ARTICLE

# Science and Regulation Co-Evolve to Combat Plastic Packaging Failures


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## Ensuring Food and Pharmaceutical Safety

A crucial factor contributing to the safety of food and pharmaceutical products is their packaging. This is often made of plastic. More than 40% of flexible and rigid plastic packaging is used for food and pharmaceutical products. They extend shelf life and prevent contamination, chemical or biological, and provide significant transportation benefits. For example, both oils and coffee are now easily transported by oceanfreight thanks to advances in packaging technology.

Of course, food or pharmaceutical products can become unsafe or unsuitable if the wrong material is used to wrap it. Physical breakages from the packaging itself in the form of plastic fragments can get into the product and be ingested by the consumer. Chemicals from the plastic can leach into the food or medicines and endanger health and the environment.

## Government Oversight

To ensure safety, nearly all countries have government agencies that standardize and regulate the performance criteria for product packaging materials. These include restrictions on chemicals and heavy metals, recycling requirements, labelling and laboratory testing. Such authorities include the Food & Drink Administration (FDA) and CFIA in North America, the SFDA in China or the European Commission to name just a few. Continuous improvement and amendment to such regulation is important for ongoing public safety. A strong relationship with the research community is therefore vital to yield updates in our understanding to keep regulation effective.

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A good example is the Food Standards Authority of Australia and New Zealand which carries out periodic analysis on food products and their packaging material. In the FSANZ's 2016 study – the 24th Australian Total Diet Study, several chemical contaminants were found in package materials. The chemicals listed by the federal department include BPA epoxidized soybean oil, phthalates, printing inks and perfluorinated compounds (PFAS).

### PFAS, PFOS, PFOA Defined

Perfluoroalkyl and polyfluoroalkyl substances (PFAS) are a group of man-made chemicals that include Perfluorooctane Sulfonate (PFOS) and Perfluorooctanoic Acid (PFOA). Because of their ability to repel fire, water, oil and stains, they were used since the 1940s to produce a variety of products, including:

- Plastic packaging
- Stain and water-resistant fabrics
- Non-Stick Coatings
- Polishes and Waxes
- Paints
- Cleaning Products
- Fire-Fighting Foams

*Figure 1: Definition of PFAS, PFOS, PFOA*

Roberto Fusetto, Applications Scientist of Chromatography at PerkinElmer in Australia notes that, "there is a rising concern about the presence of these chemical compounds. Societies are asking how these chemicals should be addressed and at what levels they should be controlled or even completely eliminated from packages."

Another example is the European Commission, which continuously improves the rules around the use of printing inks, adhesives, and coatings used in food-contact plastics.

## Leaching Out

Contaminants from packaging include; phthalates, receiver solvents (like inks), volatile organic compounds and PFAS/PFOS. The ability to moderate these contaminants is dependent on package integrity, that is, the structural layers which protect from external contamination being brought into the package and microplastic waste, which can result from it, entering the external environment.

Phthalates (PAH) are a group of chemicals used to make plastics more durable and they are commonly called plasticizers. Used to increase flexibility, transparency, durability and longevity, Phthalates are present in hundreds of products, such as vinyl flooring, lubricating oils, and personal-care products like soaps, shampoos, and hair sprays. The following molecular structure shows you the backbone structure of phthalates is simply a benzene ring with two ester bonds.

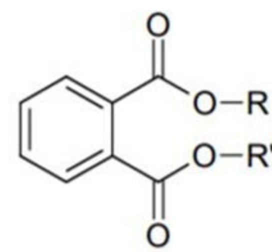


*Figure 2: Phthalates chemical composition.*

The hydrocarbon chains attached represent different substitutes which will give a different degree of flexibility and transparency to the product. Three phthalates are of major concern: Dibutyl Phthalate (DBP), Butyl Benzyl Phthalate (BBP) and Diethylhexyl phthalate (DEHP).

*Table 1: Table of Phthalates compounds.*

| Acronym | Common Name |
|---|---|
| DBP | Dibutyl phtalate |
| DIBP | Diisobutyl phtalate |
| BBP | Butyl benzyl phtalate |
| DnPP | Di-*n*-pentyl phtalate |
| DEHP | Di (2-ethylhexyl) phtalate |
| DnOP | Di-*n*-octyl phtalate |
| DINP* | Diisononyl phtalate |
| (Part of DINP)* | Di-($C_9$-rich branched $C_8$-$C_{10}$-alkyl) phtalate |
| DIDP* | Diisodecyl phtalate |
| (Part of DIDP)* | Di-($C_{10}$-rich branched $C_9$-$C_{11}$-alkyl) phtalate |

Studies have demonstrated a link between phthalates and several health problems, including asthma, endocrine disruption, reproductive abnormalities and cancers. Factors like; the type of material used, how long it has stayed wrapped, and the storage temperature can all influence the release of phthalates into food products. Additionally, it is not just the packaging material that can leach these compounds into food but also other plastic parts which can come into contact with the products during the production process, so it's a more complicated picture that needs to be addressed.

Over the years concerns have been raised by the scientific community which has led to a greater focus on how to prevent PAH contamination in food and how to safely identify them before they can become a hazard to humans. One of the first to raise the alarm was Robin Whyatt, Professor of Environmental Health Science at Columbia University, who in 2015 expressed concern about the ability of milk to extract phthalates out of the plastic tubes used in milking machines.

> *"Milking machines use a lot of plastic and DEHP is free and very lipophilic (fat soluble), and milk is full of lipids, so it just pulls the DEHP out of the plastic tubing and into the milk"*
>
> Robin Whyatt, Professor of Environmental Health Services at the Columbia University Medical Center

A combination of chromatography techniques including GC/MS and LC-MS-MS are currently employed to assess PAH levels in different food samples. The right choice of equipment will depend on whether the contamination comes from a leachable plastic container or within the sample itself.

## Inky Issues

Many flexible packages will have solvents, or inks, present because of labelling needs. The analysis of solvents in packaging material is a crucial QC step during the production process.

By law in most countries, the printed side of a packaging material cannot come into contact with food at any time. It is also important to prevent any "set off" of the ink, which means the ink cannot be carried into the layer that is in contact with food. When rolls of printed material are made, there are always two sides; the external side which has the label's printed information, and the internal side which is in contact with the food. Because these rolls form into coils, it is inevitable that the printing side contacts the internal side of the material. If the ink does not set off properly, it can be transferred into the inside of the packaging material and possibly contaminate the food.

In Europe this has been a major concern since 2005, so it is a legal requirement that producers analyze inks by gas chromatography using a combination of headspace and flame ionisation detector. Inks are therefore tested during production, with the official analytical method EN 13628-2:20041.

*Figure 3: PerkinElmer GC 2400™ with autosampler and detachable interface.*

Using this technique is straightforward. A small piece of sample/film is added to the autosampler vial which is then sealed and heated up. The solvents released in the process are quantified by GC-FID or MS and their level compared with the local regulation. The 12 key residual solvents of concern are reported in Table 2.

*Table 2: Table of solvents used in Phthalates analysis.*

| **Solvents** | |
|---|---|
| Ethanol | Methoxy Propanol |
| Isopropanol | Ethoxy Propanol |
| Methyl Acetate | Toluene |
| MEK | Butyl Acetate |
| Ethyl Acetate | m-Xylene |
| Isobutanol | o-Xilene |

## Volatiles in Recycled Products

Volatile screening, similar to NGS is carried out by experts and is generally connected to bad odours. This can become a common problem during a typical recycling process, where plastics are melted down and formed into pellets during a series of grinding, washing, heating, and extruding steps, see Figure 4. Here different long-lasting constituents within the products such as inks, coatings, additives, and adhesives, can accumulate or transform over time and accumulate or form new contaminants in the final recycled product.  Furthermore, the increasing quantity of recyclable materials present in landfills, the type of plastic-like products present in the market and the pressure by regulatory bodies on quality and safety around recycled products, requires extensive analytical testing on both raw materials (flakes and pellet resins) and final products. PerkinElmer produce a package of instruments specifically to meet the identification needs of recyclers – the Polymer Recycling package.

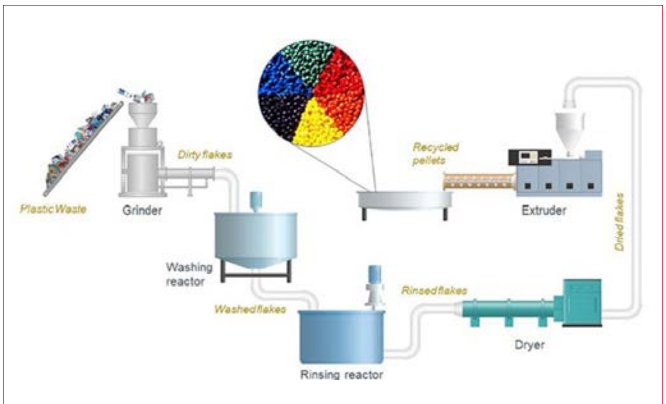


*Figure 4: Schematic of a mechanical recycling procedure.*

For example, pellets of recycled polyethylene terephthalate (PET) used to create new water plastic bottles, need to be tested for the presence of benzene, acetaldehyde, and limonene. Acetaldehyde and Benzene are both thermal degradation products of the PET polymer and polymer impurities respectively. If acetaldehyde migrates or leaches into the bottled water, it might influence the organoleptic properties of the bottled water. On the other side, Benzene is a toxic compound which needs to be strictly controlled to avoid any health concerns. Lastly, the flavour substance limonene, is one of the key substances used to identify post-consumer recyclates from soft drink containers, as most soft drinks contain this compound. Limonene levels need to be maintained at extremely low levels with recycled pellets (below 20 ppb) to avoid contaminating water and leaving an unpleasant lemon taste. A combination of Head Space, Gas Chromatography and Flame Ionisation Detector (FID) can be employed to assess flakes and resins to the required specifications.

Besides taste and smell, volatile organic compounds (VOCs) may also include toxic compounds (e.g. toluene, hexane, etc) that are not generally expected during the process or are produced at much higher levels than predicted. In this case, the introduction of mass spectrometry as a secondary level of detection (GC-MS) can help to screen for a broader range of compounds from a single sample. An example of the different types of VOCs observed on a mass spectrometry detector is reported in Figure 5.

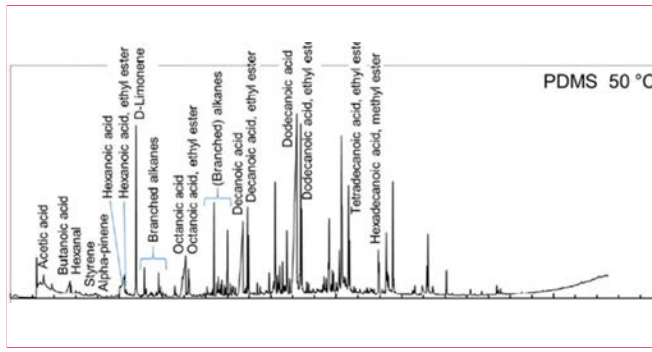


*Figure 5: SPME measurements on the agglomerated material using GC-MS Sampling temperature 50°C with PDMS fibre.*

The use of mass spectrometry makes a big difference because the detector can be used to identify an unknown peak by simply matching it against a library. This technique is particularly useful when its needed to check the efficiency of the whole recycle process. The quality of the material can be analyzed before starting the process, during the process and at the end. The different chromatographic profiles obtained at different time points of the process allows scientists to understand the efficiency of the process as well as determine what conditions could be changed to improve the final result. Furthermore, the use of different sampling strategies like solid-phase micro extraction (SPME), solvent desorption and thermal desorption can be used on the front end of the GC-MS to focus on a different class of analytes or achieve lower levels of detections. Currently, thermal desorption is the most suitable and cleaner technique to use because the contaminants are concentrated on a sorbent, and then thermally desorbed into the GC-MS. This enables the operator to avoid unessential work, and prevents the need for toxic solvents, allowing laboratories to operate in a more environmentally sustainable manner.

## Environmental Excess

Returning to the topic of PFAS/PFOS, we know that these are leachable compounds and certain components of fire retardants, such as PFOA, are leachable and can cause persistent harm to the environment if they are exposed to it. Perfluoralkyl compounds are fully fluorinated and it is the strength of the carbon-fluorine bond that renders these compounds so resistant to degradation. In the past, PFAS/PFOS chemicals were chosen for their high thermal stability which makes them ideal for packaging used in food heating/re-heating. Today, PFAS are present almost everywhere including carpets, household detergent, and food packaging. Food packaging examples of PFAS presence include microwavable popcorn packets and fast food containers.

Not only do PFAS compounds get released during contact with food, but they are also later dispersed in the environment. They enter landfills and are composted, and can then enter the food chain through the soil. Because they are both stable and long-lived, it's hard to get rid of them, and severe treatments must be carried out to remove them from the environment.

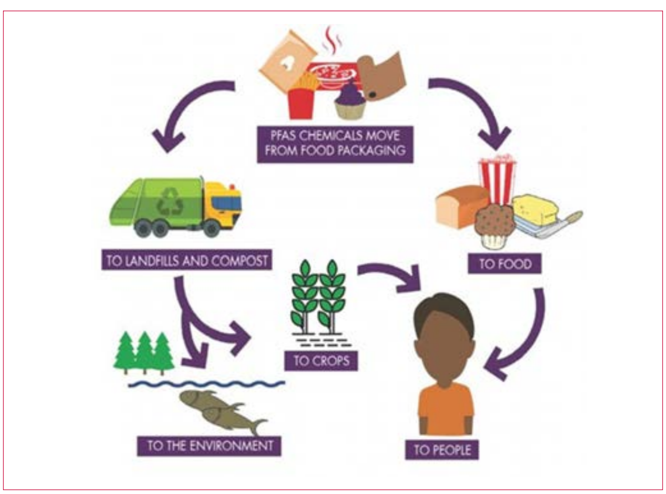


*Image Credit: ToxicFreeFuture.org https://toxicfreefuture.org/seriously-sticky-situation/*

Because this is a potential human health issues, research is ongoing to determine the best strategies so that governments can act to protect health. Since 2018 for example, the United States EPA has established strict limits requiring no more than 70 nanograms per litre be detectable in drinking water. Limits for packaging material are less well-formed. In fact by 2022 there was still no clear regulation regarding acceptable detection limits for packaging material. Scientists are still working on questions like, "how do we assess how leaching is happening?" and "how should PFAS be monitored in recycled plastics?" The issue becomes even more complicated when considering the analytical challenges. Liquid Chromotography (LC/MS/MS) is the technique of choice for PFAS/PFOS due to the extremely low limits of detection it offers.

However, consider that the instrument itself contains plastic – in the tubing of the LC and so on - and we start to see how this complicates matters in a lab. The chromatogram in figure 6 shows the injection of a few standard PFAS/PFOS (tall peaks) and next to them contaminants leaching out from the tubing inside the LC system or left behind from the previous sample run. As such, it is common practice to take the following precautions with PFAS/PFOS analysis; replacing the internal tubing in the LC system, employing a delay column, aggressive clean up after each injection and carrying careful examination of the collected data.

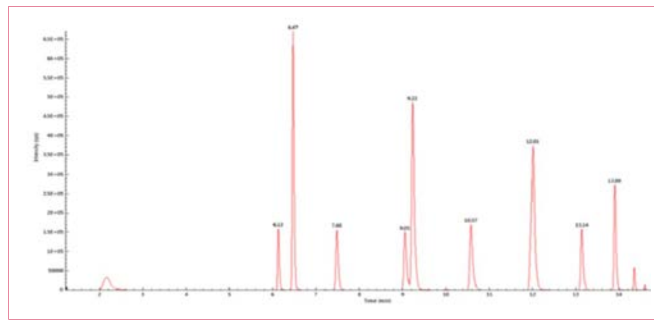

*Figure 6: PFOS/PFAS standards injected in a LC/MS/MS system. (tall peaks) Standards, (small peaks) contaminants leaching from tubes or carried over from the previous injection.*

## Maintain Your Integrity

The physical characteristics of packaging can be just as important as its chemical composition. Packaging is often formed by different layers organized in a specific manner to optimize total properties, as illustrated in Figure 7. For example, PVA plastic provides a barrier to prevent oxygen from infiltrating the packaging. Oxidation of food is what can cause it to spoil rapidly. So, maintaining integrity within the structure is crucial for safety because the wrong manufacturing of this layer could cause leaching of volatile compounds into the product, or allow external contaminants to get inside.

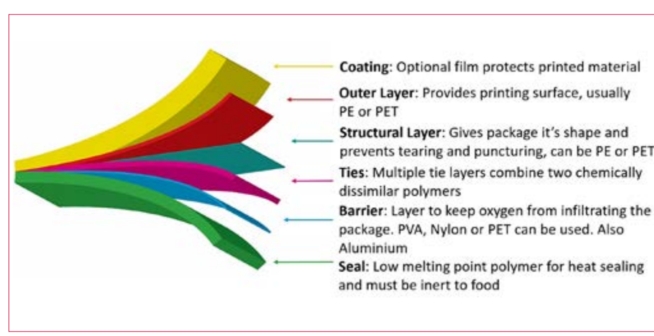


*Figure 7: Structural layers of laminated packaging typically found in food packaging.*

Layer structural analysis is typically done by an optical view via a microscope. Figure 8 shows a cross section of the packaging material under observation by using a microscope showing the different layers. The highlighted regions of the cross section correspond to the accompanying FTIR spectra.

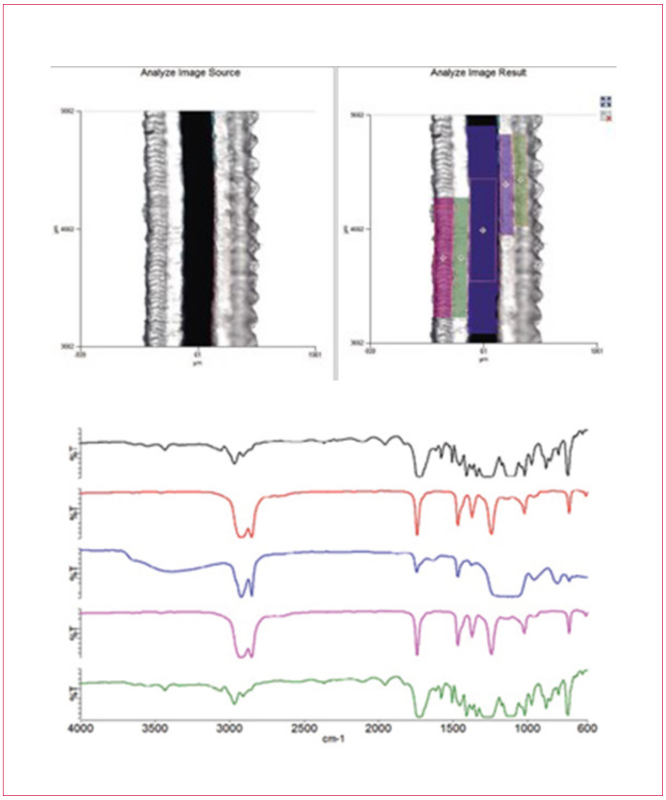


*Figure 8: Layers structural analysis using Imaging microscope.*

The combination of a microscope with infrared technology, such as the PerkinElmer Spotlight, demonstrates the ability to identify compounds by selectively picking each layer and scanning an area to produce an infrared spectrum and compare it with a library database. By doing this, scientists can assess the layer integrity to verify that each layer is assembled properly along the process, and verify if there is any breakage in the material.

The same technology can be used to study and identify foreign bodies which could be formed during the process. Figure 8 highlights a laminate compound which is comprised of five layers. After magnifying this sample and carrying out a selected infrared analysis the data can then be compared with a reference database and we can accurately identify the chemical make-up of each layer plus any contaminants.

## Microplastics Under the Microscope

Microplastics are divided into two types, primary and secondary. Primary microplastics are designed to be present in a product, so are macroscopic in size. This is the case for microplastics present in toothpaste, shampoo, face creams and some detergents. Secondary microplastics consist of particles degraded by the breakdown of larger items, such as plastic bags. Microplastics form over time and the environmental impact has been detected and studied even at the most remote locations of the ocean. Consider these examples:

- At least 60% of the fishing industry uses plastic netting and all of them can contribute to the formation of microplastics in the environment.
- More than 100,000 microbeads can be released from a single application of a single product. Some of these are then subsequently found in foods.
- Nearly all bottled liquid goods such as water, milk, honey or oils can contain a significant amount of microplastic.
- Supermarket bought mussels have been found to contain 70 microplastic particles per 100 grams.
- And teabags have reported to release high levels of microplastics and microfibers during the brewing process.

These examples illustrate how an environmental issue has become a food safety issue, because microplastics work their way up the food chain – and do not degrade in the environment. We then absorb them with our diet. Microplastics can be formed simply by cutting or tearing packaging – contrary to their main purpose of maintaining integrity (see Figure 9).

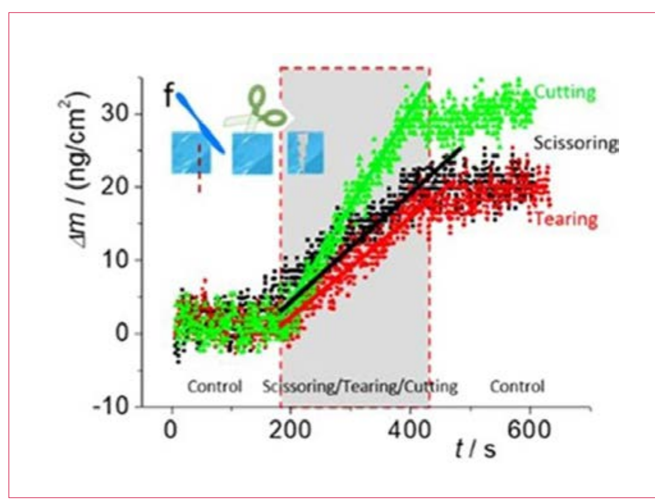


*Figure 9: Release of the number of microplastic particles as a function of time during cutting, scissoring and tearing of a plastic package.*

During a PerkinElmer study in 2018, 250 bottles from 11 different water brands were monitored for the presence of microplastic. It found that the amounts of microplastic varied considerably between brands, shown in table 2. It was interesting to note the distribution of the different polymer types arising from these results. PP made up more than 50% followed by Nylon, PS and PE microplastic (Figure 11).

*Table 2: Water bottle brands experiment - Source: Synthetic polymer contamination in bottled water, Frontiers in chemistry 2018.*

| Mineral Water Brand | Particles / L |
|---|---|
| Nestle Pure Life | 10,390 |
| Bisleri (India) | 5,230 |
| Gerolsteiner (Germany) | 5,160 |
| Aqua | 4,713 |
| Epura | 2,267 |
| Aquafina | 1,295 |
| Minalba | 863 |
| Wahaha | 731 |
| Dasani | 335 |
| Evian | 256 |
| San Pellegrino | 74 |

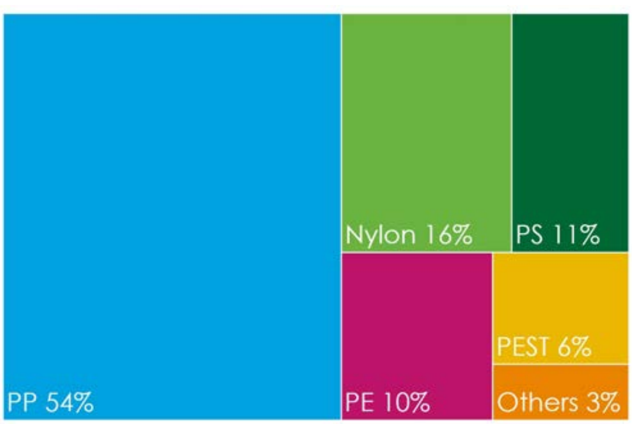


*Figure 11: Microplastic polymer type distribution from Water bottle brands experiment data.*

The study was carried out using the PerkinElmer Spotlight 200i FTIR Microscope (Figure 12). Within the sample, the process can be vastly automated, the microplastics are simply washed off into a micro mesh filter. The software can zoom in and automatically identify microplastic in a quick screening, and carry out analysis on each single microplastic particle to identify them by comparison with the infrared spectrum database.

*Figure 12: PerkinElmer Spotlight™ 200i microscope & Spectrum Two IR.*

## Summary

In summary, it's clear that plastics play an important role in food packaging as safety is critical given we ingest food every day. This white paper details food examples but the same principles apply in pharmaceutical packaging too. Chemical compounds and microplastics can leach out of packaging, and therefore it's important to prevent that from happening through analytical understanding of factors like chemical structure, temperature, storage time, humidity and physical characteristics.

Regulation is in place to identify leachable compounds, and establish the acceptable level for the safety of human health. But these regulations are also evolving as more studies reveal the health effect of these chemicals in our diet. We need to keep in mind, there are new threats like microplastic and PFAS which started as environmental issues and have rapidly evolved into consumer safety issues.

For a full compendium of research data and QA/QC methods using a range of analytical instrumentation - Click here

A range of analytical instruments are used by laboratories servicing the packaging industry; including spectroscopy, microscopy, thermal and mechanical analysis, chromatography, elemental analysis and even hyphenated solutions which link multiple technologies together in a single run. Comparison tools - like this PerkinElmer infographic - are helpful in evaluating the pros and cons at each step in the polymer production lifecycle.

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