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The Advantages of Mid-IR Spectroscopy for Polymer Recycling

Introduction

Plastics are becoming increasingly utilized in consumer and industrial products. Over five million tons of plastics are used each year. In the UK in 2010 approximately 38% of the plastics consumption was used in packaging materials, with a quarter of this in production of plastic bottles. In the automotive industry an increasing number of large parts are being made from plastics due to the demand for lighter materials to reduce the overall weight of the vehicle and reduce fuel consumption. Tons of plastics are discarded every year, often ending up in landfill sites. Across the world there are initiatives for consumers to increase the amounts of materials they recycle, rather than discard them to these landfill sites. The waste plastics will then go to plastics recycling plants where they can be identified and reused. Japan is one of the most successful countries in the world for recycling plastics. In 2010, 77% of plastic waste was recycled, over double the rate of the UK, with the US currently achieving about 20%.

The Society of the Plastics Industry introduced the Plastics Identification Code (PIC), to provide a system for categorizing polymer types and to help recycling companies separate various plastics for reprocessing.

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Table 1. Polymer Identification Codes (PIC)

	Acronym	Full Name	Example of Uses
♲ 1 PETE	PET	Polyethylene Terephthalate	Fizzy drink bottles and frozen ready meal packages.
♲ 2 HDPE	HDPE	High-Density Polyethylene	Milk and washing-up liquid bottles.
♲ 3 V	PVC	Polyvinyl Chloride	Food trays, cling film, bottles for squash, mineral water and shampoo.
♲ 4 LDPE	LDPE	Low Density Polyethylene	Carrier bags and bin liners.
♲ 5 PP	PP	Polypropylene	Margarine tubs, microwavable meal trays.
♲ 6 PS	PS	Polystyrene	Yogurt pots, foam meat or fish trays, hamburger boxes and egg cartons, vending cups, plastic cutlery, protective packaging for electronic goods and toys.
♲ 7 OTHER	Other	Any other plastics that do not fall into any of the above categories.	Melamine, often used in plastic plates and cups.

However, the PIC system is not mandatory worldwide and often plastic samples do not have the code on them, especially older materials.

In order to be successfully recycled, the plastics need to be accurately identified and sorted. Many recycling plants rely on the "experienced recycler" to identify the plastics. This can involve traditional tests such as "float test" or "burn and sniff test". The "float" test can supposedly differentiate polyolefins from other types of plastics based on whether the plastic floats on a water-detergent solution. The "burn and sniff" test involves the operator setting fire to a small amount of the plastic and sniffing the evolved fumes. Not only can this lead to misidentification of the plastic, but is extremely dangerous as the fumes from burning polymers can be extremely toxic.

Optical spectroscopic techniques offer an accurate and scientific method of identifying plastic materials. The near-infrared (NIR) region of the electromagnetic spectrum, from 12000 - 4000 cm-1, can be used for fast screening of plastic types. However, mid-infrared (MIR) spectroscopy, from 4000 - 450 cm-1, offers significant advantages for positive identification of the plastic and any other components in the plastic, such as fillers, plasticizers, surfactants, coatings, or release agents. In addition, NIR instrumentation cannot be used for identification of plastics containing even low amounts (above 2% or 3%) of carbon black. This represents a reasonable proportion of recycled plastics.

Mid-infrared spectra were collected on a Spectrum Two™ FT-IR using the Attenuated Total Reflectance (ATR) sampling technique. Measuring samples is achieved by placing the plastic on top of the sampling accessory and applying pressure to the sample in order to make contact with the diamond crystal. Measurement time is in the region of 10 seconds.

Figure 1. The PerkinElmer Spectrum Two and diamond ATR.

Figure 2 is representative mid-infrared spectra of plastics for the different PICs. Spectra 1 to 6 are spectra for PIC 1 to 6, Spectra 7 and 8 are two different materials representing PIC 7 (OTHER). These materials are polyamide (PA) and polycarbonate (PC).
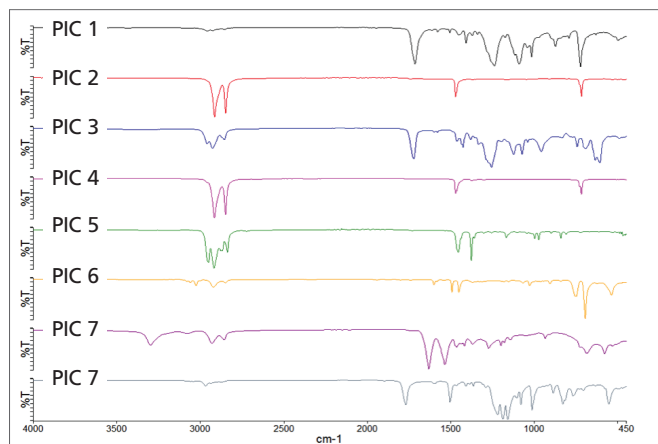

Figure 2. Mid-infrared spectra from the different PIC categories.

The spectra for each of the categories are visibly different. However, the software has the capability of identifying the plastic by comparing the unknown spectrum against a library of standard polymers. The whole routine can be deployed in a simple user interface with on-screen instructions for the plastics recycler rather than requiring expertise to analyse samples. Figure 3 shows a representative result from a library search using a standard polymer library.
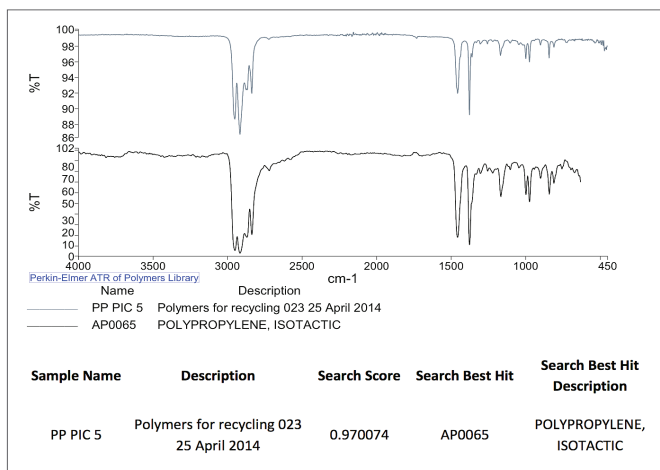

| | | | | Search Best Hit |
Sample Name	Description	Search Score	Search Best Hit	Description
PP PIC 5	Polymers for recycling 023 25 April 2014	0.970074	AP0065	POLYPROPYLENE, ISOTACTIC

Figure 3. Search result identifying the sample as Polypropylene.

Measurement of Darkly Colored Samples

Plastics sent for sorting and recycling come in an extremely wide range of colors, with the colors due to pigments or other fillers present in the material. Many of the fillers and pigments will introduce spectral features due to the chemical composition, which is mainly inorganic. A frequently used filler in plastics is carbon black. This material shows no spectral bands in the mid- or near-IR regions of the spectrum. However, in the near-IR region it leads to very intense absorption, masking any other spectral features. The mid-IR region of the spectrum does not suffer as badly from this problem. Rigid plastics will generally only contain carbon levels from a few per cent up to 25 - 30%. Mid-IR diamond ATR measurements are possible with these samples.

Figure 4 shows the mid-IR diamond ATR spectra of two samples of the same plastic type, polystyrene, with one of the samples being a clear plastic, the other is extremely black due to being carbon-filled.
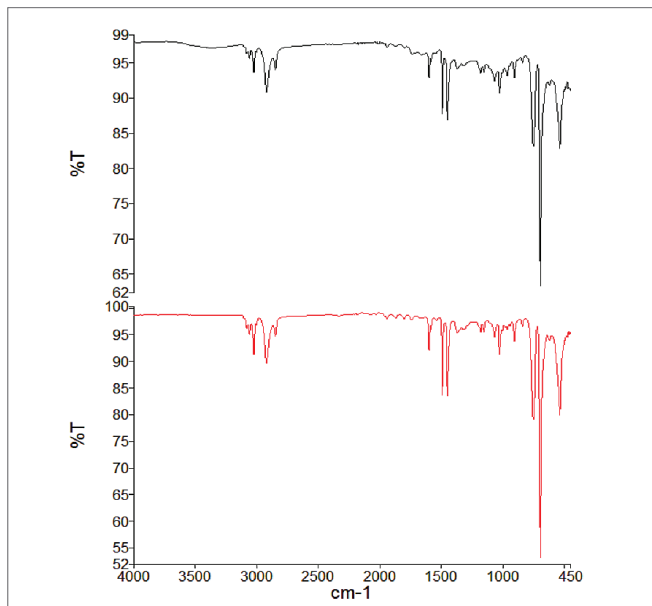

Figure 4. Diamond ATR spectra of black polystyrene (top) and clear polystyrene (bottom).

The spectra are virtually identical showing that the presence of carbon black is not having an effect on the infrared spectrum or the identification of the material. This is not the case with near-IR spectra.

Near-IR spectra of a variety of samples were measured on a PerkinElmer Frontier™ IR/NIR spectrometer configured for operation in the near-IR region. Sampling was performed in reflectance mode using the Near-IR Sampling Accessory (NIRA) over the spectral range 10,000 - 4000 cm-1 at 16 cm-1 resolution. Near-IR reflectance is the technique utilized by handheld Near-IR analysers. Figure 6 shows the Near-IR spectra of two different samples of Low Density Polyethylene (LDPE). The upper spectrum was measured on a white sample, whereas the lower spectrum was measured on a black sample.
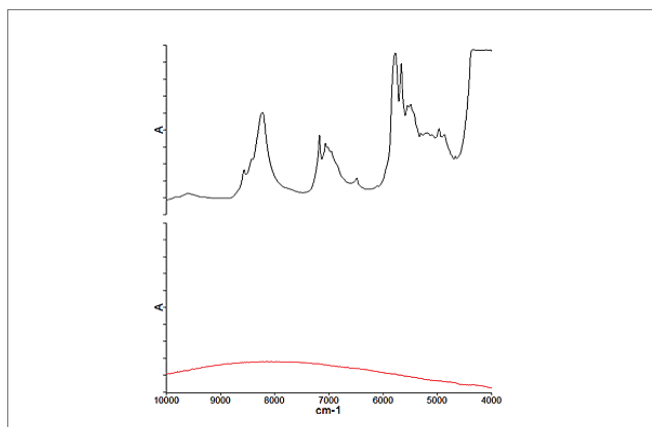

Figure 5. Near-IR spectra of white (top) and black (bottom) samples of LDPE,

The spectra here are completely different. The white LDPE sample generates a good quality spectrum that would allow for identification of the material against a library of spectra. The black LDPE sample generates a broad spectral curve with no discernable spectral features. This appearance is typical for black polymer samples measured in the near-IR spectral region, as seen in Figure 6.
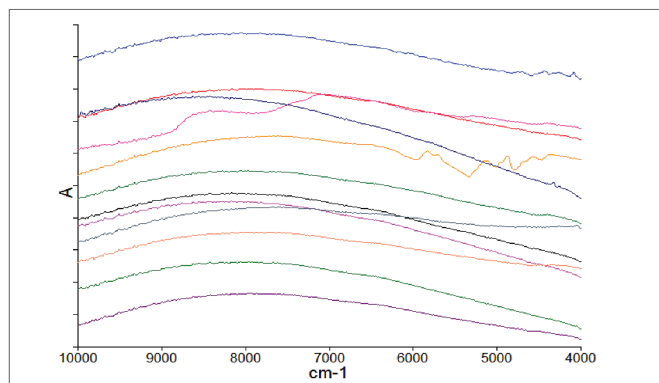

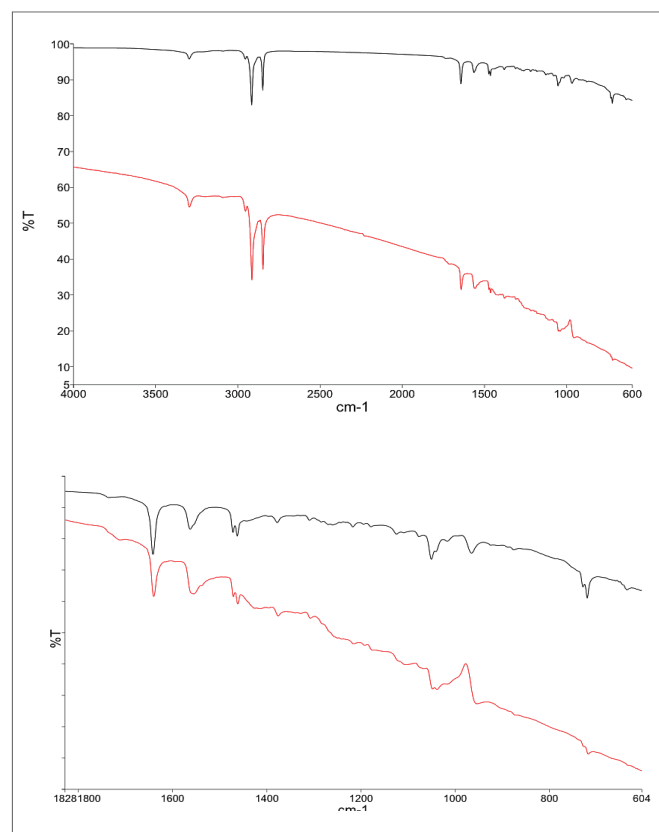*Figure 6.* Near-IR reflectance spectra of black plastics.

Figure 7. Spectra of carbon-filled o-ring on germanium crystal (upper) and diamond crystal (lower).

Only a couple of the samples measured showed any spectral features in this region of the spectrum. It would be impossible to identify any of the other samples using this near-IR data.

Softer rubber-like materials with high carbon content can be measured by ATR in the mid-IR region of the spectrum, but it requires the use of germanium as the crystal type rather than diamond. The higher refractive index of germanium means the IR beam will have a lower penetration depth into the sample, preventing high absorption due to the carbon.

Figure 7 displays a sample of a carbon-filled rubber o-ring. The spectra were collected on the same sample, using both germanium and diamond as the crystal material. Both of the spectra exhibit a baseline slope, with the slope on the spectrum collected from the diamond crystal being considerably worse. Expanding the spectra to look only at the spectral region from 1800 - 650 cm-1 shows that there are also severe distortions in the spectrum collected using the diamond crystal, especially in the region around 1000 cm-1. This leads to significant loss of information.

For the spectrum collected on the germanium crystal it is possible to apply simple, automated baseline correction to generate the best quality spectrum, as shown in Figure 8. This would not be possible for the spectrum collected on the diamond crystal due to the spectral distortions.
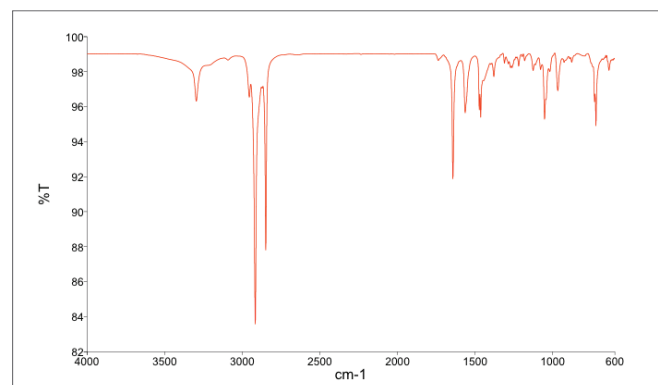

Figure 8. Baseline corrected spectrum of o-ring collected using the germanium crystal.
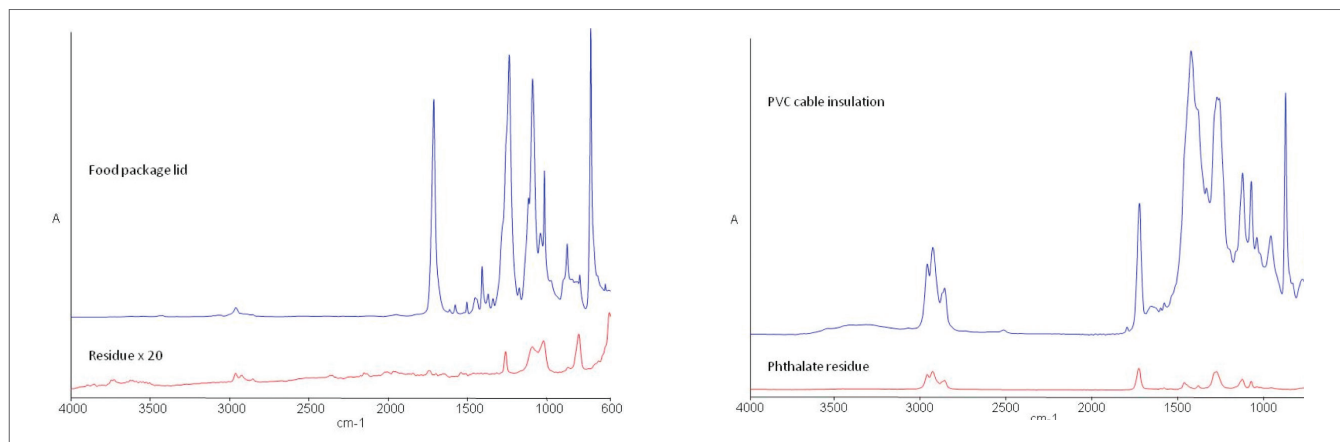
Identification of Additives

Figure 9. Examples of spectra of bulk material and additives from plastic samples.

The process of running a sample on the ATR accessory involves applying pressure onto the sample in order to get contact between the sample and the ATR crystal. This process can often squeeze out additives that remain as a residue when the sample is removed. This requires a quick clean of the crystal between samples. However, this also allows for the possibility of identifying the additive(s) by means of scanning the residue spectrum. Figure 9 shows two such examples where the plastic sample spectrum is obtained and the material can be identified, but also the residuals can be identified. In the case of the food packaging lid, the additive has been identified as a silicone, often used as releasing agents. In the case of the PVC insulation cable the additive has been identified as a common PVC additive, a phthalate plasticiser.

Summary

Molecular spectroscopic techniques offer fast and easy measurement and identification of plastic types. Both mid- and near-IR instrumentation can be deployed for this task for a wide range of sizes and shapes of samples. However, if the samples are carbon-filled then near-IR technology, both handheld and laboratory instruments, it is unlikely to yield useable spectra.

In addition, with the use of a germanium crystal in the ATR instead of a diamond, very heavily carbon loaded rubber materials can be identified in the mid-IR region. An instrument with an ATR that is capable of using multiple crystal types for different sample types would be recommended.

Mid-IR instrumentation using ATR will also be capable of identifying a range of additive materials based on the infrared spectrum of the residual left on the crystal after measurement of the bulk material.

	Near-IR	Mid-IR
Identification of common plastics (non-black)	✓	✓
Identification of common plastics (black)	X	✓
Identification of carbon-filled rubber materials	X	✓ *
Identification of common additives	X	✓
Using Ge crystal		

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