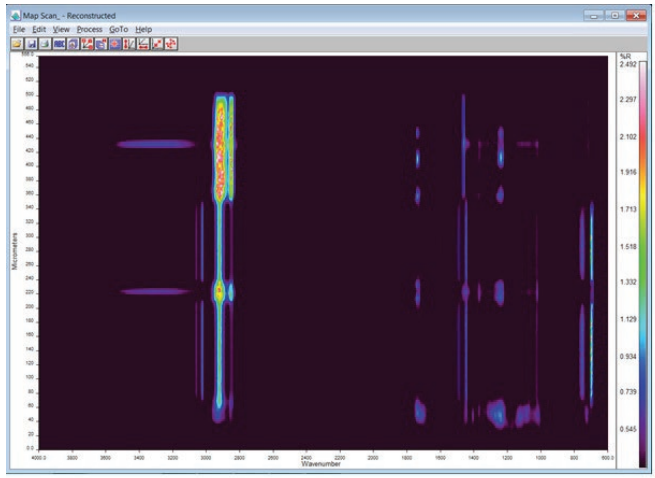


Figure 2: Linescan data for polymer laminate transmission measurements.

The results indicated that several different polymer types were present in the sample as shown in Figure 3. These were identified using Search libraries as; PET, modified PS, PE, ethylene-vinyl acetate (EVA), and ethylene-vinyl alcohol (EVOH).

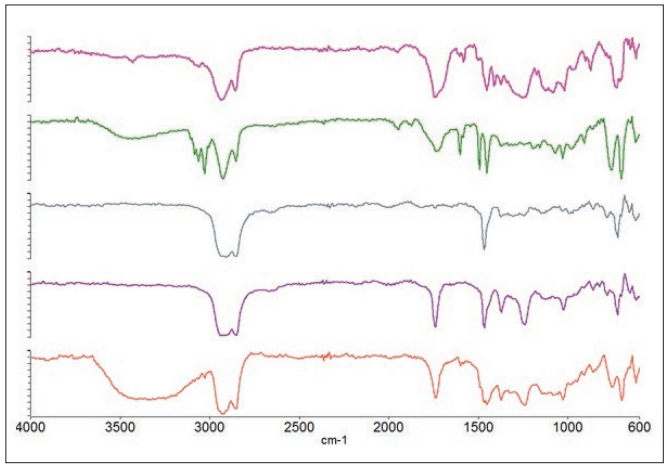


Figure 3: Spectra of the polymers present in the different laminate layers.

Profiles can be generated to show the distribution of the different polymer types throughout the laminate giving significant structural information. The profiles for polystyrene (1600 cm^{-1}), polyethylene (1450 cm^{-1}), ethylene-vinyl acetate copolymer (1746 cm^{-1}), and ethylene-vinyl alcohol copolymer (3334 cm^{-1}) are shown as Figure 4.

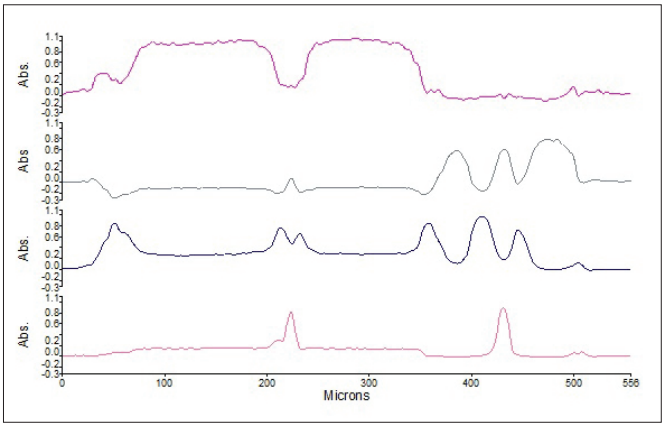


Figure 4: Distribution profiles for polymer types in laminate. From top to bottom: polystyrene, polyethylene, ethylene-vinyl acetate co-polymer and ethylene-vinyl alcohol co-polymer.

If the only requirement for the analysis is to detect and identify the layers in the laminate, then the Analyze Image function within the Spectrum 10 software can be used. This function will analyze the visible image of the sample, detect the layers present, and maximize the measurement area for each layer, all completed automatically. In the case of a multilayer sample, it will collect a single spectrum for each layer, giving the maximum signal-to-noise and significantly reduce the analysis time compared to mapping or measuring a linescan on the same sample. Figure 5 shows an example of a five-layer laminate.

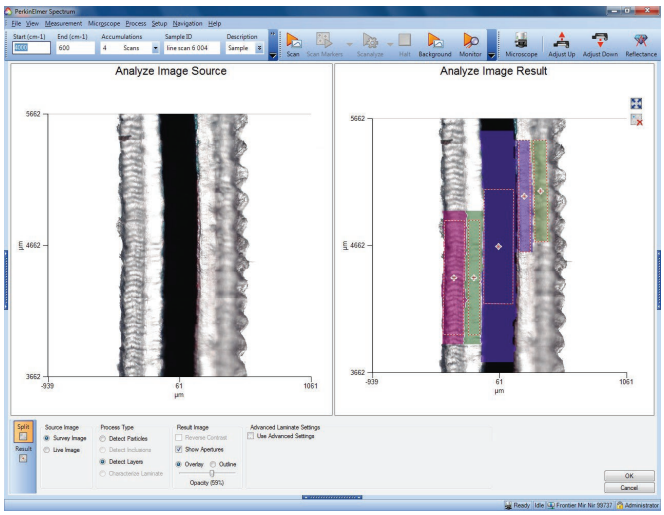


Figure 5: Automatic detection of layers in a laminate shows five layers.

After detection of the laminate layers, spectra were automatically recorded at the marker positions, shown in Figure 6. An automatic library search identified each of the layers as polyethylene terephthalate (layers 1 and 5), ethylene-vinyl acetate copolymer (layers 2 and 4), and silica-loaded polyethylene (layer 3).

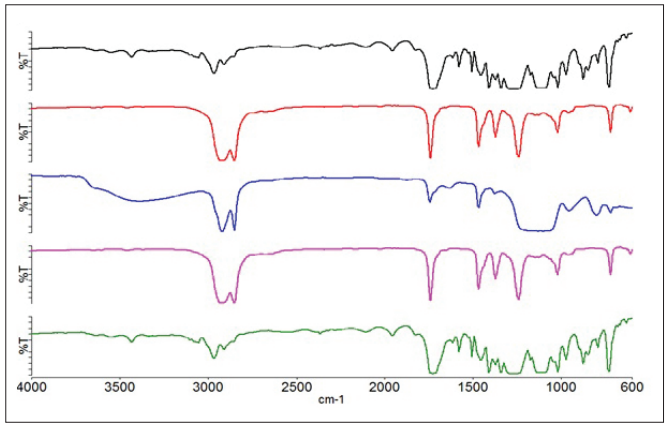


Figure 6: Spectra of layers 1 are shown (top) to 5 (bottom) in polymer laminate.

ATR Measurements of Polymer Laminates

ATR provides a fast and easy way of measuring an infrared spectrum of a material. ATR on an infrared microscope is capable of measuring spectra of very small materials down to just a few micrometers in size. A macro ATR crystal/accessory for the microscope has been utilized to collect data on food packaging laminates. This ATR accessory can generate spectra at a significantly better spatial resolution than transmission measurements [1]. For the ATR measurements the samples were embedded in a resin and polished to give a flat, clean surface for the ATR measurement. Embedding the sample generates a stronger multilayer surface than simply clamping the sample and prevents deformation or compression of the sample under ATR pressure.

A sample of a multilayer food package manufactured using "traditional" polymers was prepared for ATR measurement in the Spotlight 200i. The visible image of this sample was measured and is shown as Figure 7. The width of the laminate is seen to be approximately 200 micrometers and consists of several polymer layers.

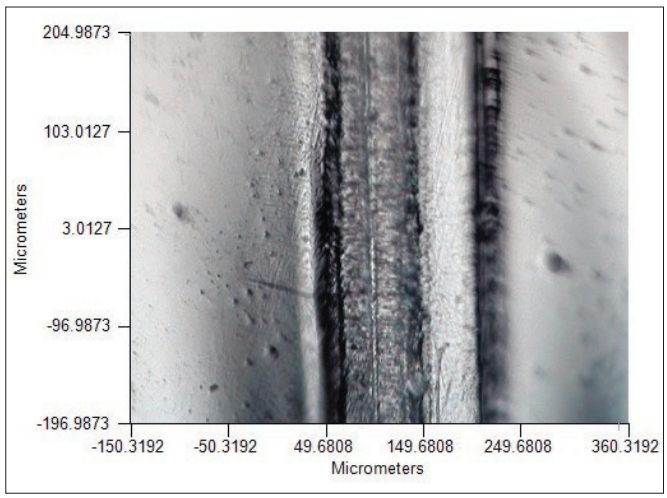


Figure 7: Visible image for multilayer food packaging material.

The macro ATR crystal for the IR microscope was placed in contact across the entire width of the sample. Spectra were collected across the laminate with an effective aperture size of 5 x 5 micrometers at a step size of 5 micrometers. The linescan data collected is shown as Figure 8.

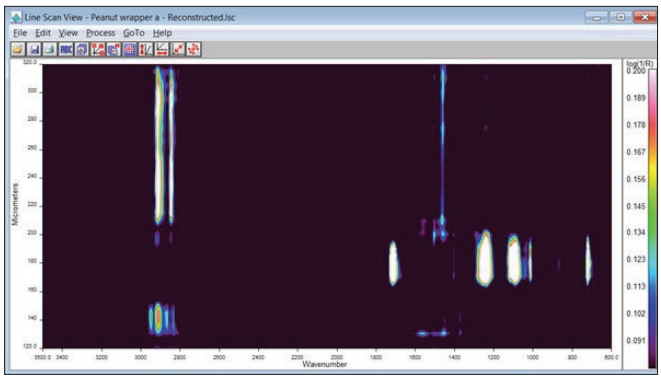


Figure 8: Linescan data for food packaging material.

Several different polymer types seem to be present in the sample. The spectra obtained from the major layers are shown in Figure 9. A search against polymer databases identifies the layers as polypropylene, polyethylene terephthalate, polyethylene, and modified polyethylene.

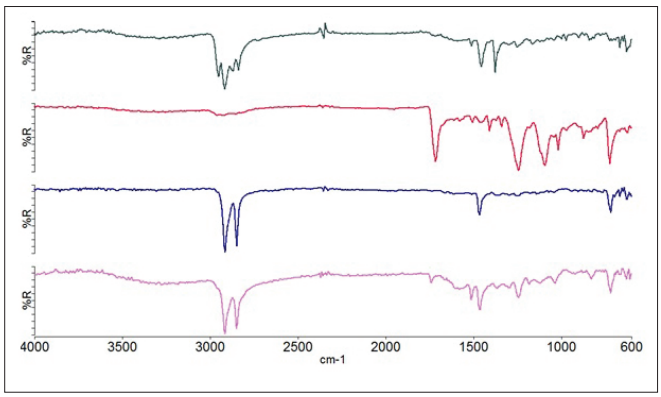


Figure 9: Spectra of major layers are identified as PP, PET, PE and modified PE.

In addition, several other minor layers were detected and their infrared spectra shown as Figure 10. A region of the data (around 160 micrometers in the display) gave no spectral details at all, as it was a thin foil layer.

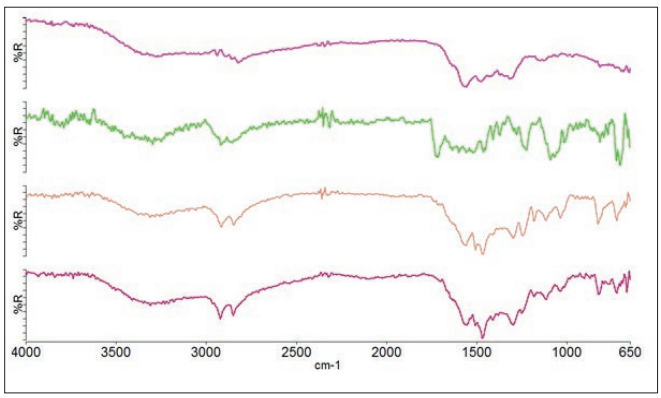


Figure 10: Spectra of minor layers in multilayer food packaging material.

A new generation of biodegradable polymer materials has been developed as a replacement for the "traditional" polymer packaging material. A compostable food packaging material has been analyzed on the Spotlight 200i. The sample was prepared for IR-ATR microscopy in the same way as the "traditional" packaging material that was shown previously.

The visible image of the embedded sample appears as Figure 11. The laminate is seen to be approximately 80 micrometers wide, consisting of a small number of visible layers.

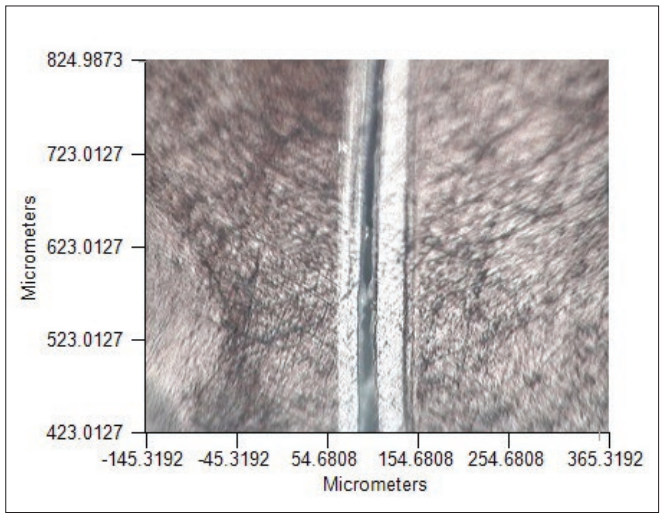


Figure 11: Visible image of a compostable food packaging laminate.

The infrared data collected on the sample is shown as Figure 12. The sample consists of three major layers each of approximately 25 micrometers width.

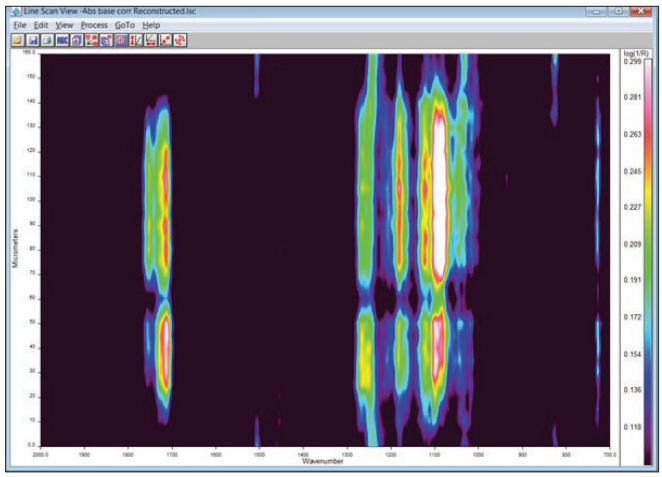


Figure 12: Linescan data for compostable laminate sample.

The spectra are shown as Figure 13. The spectra of the layers all look similar, however, they exhibit spectral differences in the C=O region between 1700-1760 cm^{-1}. The materials are known to be polylactic acid (PLA)-based copolymers. The region at approximately 60 micrometers in the display does not exhibit spectral features, as there is a thin layer of foil present in the sample.

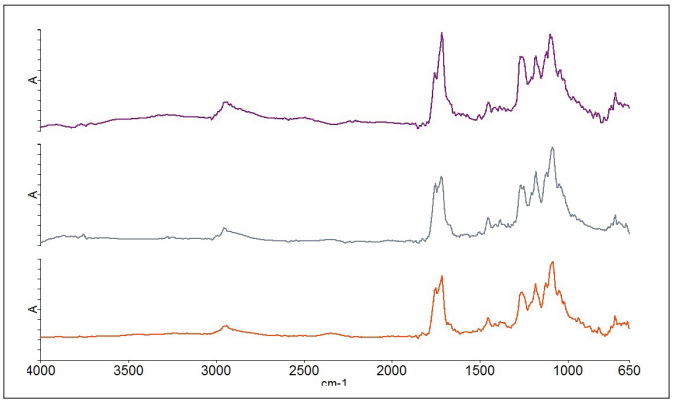


Figure 13: Shown here are spectra of the three different layers in the compostable polymer laminate.

Summary

Packaging materials, especially food packaging, are complex materials in order to satisfy the numerous requirements for the product contained within. Multilayer laminates are a means of fulfilling these requirements. However, disposal of food packaging materials is a significant environmental problem. Biodegradable packaging materials are a possible solution.

IR microscopy has been shown to be an excellent technique for the characterisation of these "traditional" and newer multilayer materials. Transmission or ATR measurements can easily be deployed depending on the sample preparation that is available.

Reference

1. PerkinElmer Technical Note 007641A_03, Spatial Resolution in ATR Imaging

PerkinElmer, Inc.
940 Winter Street
Waltham, MA 02451 USA
P: (800) 762-4000 or
(+1) 203-925-4602
www.perkinelmer.com

PerkinElmer®

For a complete listing of our global offices, visit www.perkinelmer.com/ContactUs

012074_01 PKI

APPLICATION NOTE

FT-IR Microscopy

Author:

Kieran Evans

PerkinElmer, Inc.
Seer Green

Analysis of Multi-Layer Polymer Laminates with Infrared Microscopy

Introduction

Polymer laminates are materials consisting of multiple layers of different polymers. These materials are ubiquitous in modern day life with a substantial amount of food and pharmaceutical packaging containing laminates. A common requirement of food packaging is that the internal layer must be appropriate to be in contact with food and the external layer must be suitable for printing product information. The middle layers of the laminate can also vary depending on requirements regarding the flexibility of the packaging. Due to the large amount of variation present in the parameters of a polymer laminate, the number of combinations is innumerable making detailed analysis of these materials incredibly important.

The PerkinElmer Spotlight™ 400 Imaging System (Figure 1) with the ATR imaging attachment allows layers with thicknesses down to 2-3 µm to be investigated.

Figure 1. Spotlight 400 IR Imaging System.

PerkinElmer®
For the Better

Experimental

Samples were placed vertically in a sample clamp and cut horizontally, flush to the clamp surface, to reveal a flat surface for analysis. The instrumental parameters used are shown in Table 1.

ATR imaging allows a much smaller pixel size (1.56 x 1.56 µm) to be used than conventional, non-contact imaging techniques (6.25 x 6.25 µm), providing the opportunity to image much thinner layers.

Two different polymer laminate samples were imaged as part of this study.

Table 1. Data collection parameters used for measurement of polymer laminates.

Parameter	Value
Spectral Range	4000 – 500 cm^{-1}
Spectral Resolution	8 cm^{-1}
Pixel size	1.56 x 1.56 µm

Results and Discussion

Sample 1

The first laminate sample comprised of five polymer layers with a total thickness of approximately 125 µm. A visible image of the laminate is shown in Figure 2.

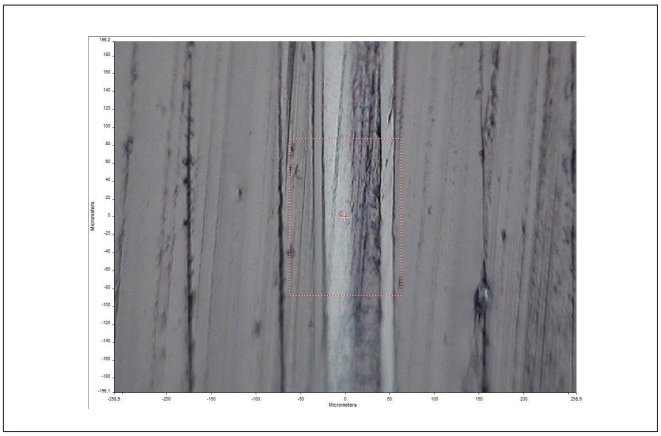


Figure 2. Visible image of polymer laminate 1.

It can be seen in Figure 2 that little information about the polymer could be deduced simply from looking at a visible image. The infrared image obtained using the Spotlight 400 system is shown in Figure 3.

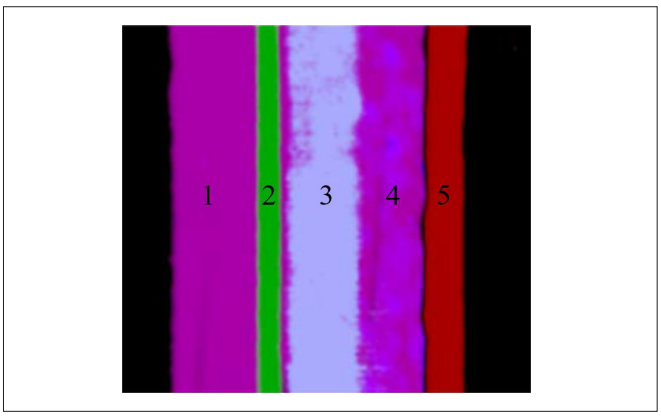


Figure 3. PCA processed ATR-image of laminate 1.

Table 2 shows the identities and thickness of each layer in laminate 1. The identities were determined by comparing the spectra obtained to a library of reference polymer spectra.

Table 2. Identities and thicknesses of the layers present in laminate 1.

Layer	Identity	Thickness (µm)
1	Polyethylene	37
2	Polyethylene + TiO_2	32
3	EVOH	10
4	Polyethylene + Ultramarine pigment	30
5	PET	14

The show structure images and corresponding spectra for each individual layer of laminate 1 are shown in Appendix 1.

Sample 2

The second laminate consisted of eight layers with a total thickness of around 100 µm. The visible image of this laminate is shown in Figure 4.

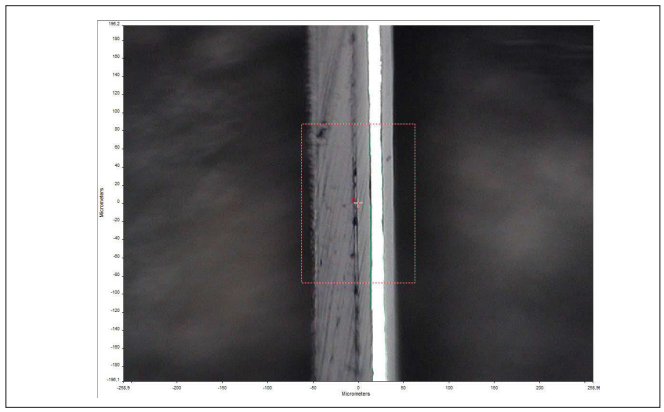


Figure 4. Visible image of laminate 2.

This visible image offers slightly more information than for the first laminate in that it could be reasonably assumed that the reflective layer is some sort of metallic foil. The infrared image is shown in Figure 5.

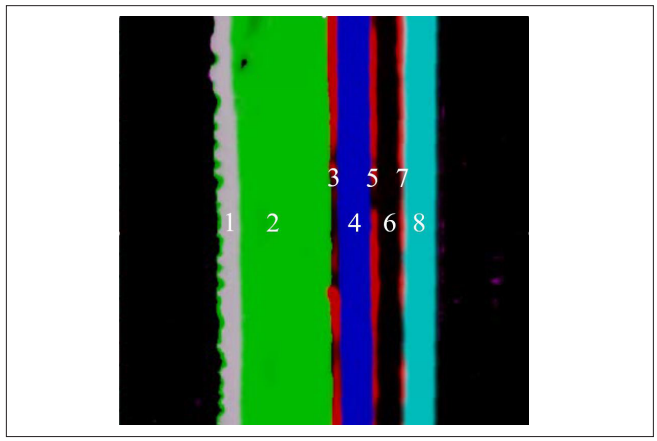


Figure 5. PCA processed ATR-image of laminate 2.

Table 3 shows the identies and thicknesses of each layer in laminate 2. This particular sample demonstrates the ability of ATR-Imaging to resolve sections of sample less the 3 µm in thickness.

Table 3. Identities and thicknesses of layers in laminate 2.

Layer	Identity	Thickness (µm)
1	Polyethylene/Polypropylene Copolymer	6
2	Polypropylene	40
3	Polyurethane	3
4	Polyamide (Nylon) 6	15
5	Polyurethane	2
6	Aluminium	14
7	Polyurethane	3
8	PET	14

The 'show structure' image and corresponding spectrum for each layer of laminate 2 is shown in Appendix 2.

Conclusion

The PerkinElmer Spotlight 400 infrared imaging microscopy with ATR imaging may be used to provide detailed information about the micro-level structure of polymer laminates. SpectrumIMAGE™ software allows the user to perform data analysis with ease in order to unlock valuable information about their samples.

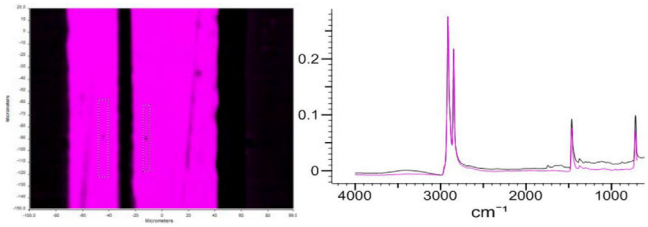
Reference

1. Chanda, M., & Roy, S. K. (2008). Industrial polymers, specialty polymers, and their applications. London: CRC Press

Appendix 1

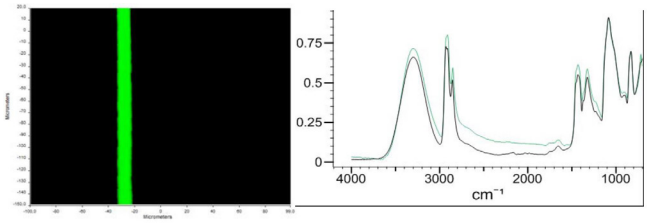
In each case, the collected spectrum is shown in the same colour as the image, while the reference spectrum is shown in black.

Layer 1 – Polyethylene (37 µm)

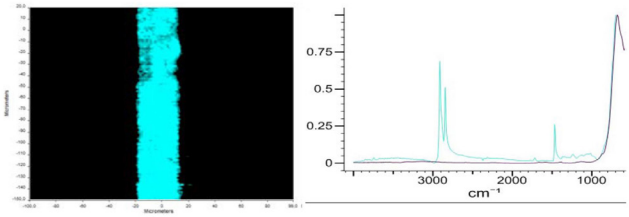


Layer 2 – Polyethylene w/ TiO_2 (10 µm)

In this layer, the reference spectrum is that of TiO_2, showing the influence the addition of this pigment has on the spectrum.

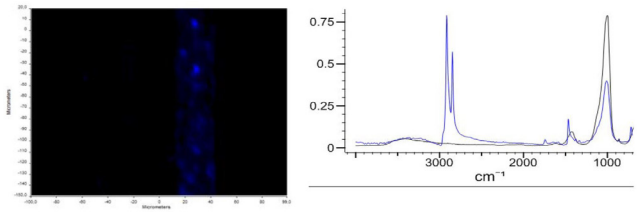


Layer 3 – Poly(ethylene vinyl alcohol) (32 µm)

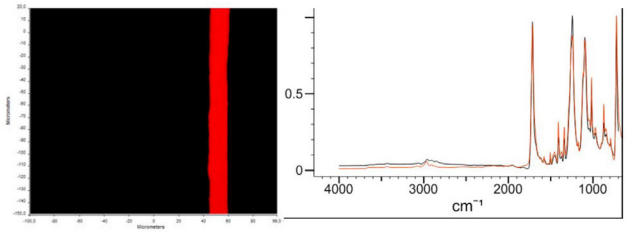


Layer 4 – Polyethylene w/ ultramarine pigment (30 µm)

In this layer, the reference spectrum is that the ultramarine pigment, showing the influence the addition of this pigment has on the spectrum.

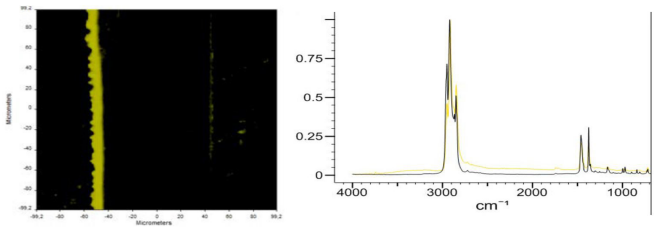


Layer 5 – Polyethylene Terephthalate (14 µm)

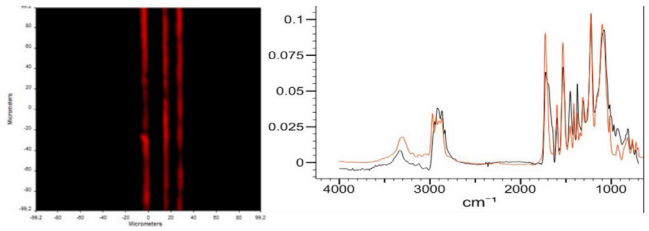


Appendix 2

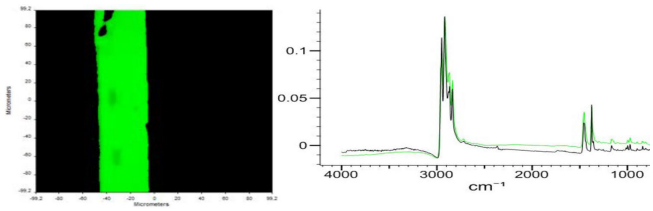
Layer 1 – Polyethylene/Polypropylene copolymer (6 µm)



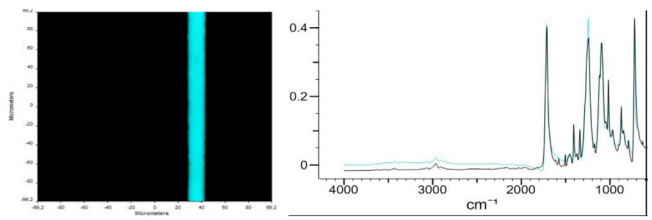
Layers 3, 5 and 7 – Polyurethane (3, 2 and 3 µm respectively)



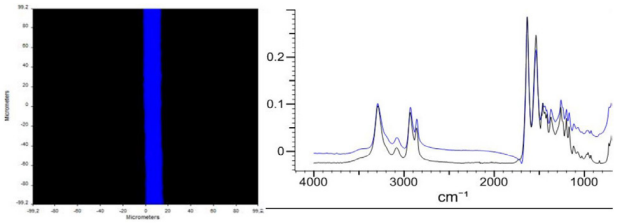
Layer 2 – Polypropylene (40 µm)



Layer 8 – Polyethylene Terephthalate (14 µm)



Layer 4 – Polyamide 6 (15 µm)



PerkinElmer, Inc.
940 Winter Street
Waltham, MA 02451 USA
P: (800) 762-4000 or
(+1) 203-925-4602
www.perkinelmer.com

For a complete listing of our global offices, visit www.perkinelmer.com/ContactUs

68185 PKI

APPLICATION NOTE

Thermal Analysis

Author:

Bruce Cassel

Kevin Menard

PerkinElmer, Inc.
Shelton, CT

TMA of Packaging Materials

Background

The packaging of food and other consumer products is a competitive and rapidly evolving business. The use of plastic containers, plastic wrappers, bubble wrap, etc. allows products to be displayed to best advantage along with printed messaging, consumer information and logos. Besides the display requirements, plastic packaging must seal in the product using a rapid, automated process; it must be cost effective, and increasingly there are requirements for recyclability. Thermal analysis, including dynamic mechanical analysis, has played a role in developing new packaging materials and adapting existing materials to new packaging products and processes. One piece of the materials puzzle is a dimensional piece, namely, determining the dimensional changes that take place in the material as a function of temperature as a result of stresses built up during the production and sealing processes. PerkinElmer has recently developed a moderate cost thermomechanical analyzer (TMA), the TMA 4000, described elsewhere, which is well adapted to testing coefficients of expansion and stress relief dimensional changes which are often of critical interest in the varied fields of plastics processing.

PerkinElmer®
For the Better

This note presents examples of analysis of plastic film products using the PerkinElmer TMA 4000. In each case a sample of a roughly 10 mm finished piece of packaging material is analyzed in extension in the X and Y plane, and in compression in the Z direction perpendicular to the plane. The force applied to the TMA probe is minimal to allow the accumulated stress in the material to be relieved by way of expansion or contraction. Because the authors have little technical information on the material being tested the emphasis here is on the analytical method and instrumental performance. As used in an industrial setting, the TMA focus would likely be on problem solving and specific packaging product improvements.

Food wrapper

Typical requirements of a food wrap are, first, barrier properties to ensure taste quality and safety from contamination, and then also printability, transparency, ease of opening, and critically, processing throughput. To achieve these disparate goals a multilayer film is often employed. Because the film layers will have different coefficients of thermal expansion (CTE) the sealing process might be expected to produce stress that will result in deformation on softening.

To interpret behavior at an inter-molecular level may require analysis by both differential scanning calorimetry (DSC), to interpret heat flow, and by TMA to record dimensional change. The DSC 8000 was used to observe the heat flow behavior, including interpret the glass transition (Tg) region and crystalline melting. The Pyris software facilitates comparing data from multiple thermal analysis techniques, such as DSC, TMA, TGA and STA.

Figure 1 shows the DSC heat flow scan of an aluminized, multilayer polyethylene terephthalate (PET) wrapper used for an individually wrapped health food bar. From the DSC data can be seen two distinct melting endotherms, the high temperature one of which is likely polyethylene terephthalate (PET). The absence of an exotherm indicates the PET is in a crystallized form such as that of biaxially-oriented polyester familiar to many under the trade name Mylar™.

Figure 2 shows the TMA analysis of this snack food wrapper analyzed in compression, observing the softening and contraction of the film in the z-direction, perpendicular to the plane of the film. Six layers of film were sandwiched in a DSC pan to amplify the displacement while avoiding any cleanup after the melt.

Figure 3 shows the TMA machine and transverse-direction of the same wrapper. For the first 60 °C the wrapper shows expansion in both machine and transverse directions. At 150 °C there is differential contraction accompanying the first melt.

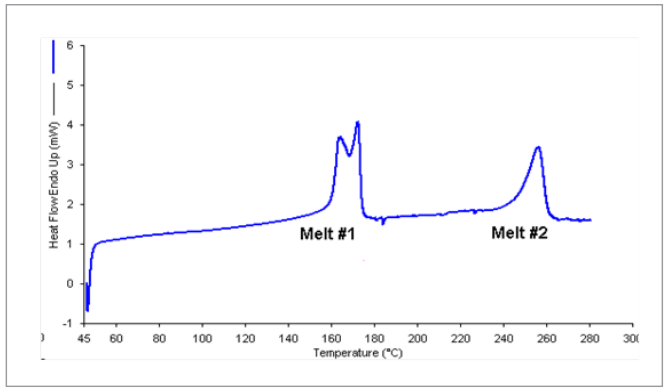


Figure 1. DSC heat flow analysis (endothermic up) of pictured snack food wrapper

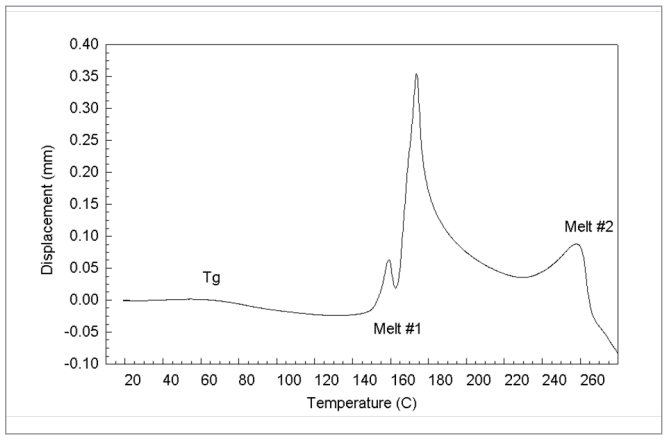


Figure 2. Z-axis expansion and shrinkage of 26 micron film used as snack food wrapper

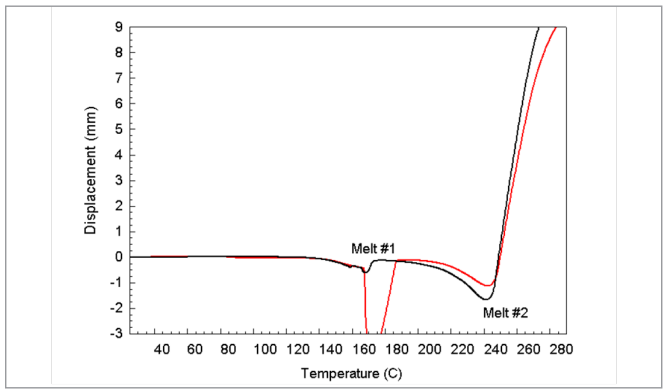


Figure 3. TMA extension of snack food wrapper in machine and transverse direction. Downward slope indicates contraction; upward slope indicates softening or elongation

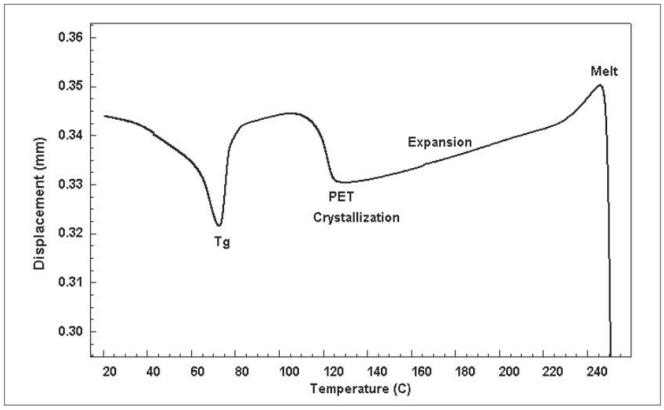


Figure 4. TMA data of PET clamshell showing displacement in Z-direction under compression

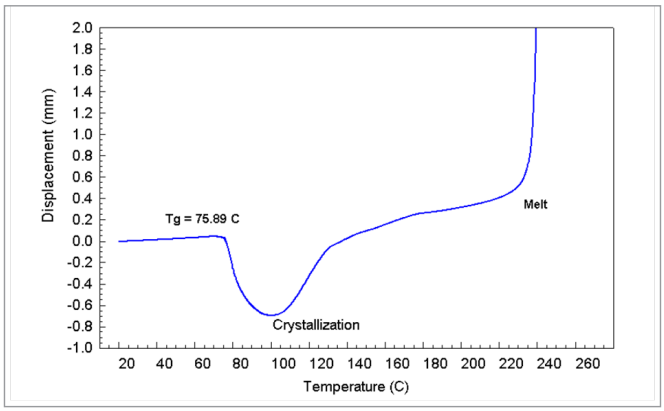


Figure 5. TMA data of PET clamshell showing displacement in the XY plane in extension

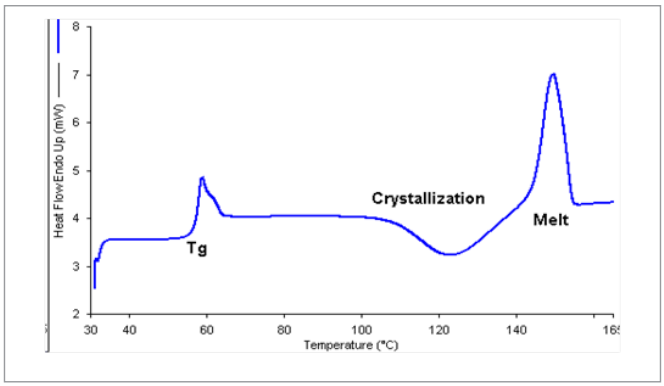
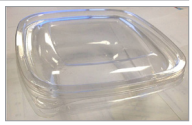


Figure 6. DSC of PLA showing heat flow (positive deflection is heat absorbed)



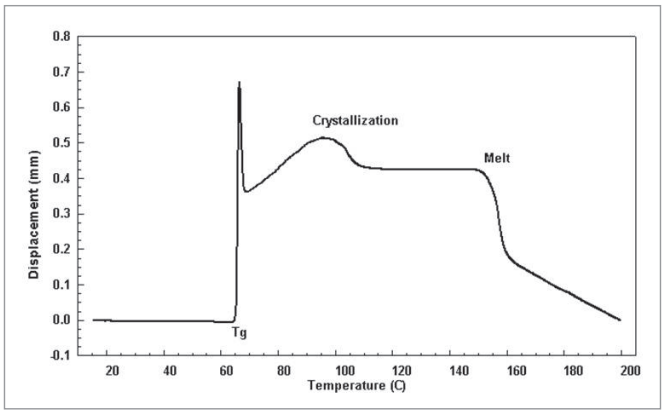


Figure 7. PLA clamshell in Z-direction – zero force in compression

Further heating results in contraction up to the extension at the final melt. Because of the wide dynamic range of the TMA 4000 the displacement can be followed for several millimeters either expansion or shrinkage. Because of the damped suspension, low force (~1g) can be employed without inducing undue noise. There is very little stress relief at Tg since the stress has been relieved in the rolled and drawn film production.

Clam shell packaging

Clam shell packaging—typically of amorphous PET—displays a different story to that described for the PET food wrapper. Here there is substantial stress release at the glass transition from the molding process followed by a reciprocal dimensional recovery during cold crystallization. See Figures 4 and 5.

A newcomer to the clamshell scene is the amorphous PolyLactic Acid (PLA) clamshell which is used in carry-out applications where recycling is problematic. The PLA clamshell material is biodegradable in a weathering environment. While manufacturing problems for PET have been largely worked out over the past decades, thermal information on PLA is less extensive. Figure 6 shows the DSC heat flow scan at 10 °C/min showing some of the same characteristics of amorphous PET, namely, a predominate glass transition followed by crystallization, followed by melt. These events can also be seen in the TMA expansion in the Z-direction shown in Figure 7.

Figure 8 shows the expansion of PLA in the XY plan, showing two samples taken at 90 degrees to one another, one radial with respect to the center of the clamshell, the other tangential.

Tips for running films in extension

When running fibers or fragile film samples the key to obtaining good dimensional change data under low load is attention to careful sample preparation and mounting. The sample should be cut to dimension without creating stress, and it should be mounted linearly in the clamps with the analyzer force evenly distributed. The clamps should be absolutely parallel and in line to one another. The loading fixture shown in Figure 9 is invaluable to perform this task. This fixture which was designed for performing dynamic mechanical analysis in extension forces the clamps to be perfectly parallel and rigidly held as the sample is clamped in place and its length measured.

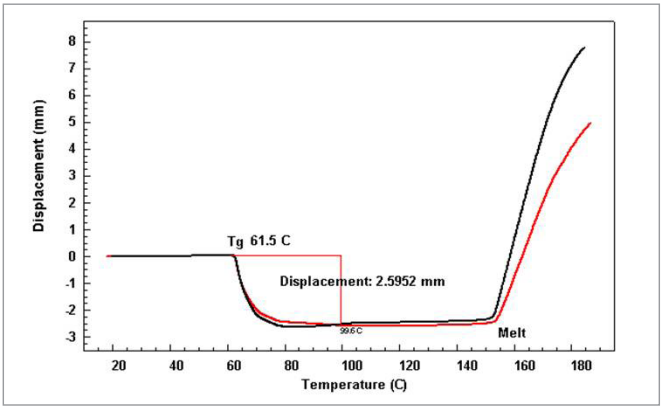


Figure 8. PLA clamshell measured in the XY (radial & tangential) plane of the film in extension

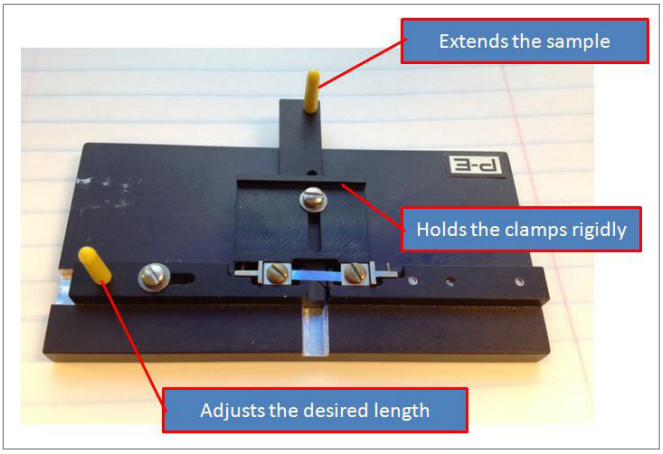


Figure 9. Aligning clamp fixture for extension

Summary

While dynamic mechanical analysis can determine the modulus of a plastic product, such as a film used in packaging, often the TMA, a much simpler technique, can more easily reveal the source of production problems related to the mechanical aspects of processing, especially those related to stress relief. It is clear from the above examples that finished plastic films exhibit measurable dimensional changes due to stress relief upon heating. The TMA 4000 thermomechanical analyzer was designed for the demanding sensitivity of measuring the small coefficients of expansion of materials used in the electronics industry, but it also has the wide dynamic range and low force capability to analyze production problems in the packaging industry, or in other plastics industries.

PerkinElmer, Inc.
940 Winter Street
Waltham, MA 02451 USA
P: (800) 762-4000 or
(+1) 203-925-4602
www.perkinelmer.com

PerkinElmer®

For a complete listing of our global offices, visit www.perkinelmer.com/ContactUs

011202_01

APPLICATION NOTE

Gas Chromatography/
Mass Spectrometry

Author:

Kira Yang

PerkinElmer, Inc.
Shanghai, China

Determination of the Migration of Phthalate and Polycyclic Aromatic Hydrocarbon from Food Contact Plastic Bags by GC/MS

Introduction

Plastic bags are widely used in food packaging due to cost and flexibility, for example breakfast items such as hot steamed buns, oil cake and soybean milk are typically packaged in plastic. Leftovers, supermarket cooked food and even beer, are also packaged with plastic bags. Plastic packaging is very convenient but plasticizers and other additives dissolve and migrate into food during processing, heating and packaging, which can result in food contamination and permanent damage to human health and the environment.

This application demonstrates a method for the determination of 16 phthalates (PAEs) and 16 polycyclic aromatic hydrocarbons (PAHs) leaching from plastic bags using the PerkinElmer Clarus® SQ 8 GC/MS with electron ionization (EI) source. The method is based on the Chinese National Standards GB 31604.1-2015, GB 31604.30-2016 and GB 5009.265-2016.[1-3] Toluene is used as a solvent to extract the target compounds from the food simulants.

PerkinElmer®
For the Better

Experimental

The PerkinElmer Clarus 680 SQ 8 GC/MS operating in electron ionization (EI) mode was used to perform these experiments with the conditions presented in Table 1. SIFI MS mode was used to analyze samples qualitatively and quantitatively with the operating parameters for SIM mode shown in Table 2. A PerkinElmer Elite 5MS column (30 m × 0.25 mm × 0.25 µm) was used to separate the compounds. Five food simulants are used in this study (shown in Table 3) according to GB 31604. 1-2015, General rules for food contact materials and articles.

Calibration standards (sixteen PAE and sixteen PAH mixture) were purchased from ANPEL Laboratory Technologies (Shanghai) Inc. Chromatographic grade toluene (HPLC grade, Fisher Scientific) was used for all standard dilutions and as a solvent to extract target compounds from simulants. The concentration ranges for the standards are 0.05 mg/L – 10 mg/L for PAEs and 5 µg/L -100 µg/L for PAHs. Plastic bags (polyethylene) were obtained from a local breakfast store and vegetable market. Each bag was cut into 0.6 dm^2 pieces and submerged in 10 mL of food simulants with the storage conditions for each plastic in the five food simulants shown in Table 4. The glass containers for the food simulants were sealed to prevent loss due to evaporation.

After the migration test, the plastic pieces were removed from the simulants. The isooctane simulant was placed directly into vials for analysis without further preparation. A toluene extraction was performed for the other stimulants using the following procedure; add 2 mL of toluene to the simulants followed by mechanical shaking. The extract was then separated under centrifuge with the toluene layer sampled for analysis by GC/MS.

Table 1. Analytical parameters.

GC Parameters	
Injector Type	Capillary injector with capillary splitless deactivated glass liner with deactivated wool
Inlet Temp	280 °C
Carrier Gas Flow	1 mL/min
Split Flow	Splitless
Injection Volume	1 µL
Initial Oven Temp	50 °C
Oven Hold	1.0 min
Ramp	20 °C/min
2nd Oven Temp	220 °C
Oven Hold	1.0 min
Ramp	5 °C/min
3rd Oven Temp	250
Oven Hold	1.0 min
Ramp	20 °C/min
4th Oven Temp	290 °C
Oven Hold	5.0 min
MS Parameters	
Ionization	EI
GC Inlet Line Temp	290 °C
Ion Source Temp	260 °C
Function Type	SIFI
Mass Range	45 to 450 amu
Scan Time	0.05 s
Solvent Delay Time	3 min

The spike recovery experiment was carried out by spiking 10 mL of food simulants to give expected concentrations of 0.2 mg/L and 5 mg/L PAE and 20 µg/L PAH in toluene.

Table 2. Operating parameters for SIM MS mode.

Compound Name	Quantitation Ion (m/z)	Dwell Time (s)	Retention Window (min)
Naphthalene	128	0.1	4.70 - 6.13
DMP	163	0.03	6.50 - 8.00
Acenaphthylene	152		
Acenaphthene	154		
DEP	149	0.05	7.65 – 8.60
Fluorine	166		
Phenanthrene	178	0.03	9.00 – 12.20
Anthracene	178		
DIBP	149		
DBP	149		
DMEP	149		
BMPP	149		
Fluoranthene	202		
DEEP	149		
DPP	149		
Pyrene	202		
DHXP	149	0.03	12.70 – 16.40
BBP	149		
DBEP	149		
Benz[a]anthracene	228		
Chrysene	228		
DCHP	149		
DEHP	149		
DPhP	225		
DNOP	149	0.03	16.80 – 20.20
Benz[b]anthracene	252		
Benz[k]anthracene	252		
Benzo[a]pyrene	252		
DNP	149		
Indeno(1,2,3-cd)pyrene	276	0.03	20.60 – 23.00
Dibenz[a,h]anthracene	278		
Benzo[g,h,i]perylene	276		

Table 3. Food simulants.

Type of Food		Food Simulants
Aqueous	pH ≥5	10% Ethanol (v/v)
	pH <5	4% Acetic acid (v/v)
Alcoholic	The amount of Ethanol ≤20% (v/v)	20% Ethanol (v/v)
	20%<The amount of Ethanol ≤50% (v/v)	50% Ethanol (v/v)
Oil and food with oil on the surface	Isooctane *	1 µL

** Vegetable oil is the simulant for oil and food with oil on the surface which can be replaced by 95% ethanol (v/v), hexane, n-heptane and isooctane. Here isooctane is used as a simulant.*

Table 4. Storage conditions.

Time (Hours)	Temperature (°C)		
0.5	20	40	70
2	20	40	70
6	20	40	70

Results and Discussion

The overlaid extracted ion chromatograms (Figure 1) show the elution of the PAEs and PAHs. The calibration curves were plotted as the peak area versus the amount of analyte and the obtained determination coefficients (r^2) for all compounds were over 0.997, showing the reliability of the analysis in the concentration range. Table 5 and 6 summarizes the results for linearity of PAEs and PAHs.

In this study, hexane, dichloromethane and toluene were the solvents evaluated for extraction efficiency. Hexane showed lower extraction efficiency than toluene and dichloromethane because of the weak polarity of the solvent. The dichloromethane layer was under the simulants layer since dichloromethane is denser than the simulants and as such it proved difficult to transfer the extract into autosampler vials. Therefore, toluene was chosen as a solvent in this paper. The recoveries per storage conditions were calculated to be in the range of 85.5 – 116.0% for most PAEs and all PAHs (Table 7 and 8). The slightly polar compounds such as DEP, DMP and DMEP showed lower recoveries. Three phthalates, DIBP, DBP and DCHP, were detected under the different storage conditions and there was a measurable increase in leaching with increased storage time and storage temperature. The strongest leaching result was obtained in 50% of ethanol when comparing the other food simulants. Figure 2 shows the obtained total ion chromatograms of the phthalates. The phthalate extract was obtained using a migration test with samples heated at 40 °C in 50% ethanol for different times. The migration of PAEs in plastic bags summarized (Table 9) is very low even when the simulants were stored at high temperature for an extended time. Specific migration limit (SML) in the Chinese national standard for phthalates are 0.3 mg/kg for DBP, 1.5 mg/kg for DEHP, 0.01 mg/kg for DAP and 9.0 mg/kg for DINP.[4] The amount of DBP is lower than the SML. The other two phthalates weren't prescribed SML in Chinese standard. No PAHs were detected from any of the simulants.

Table 5. PAEs results for retention time and linearity.

Compound Name	Retention Time (min)	Quantitation Ion (m/z)	Linearity	
			Calibration Curve	r^2
DMP	7.24	163	24916.6x - 716.13	0.9991
DEP	8.08	149	27373.9x - 1027.87	0.9990
DIBP	9.57	149	40998.3x - 2395.72	0.9992
DBP	10.11	149	48816.0x - 3210.09	0.9990
DMEP	10.34	149	24828.4x - 1956.98	0.9982
BMPP	10.88	149	24774.7x - 2348.26	0.9994
DEEP	11.18	149	11755.0x - 1044.41	0.9989
DPP	11.51	149	52400.1x - 3993.44	0.9993
DHXP	13.32	149	51978.3x - 5754.94	0.9993
BBP	13.41	149	20601.9x - 2406.26	0.9992
DBEP	14.70	149	8662.19x - 1362.36	0.9990
DCHP	15.25	149	36741.1x - 4353.72	0.9992
DEHP	15.47	149	32189.0x - 2720.40	0.9993
DPhP	15.55	225	22867.3x - 2229.54	0.9993
DNOP	17.91	149	46799.4x - 8164.74	0.9989
DNP	19.56	149	50894.5x - 7911.87	0.9991

Table 6. PAHs results for retention time and linearity.

Compound Name	Retention Time (min)	Quantitation Ion (m/z)	Linearity	
			Calibration Curve	r^2
Naphthalene	5.50	128	43.42x - 142.42	0.9994
Acenaphthylene	7.37	152	28.55x - 97.55	0.9968
Acenaphthene	7.55	154	19.71x - 67.34	0.9967
Fluorine	8.18	166	18.66x - 68.49	0.9985
Phenanthrene	9.31	178	29.60x - 125.86	0.9988
Anthracene	9.38	178	27.02x - 107.53	0.9991
Fluoranthene	11.09	202	30.87x - 151.234	0.9994
Pyrene	11.53	202	32.62x - 151.56	0.9992
Benz[a]anthracene	14.79	228	20.00x - 126.54	0.9991
Chrysene	14.90	228	26.35x - 163.96	0.9995
Benz[b]anthracene	18.34	252	16.43x - 106.02	0.9975
Benz[k]anthracene	18.42	252	23.84x - 162.02	0.9986
Benzo[a]pyrene	19.09	252	15.74x - 99.15	0.9991
Indeno(1,2,3-cd)pyrene	21.46	276	10.65x - 82.70	0.9973
Dibenz[a,h]anthracene	21.57	278	11.39x - 84.94	0.9983
Benzo[g,h,i]perylene	22.07	276	14.33x - 94.20	0.9992

Table 7. PAEs recoveries (%) (n=3).

Compound Name	4% Acetic Acid		10% Ethanol		20% Ethanol		50% Ethanol		Isooctane	
	0.2 ppm	5 ppm	0.2 ppm	5 ppm	0.2 ppm	5 ppm	0.2 ppm	5 ppm	0.2 ppm	5 ppm
DMP	88.5	110.4	95.5	97.1	106.0	108.0	-	86.0	85.4	110.6
DEP	-	-	-	94.7	-	85.7	-	-	85.8	86.6
DIBP	92.5	103.7	100.5	99.0	103.0	94.1	111.5	104.0	104.3	98.6
DBP	105.5	102.5	100.0	98.9	102.5	93.9	116.0	106.0	105.1	97.6
DMEP	85.5	97.4	89.0	93.1	90.5	86.0	-	-	103.6	98.0
BMPP	87.0	104.7	99.5	98.7	103.0	95.2	114.5	113.0	100.2	97.4
DEEP	87.0	103.4	95.5	98.9	99.5	92.6	89.5	88.2	99.7	95.4
DPP	88.5	101.4	95.5	97.9	101.0	93.3	113.0	106.0	99.6	95.0
DHXP	88.5	104.7	98.0	97.7	97.0	92.8	106.5	111.2	100.3	95.0
BBP	85.7	108.3	98.0	100.9	100.5	95.8	110.5	110.8	99.5	95.6
DBEP	85.5	104.4	98.0	98.3	111.5	91.9	113.8	110.0	90.3	94.0
DCHP	88.0	103.0	100.0	98.2	103.5	94.6	113.5	108.0	95.1	95.0
DEHP	94.5	104.1	103.0	97.2	109.5	93.4	112.2	114.0	88.6	93.6
DPhP	85.5	104.1	95.5	98.0	100.5	93.0	106.5	102.7	100.4	95.0
DNOP	88.0	101.7	101.0	96.5	107.0	89.5	108.5	111.0	95.2	95.4
DNP	88.5	102.8	100.5	98.2	105.0	91.3	104.5	114.0	89.9	93.0

Table 8. PAHs recoveries (%) (n=3).

Compound Name	4% Acetic acid	10% Ethanol	20% Ethanol	50% Ethanol	Isooctane
Naphthalene	96.89	107.00	103.80	102.40	95.00
Acenaphthylene	95.50	92.75	91.20	89.00	100.20
Acenaphthene	88.65	86.35	85.80	88.25	93.50
Fluorine	98.90	92.45	102.90	96.50	96.76
Phenanthrene	97.50	97.00	105.75	106.15	96.75
Anthracene	92.70	93.70	96.50	105.60	100.55
Fluoranthene	95.60	91.55	94.50	93.80	103.40
Pyrene	96.50	93.40	95.50	104.10	98.05
Benz[a]anthracene	89.50	87.55	86.85	85.30	90.65
Chrysene	98.50	94.25	94.00	106.75	101.85
Benz[b]anthracene	91.80	91.60	101.25	110.90	89.10
Benz[k]anthracene	99.85	91.55	94.30	103.25	92.25
Benzo[a]pyrene	100.20	95.95	98.00	106.70	93.95
Indeno(1,2,3-cd)pyrene	88.50	97.10	95.90	104.35	93.30
Dibenz[a,h]anthracene	95.70	98.35	104.25	113.75	95.75
Benzo[g,h,i]perylene	87.15	90.70	91.90	94.20	94.35

Table 9. The migration of PAEs in plastic bags.

Compound Name	Food Simulants	Amount (mg/kg)								
		70 °C			40 °C			20 °C		
		0.5 Hour	2 Hours	6 Hours	0.5 Hour	2 Hours	6 Hours	0.5 Hour	2 Hours	6 Hours
DIBP	4% Acetic Acid	0.064	0.092	0.111	0.003	0.005	0.008	0.003	0.004	0.004
	10% Ethanol	0.071	0.091	0.173	0.006	0.006	0.008	0.003	0.004	0.004
	20% Ethanol	0.147	0.188	0.247	0.010	0.016	0.017	0.004	0.007	0.009
	50% Ethanol	0.197	0.238	0.266	0.007	0.017	0.020	0.006	0.007	0.010
	Isooctane	0.201	0.256	0.287	0.005	0.011	0.016	0.005	0.006	0.007
DBP	4% Acetic Acid	0.208	0.219	0.280	0.008	0.011	0.014	0.008	0.009	0.009
	10% Ethanol	0.184	0.199	0.230	0.010	0.010	0.011	0.003	0.004	0.004
	20% Ethanol	0.317	0.347	0.490	0.020	0.022	0.019	0.010	0.009	0.010
	50% Ethanol	0.628	0.815	1.033	0.020	0.029	0.031	0.014	0.017	0.018
	Isooctane	0.420	0.493	0. 578	0.012	0.023	0.027	0.008	0.011	0.013
DCHP	4% Acetic Acid	0.009	0.009	0.012	-	-	-	-	-	-
	10% Ethanol	0.004	0.008	0.048	-	-	-	-	-	-
	20% Ethanol	0.007	0.009	0.010	-	-	-	-	-	-
	50% Ethanol	0.299	0.317	0. 456	0.011	0.011	0.035	0.010	0.008	0.011
	Isooctane	0.130	0.404	0.682	-	-	-	-	-	-

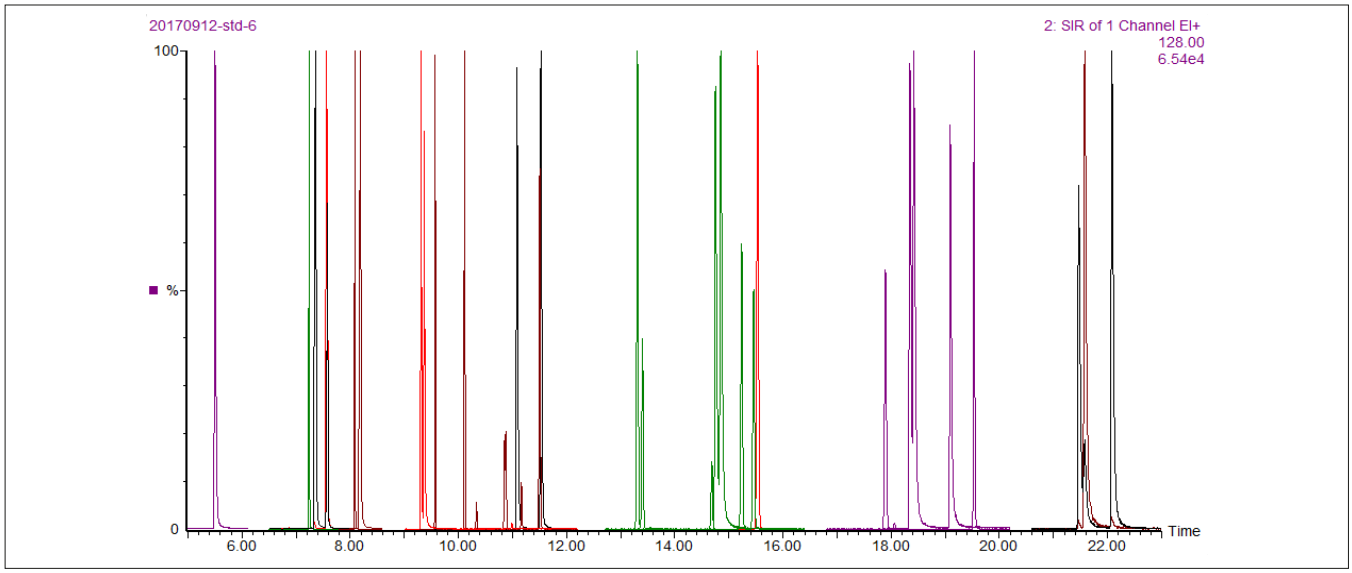


Figure 1. The overlaid extracted ion chromatogram in selected ion monitoring mode of a 5 mg/L PAE standard and 50 µg/L PAH standard.

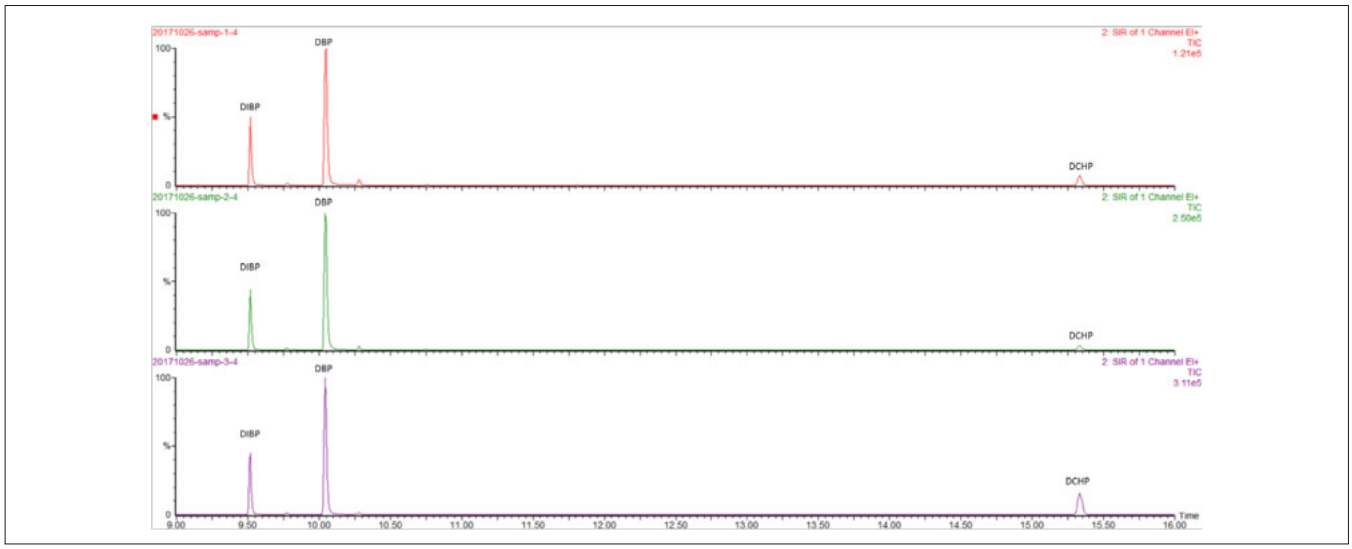


Figure 2 Total ion chromatogram of the sample at 40 °C in 50% ethanol for 0.5, 2, 6 hours. (The red one is for 0.5 hour. The green one is for two hours. The violet one is for six hours.)

Summary

In this paper, a method for the determination of 16 phthalates (PAEs) and 16 polycyclic aromatic hydrocarbons (PAHs) leaching from plastic bags was established using the PerkinElmer Clarus® SQ8 GC/MS with electron ionization (EI) source. Toluene was shown to be a suitable solvent with good recoveries for this application. The phthalate leaching from the plastic bags into food is lower than the SML in GB 9685-2008.

References

1. GB 31604.1-2015, General rules for food contact materials and Articles.
2. GB 31604.30-2016, Food contact materials and articles - Determination of phthalates and migration.
3. GB 5009.265-2016, Determination of polycyclic aromatic hydrocarbons in foods.
4. KGB 9685-2008, Hygienic standards for uses of additives in food containers and packaging materials.

PerkinElmer, Inc.
940 Winter Street
Waltham, MA 02451 USA
P: (800) 762-4000 or
(+1) 203-925-4602
www.perkinelmer.com

PerkinElmer®

For a complete listing of our global offices, visit www.perkinelmer.com/ContactUs

013869_01 PKI

PerkinElmer, Inc.
940 Winter Street
Waltham, MA 02451 USA
P: (800) 762-4000 or
(+1) 203-925-4602
www.perkinelmer.com

For a complete listing of our global offices, visit www.perkinelmer.com/ContactUs

147008 PKI