It's all made of plastic!

«Plastic» has become something of a dirty word. It makes us think of trash and environmental pollution, inferior quality, mass-produced goods, and excess. But if you take a look around, you will realize that a lot of the objects that surround us – including those that we couldn't live without – are also made of plastic.

That's no accident: as synthetic organic polymers, plastics have the advantage that their properties can be perfectly adapted to their intended use – unlike most natural materials – and they can also be manufactured inexpensively. Thanks to their versatility, plastics have become established in all areas of our lives.

Whatever their use – whether it is food packaging, flooring, or textile fibers – plastics have to meet quality criteria which are often determined by standards. To ensure that they satisfy the quality requirements, analyses must be carried out at every stage of production, from the raw materials to the reaction conditions and intermediate products, right up to the final product.

Quality control for raw materials

Identifying the raw materials

High-quality raw materials form the basis of a good product. Before being processed, the raw materials must be identified reliably and undergo quality control. When the goods are received, spectroscopic methods – particularly Raman spectroscopy – can be used to confirm that the raw materials are correct. Practical hand-held instruments such as the Mira M-1 from Metrohm make this especially easy. They measure the Raman spectrum of the sample and identify the sample by comparing the spectrum with a spectrum database – all within a few seconds.

How does Raman spectroscopy work?
The spectrometer first shines monochromatic light on the sample and then detects the scattered photons. When detected, elastically scattered photons have the same frequency as they did before being scattered on the sample, so they do not provide any information about the properties of the sample. They are of no value for the determination. In the case of inelastic scattering, however, the photons transfer part of their energy to the sample, changing their own frequency. The change in frequency provides information about the sample, as the energy absorbed induces rotational and vibrational states which are characteristic of the molecular structure and require specific amounts of energy. The absorption pattern – the Raman spectrum – of each substance is unique, and the determination is therefore unambiguous. Figure 1 shows the Raman spectra of some common monomers.

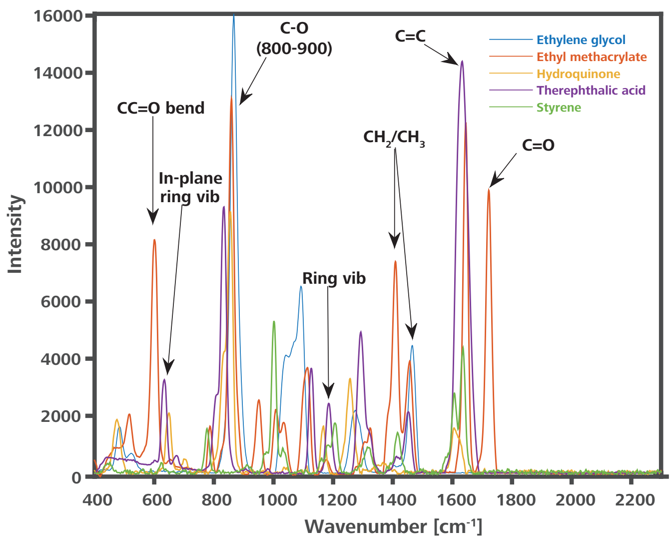


Figure 1. The Raman spectra of some common monomers are depicted. The peak positions of the Raman spectra provide information about functional groups of the sample molecule: the difference between the frequency of the scattered photons and the starting frequency corresponds to vibrations and rotations which are characteristic of them, and which are initiated using a specific amount of energy which is absorbed from the photons.

Quality of the raw materials

The quality control involves examining a wide range of physical and chemical parameters, from pH value and viscosity to determining the functional groups of the monomer, to contaminants, polymerization inhibitors, and the proportion of dimerized/oligomerized raw material.

> «*A significant proportion of the acrylic acid from which, for example, polyacrylic acid is produced, may be in the form of a dimer. This reduces the polymerization speed.*

Determining monomer quality through end-group titration
Acrylic acid is used to manufacture polyacrylic acid – the «superabsorber» that can be found in diapers – as well as many copolymers which are employed as photo-resistant and hydrolysis-resistant industrial coatings. Acrylic acid polymers also have countless applications in medical products such as creams and gels. Acrylic acid dimerizes spontaneously (Figure 2). Even when inhibitors are used (usually monomethyl ether hydroquinone, or MEHQ for short) and optimum storage conditions are ensured, this cannot be avoided entirely. Depending on the storage time, a significant proportion of the raw material may be in the form of a dimer, which reduces the polymerization speed. Determining the dimer content is, therefore, a key part of the quality control for acrylic acid.

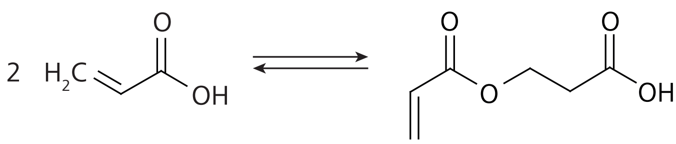


Figure 2. The acrylic acid monomer dimerizes spontaneously. The dimer content must therefore be determined as part of the raw material quality control when the goods are received.

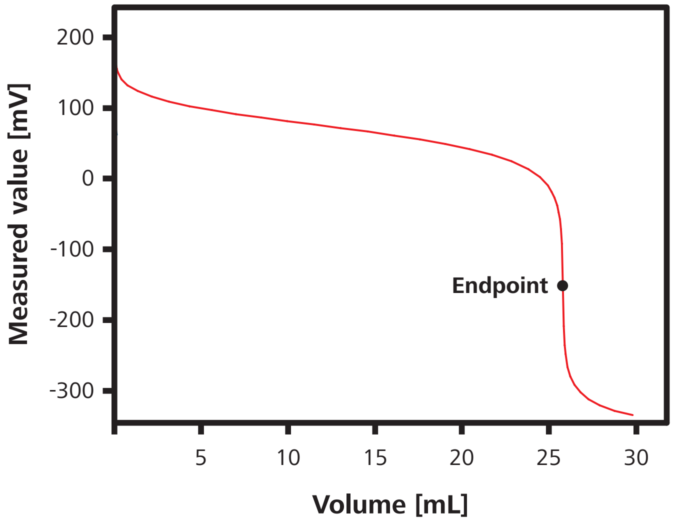


Figure 3. Acid number determination in acrylic acid monomer

«The Solvotrode enables precise potentiometric endpoint determination even in a nonaqueous medium with low conductivity.

When acrylic acid dimerizes, the acid group of one of the monomers reacts with another monomer to form a carboxylic ester. The number of free acid functions per gram of material thus reflects the dimer content. The acid number – i.e., the amount of potassium hydroxide (KOH) in milligrams which is required to neutralize one gram of sample – is therefore determined as a quality indicator. This is done by end-group titration (Figure 3). The titration takes place in a nonaqueous solution. The low conductivity of the medium makes it harder to determine the endpoint potentiometrically, but suitable sensors such as the Solvotrode from Metrohm enable precise determinations nonetheless. The process can be fully automated.

End-group titration can also be used to determine other functional groups in a similar way to the acid functions. For the polymer industry, the most important of these groups are hydroxyl and isocyanate groups (hydroxyl and isocyanate number). Their titrimetric determination complies with the ASTM and ISO standards.

Contamination of the raw material

In addition to dimers and oligomers, there are other contaminants present in raw materials which, in some cases, can significantly hinder the production process. These include water, which can be quantified using Karl Fischer titration regardless of the physical state of the monomer, as well as certain metals with catalytic activity such as iron (determined by voltammetry) or sodium and potassium (determined by ion chromatography, Figure 4).

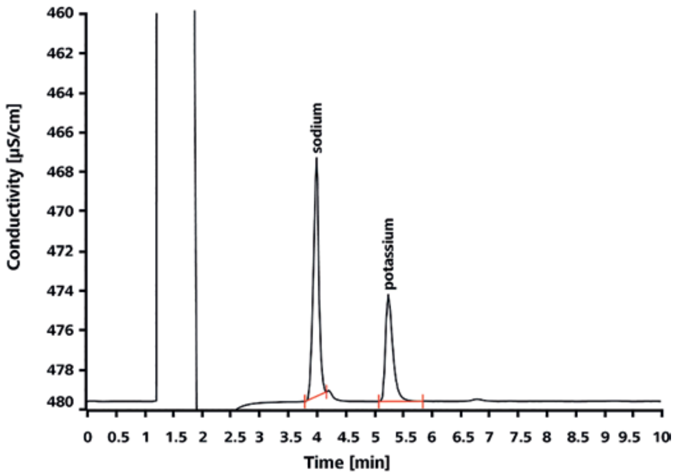


Figure 4. Determination of sodium and potassium in a polyol solution. Polyols are raw materials used in the production of polyurethane.

Reaction monitoring

Process optimization through real-time analyses

During polymer production, real-time analyses help to achieve the desired product quality and ensure an efficient production process. Online analyses, which provide results continuously and immediately, make it possible to monitor reaction conditions, for example. If necessary, these conditions can then be optimized without delay.

Viscose production: Conditions in the wet-spinning bath

More than four million tonnes of viscose fibers are produced worldwide each year for the textiles industry. Viscose is produced from cellulose, a natural polymer which is obtained from pulp. The fibers are produced using the wet-spinning method in a bath containing sulfuric acid, sodium sulfate, and zinc sulfate. Each of these substances has a different task in the production process. Altering their concentrations changes the properties of the fibers, enabling different types of viscose fibers to be produced. Online determination of the acid and zinc concentrations is essential for controlled production. Online determination of sulfuric acid and zinc can be carried out simultaneously with the ADI 2045TI Process Analyzer from Metrohm Process Analytics. Being an online analyzer, the ADI 2045TI works fully independently. Its robust design makes it well-suited to the harsh conditions in the process.

The production of nylon and nylon products can be optimized with process monitoring using near-infrared spectroscopy.

Near-infrared spectroscopy

Alongside wet-chemical methods, near-infrared spectroscopy (NIRS) is ideal for process monitoring. It works with mathematical models which correlate the measured spectra with reference methods. This enables NIRS to measure both chemical and physical parameters within seconds. One measurement can determine numerous parameters.

When manufacturing nylon fibers, NIRS helps to achieve the best possible properties: as the protective oil layer is being applied to the fibers, its thickness can be monitored in real time. This means that the process can be stopped as soon as the optimum thickness is reached.

The ADI 2045TI Process Analyzer carries out analyses automatically and is ideally adapted to the harsh conditions in the process.

Quality control for the finished polymers

Analyses before and during plastics production form the basis of a high-quality product. A final quality control step provides assurance that the production process has gone as planned and that the plastic meets the requirements of its intended application.

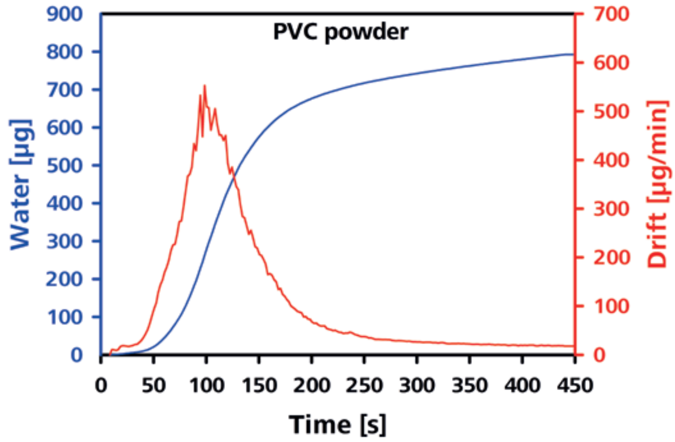


Figure 5. Curve for a coulometric Karl Fischer titration in PVC. The determination was carried out using the oven method, i.e., the sample was heated to extract the water by means of evaporation before determining the water content.

«Each polymer contains a small amount of residual monomer. In the case of the toxic styrene monomer, this can be a problem.

Residual monomer in the finished product
Each polymer contains a small amount of residual monomer which has not reacted. In the case of polystyrene, which is used for food packaging such as yogurt pots among other things, this can be a problem, as styrene is toxic and carcinogenic. It goes without saying, therefore, that sensitive determination of the monomer as part of quality control is indispensable. Voltammetry is a cost-effective, reliable analysis technique that is well-suited to this task, and can be used to determine quantities of styrene as small as of 5 mg/L. This sensitive analysis technique can also determine traces of metallic contaminants.

Polymer water content
The water content of the finished plastic affects its properties. Sensitive coulometric Karl Fischer titration is the ideal method for determining the low water content. As most polymers are not soluble, the water determination is carried out using the Karl Fischer oven method: the residual moisture in the plastic is heated in order to evaporate it and then titrated. Figure 5 shows the progression of the Karl Fischer titration for a PVC sample. Before the analysis, the sample was ground into a powder to ensure complete extraction of the contained water.

Halogens and sulfur: Safety in the event of a fire
Plastics that contain halogens and sulfur release dangerous toxic gases when they burn. Halogen-free plastics are therefore becoming increasingly popular for certain applications, such as power cables. Determining the sulfur and halogen content is an indispensable part of quality control in this case, and combustion ion chromatography, or CIC, can be used to complete this task. The sample is burned and the resulting gases are absorbed by a carrier solution which is ultimately analyzed using ion chromatography. Figure 6 shows a schematic depiction of the entire process. Metrohm provides a complete CIC solution that combines sample digestion and analysis. This saves time and ensures highly accurate analysis: a certified polyethylene granulate was used to demonstrate that the recovery rate of the method lies between 99 and 102.4%.

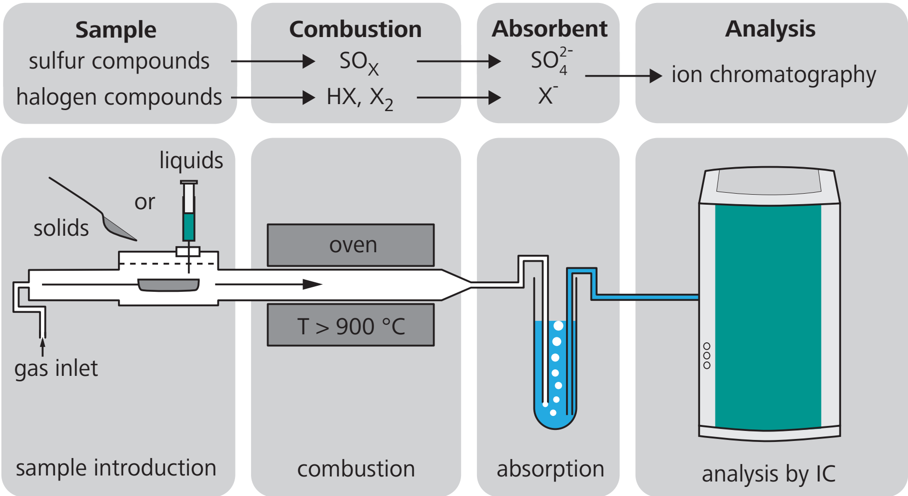
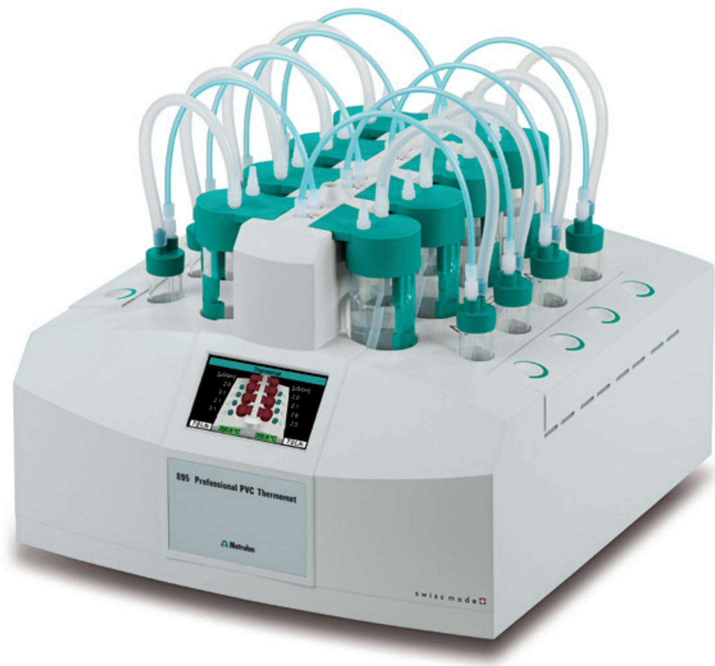


Figure 6. Combustion ion chromatography is used to analyze sulfur and halogens in solids and liquids. Once the sample has been added, the complete solution from Metrohm carries out the sample digestion and the analysis by itself: First, the sample is burned and the resulting gases are absorbed by a solution. The solution is then automatically injected into the integrated ion chromatograph where it is analyzed.

Heat resistance of PVC
PVC and other polymers which contain chloride can also release toxic gases – specifically, hydrogen chloride (HCl) – when exposed to elevated temperatures. However, these polymers are still widely used, as they are particularly versatile. The «dechlorination» effect can be prevented using heat stabilizers. To ensure quality control in accordance with ISO 182 Part 3, Metrohm offers the PVC Thermomat, which heats the sample and transfers the resulting HCl gas into a solution where it is detected by conductivity measurement.

Electrically conductive polymers
The field of electrically conductive polymers is still in its infancy. They were discovered in 1977 by the researchers Alan J. Heeger, Alan G. MacDiarmid, and Hideki Shirakawa, who were awarded the Nobel Prize in 2000 in honor of this discovery. The conductivity in these plastics is created by conjugated double bonds. There are many promising applications for conductive polymers – organic light-emitting diodes (OLEDs), photovoltaic cells, and rechargeable batteries to name but a few. When it comes to studying the electrochemical properties of polymers, cyclic voltammetry and electrochemical impedance spectroscopy are the methods of choice.

The PVC Thermomat (right) tests samples of polymers which contain chloride, e.g., PVC, to examine their heat resistance.



A future with or without plastic?

Almost all of the items that we use every day contain plastic. And their presence is likely to continue to grow: new areas of application are constantly being opened up for synthetic polymers, with notable developments in the applications of conductive polymers as just one example. With their low costs and flexible properties, plastics are attractive materials. That does not mean, however, that we should become blind to the problems they pose. In most cases, plastics are produced using fossil fuels as raw materials, which means that they consume valuable resources. They also create waste that takes a long time to decompose in the environment – from several decades (plastic bags) to many centuries (drink bottles).

Recycling provides a partial solution to this problem. Here, chemical analyses come into play again: for plastics to be recycled, they need to be sorted by material. Raman spectroscopy, which identifies substances within seconds, is ideal for this type of application.

« Plastics have long been an essential part of our everyday lives. The important thing now is to make plastics sustainable.

In the future, bioplastics could be the way forward: these are polymers that are based on renewable raw materials or are completely biodegradable – ideally, both. Examples include polyhydroxyalkanoates (PHA) and polylactic acids (PLA). Their properties are similar to those of conventional plastics, which means that they can be used in similar ways. Bioplastics are already in use in some areas, but they are a long way from covering the broad range of applications of conventional plastics. Bioplastics are constantly being optimized through intensive research, both in terms of their application properties and their degradation.

Plastics have long been an essential part of our everyday lives. The important thing now is to make plastics sustainable in order to minimize environmental pollution and oil consumption. Chemical analysis plays a central role not only in the development of sustainable, biodegradable plastics, but also in recycling and in routine work within the polymer industry. Metrohm offers suitable solutions at all stages of research, development, production, and further processing.

You can find detailed information about analytics in the polymer industry at **www.metrohm.com/Industries**