SAMPLE PREPARATION EQUIPMENT

# Thin Film Production of Plastic / Polymer Materials Using the Mini-Film Maker Accessory

## Introduction

IR spectroscopy is a useful tool for group chemical species identification of a wide variety of sample materials, particularly for the classification of “organic” chemical materials based upon carbon atoms being present in the molecular structure. Many plastic and polymeric type samples which can be included in the category of organic molecular materials can be classified into a particular “family” groupings and it is possible to identify the sample family types both qualitatively and quantitatively by use of the Attenuated Total Reflectance (ATR) technique as an IR measurement. (See - Specac Application Note 42).

The ATR technique is a surface measurement of a sample type with typically a penetration depth of circa 2 microns into the sample surface using a diamond (or ZnSe) crystal, giving an effective pathlength measurement distance of circa 4.5 microns for a single reflection event of the sample area under study. From an ATR measurement of a plastic/polymer type sample, although it may be possible to determine the polymer family type, the sensitivity of the measurement for the effective pathlength allowed may be insufficient to determine any specific sample constituents (additives, fillers, etc.) in the make-up of the polymer material that are present at a low concentration. Therefore it may be necessary to create a thin film of the plastic/polymer sample for transmission study from a suitable film making accessory.

## Application

For specific use of the Mini-Film Maker Kit (p/n GS03970), to create a thin film of the plastic/polymer sample must melt/soften for pressing at a temperature below the maximum of 250°C that can be set on the equipment. The pressing force against the molten plastic sample within the film maker assembly of parts is applied from use of the dedicated press with a 2 tons maximum pressing capability in the complete kit. If a thin thin film diameter of larger than 15mm is required, the alternative film maker accessories from Specac can be employed. The constant Thickness Film Maker Accessory (p/n GS15640) is used with the larger 15 ton Manual Hydraulic Press (p/n GS15011) fitted with Heated Platens (p/n GS15515), to allow for the formation of polymer films up to 29mm in diameter and at melt temperatures up to 300°C. Similarly, the High Temperature Film Maker Accessory (p/n GS15800) is also used in a 15 ton Manual Hydraulic Press (p/n GS15011), but this film maker has its own set of heated platen surfaces to produce 29mm diameter films at melt temperatures up to 400°C.

**Specac’s Mini-Film Maker Accessory (p/n GS03970)**

## Equipment and Method

The Specac Mini-Film Maker Kit (p/n GS03970) was used for the thin film preparation of a variety of plastic/polymer sample types at a “nominal” 50 micron film thickness and 15mm in diameter. The plastic polymer material types were the same set of samples that had been identified for their polymer family types from the Quest ATR study. (See Specac Application Note 42).

Transmission spectra over the spectral range between 4000cm$^{-1}$ and 40cm$^{-1}$ for the nominal 50 micron thick film formed were collected on a Thermo Nicolet iS5 instrument using the standard room temperature detector system set at a resolution of 4cm$^{-1}$ for 32 scans.

The samples used for this study are shown from the following images as to their form before attempting to produce them as 50 micron thick films.


Sample 1


Sample 2


Sample 3


Sample 4


Sample 5

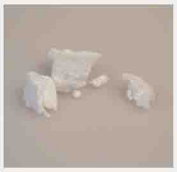

Sample 6


Sample 7

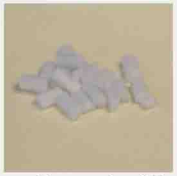

Sample 8


Sample 9


Sample 10


Sample 11


Sample 12


Sample 13

From the 13 different samples chosen to study and use, there are 7 different basic polymer family types. They have been colour coded as similar family types for their sample number as seen in table 1. (e.g. the 2 polycarbonate type samples of the 13 sample types are coded for a red colour). The sample types identified from the ATR measurement and used for formation into 50 micron films for transmission spectral measurement and collection are tabulated as follows.

Table 1

| Sample Number | Description | Polymer Family Type | Nominal 50µm Film Sample/Spectrum |
|---|---|---|---|
| 1 | Dark grey colour power cable | Polyvinylchloride (PVC) | Filmsample1B.spa |
| 2 | Light grey colour power cable | Polyvinylchloride (PVC) | Filmsample2B.spa |
| 3 | Green colour hard pellet/rod | Polycarbonate | Filmsample3B.spa |
| 4 | Blue colour pen cap fragments | Polypropylene | Filmsample4B.spa |
| 5 | FX4422CUV colourless clear bead | Polyester | Filmsample5B.spa |
| 6 | 160175 colourless opaque bead | Polypropylene | Filmsample6B.spa |
| 7 | Green colour bottle cap fragments | Polyethylene | Filmsample7B.spa |
| 8 | Blue colour bottle cap fragments | Polyethylene | Filmsample8B.spa |
| 9 | Lilac colour hard bead | Polycarbonate | Filmsample9B.spa |
| 10 | White colour packing chip | Cellophane | N/A |
| 11 | White colour tile | Polystyrene | N/A |
| 12 | Green/yellow colour power cable | Polyvinylchloride (PVC) | Filmsample12B.spa |
| 13 | Pale grey coulour hard pellet/rod | Polypropylene | Filmsample13B.spa |

**Note:** Samples 10 and 11 (Cellophane chip and polystyrene tile respectively), could not be made into a thin film because the of their original sample state and form. Only an ATR spectrum for spectral collection and information can be obtained for such sample types.

For any thin film production, it is important to define a methodology and specific procedural steps in the sample preparation to obtain a consistency of result from the spectral analysis. Key points for the method steps in sample preparation involve:

1) Choice of sizing ring to make the nominal thickness of film.
2) Melting point temperature of the plastic/polymer sample material.
3) Amount of sample used with specific sizing ring.
4) Tonnage load applied when sample is melted and being pressed.
5) Duration of the tonnage load being applied.
6) Cooling down stage (is a load being applied) and when access can be gained to the film.

For this application study, the steps from 2 to 6 were kept as consistent as possible for each sample. The conditions for the procedural steps taken in the method are tabulated on table 2.

Table 2

| Sample Number | Melting Point | Sizing Ring | Sample Size | Load Applied | Load Duration | Cooling Down Stage (*) |
|---|---|---|---|---|---|---|
| 1 | 180°C | 50 Microns | Sliced section | 0.75 Tons | 20 seconds | Film Assembly Placed on Cooling Block |
| 2 | 180°C | 50 Microns | Sliced section | 0.75 Tons | 20 seconds | Film Assembly Placed on Cooling Block |
| 3 | 200°C | 50 Microns | One pellet | 0.75 Tons | 20 seconds | Film Assembly Placed on Cooling Block |
| 4 | 180°C | 50 Microns | Small fragment | 0.75 Tons | 20 seconds | Film Assembly Placed on Cooling Block |
| 5 | 180°C | 50 Microns | One bead | 0.75 Tons | 20 seconds | Film Assembly Placed on Cooling Block |
| 6 | 160°C | 50 Microns | One bead | 0.75 Tons | 20 seconds | Film Assembly Placed on Cooling Block |
| 7 | 200°C | 50 Microns | Small fragment | 0.75 Tons | 20 seconds | Film Assembly Placed on Cooling Block |
| 8 | 200°C | 50 Microns | Small fragment | 0.75 Tons | 20 seconds | Film Assembly Placed on Cooling Block |
| 9 | 210°C | 50 Microns | One bead | 0.75 Tons | 20 seconds | Film Assembly Placed on Cooling Block |
| 12 | 180°C | 50 Microns | Sliced section | 0.75 Tons | 20 seconds | Film Assembly Placed on Cooling Block |
| 13 | 180°C | 50 Microns | One pellet | 0.75 Tons | 20 seconds | Film Assembly Placed on Cooling Block |

(*) For the Cooling Down Stage step, specifically, when the 0.75 tons load being applied from the press was released at the melting point temperature, the film maker assembly of parts was removed from the press whilst hot and placed on the black coloured cooling block disc of the kit of parts. Access to the film from peeling away the two aluminium foils was achieved when the film was near to room temperature conditions.

All prepared films were mounted in a Specacard (p/n GS03800) to be placed appropriately into the IR spectrometer sample compartment for spectral collection.

As a cross check for the actual film thickness prepared from use of the 50 micron size spacing ring, each film when mounting in a Specacard was measured for it's thickness using a digital micrometer depth gauge. The actual film thicknesses measured for each sample is tabulated in table 3.

The 11 plastic/polymer samples that were prepared as nominal 50 micron thick and 15mm diameter films mounted in the Specacard are shown as follows.

## Spectral Data

The transmission spectra collected for the 11 film samples prepared using the 50micron thick sizing ring under the specific method and sample preparation procedural steps are presented in the following pages.

Table 3

| Sample Number | Sizing Ring | Actual Film Thickness as Measured (Digital Micrometer Gauge - tolerance +/- 2 microns |
|---|---|---|
| 1 | 50 microns | 47 microns |
| 2 | 50 microns | 45 microns |
| 3 | 50 microns | 52 microns |
| 4 | 50 microns | 49 microns |
| 5 | 50 microns | 46 microns |
| 6 | 50 microns | 48 microns |
| 7 | 50 microns | 45 microns |
| 8 | 50 microns | 42 microns |
| 9 | 50 microns | 55 microns |
| 12 | 50 microns | 50 microns |
| 13 | 50 microns | 50 microns |

Filmsample1B

Filmsample2B

Filmsample3B

Filmsample4B

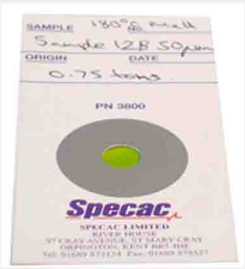
Filmsample5B

Filmsample6B

Filmsample7B

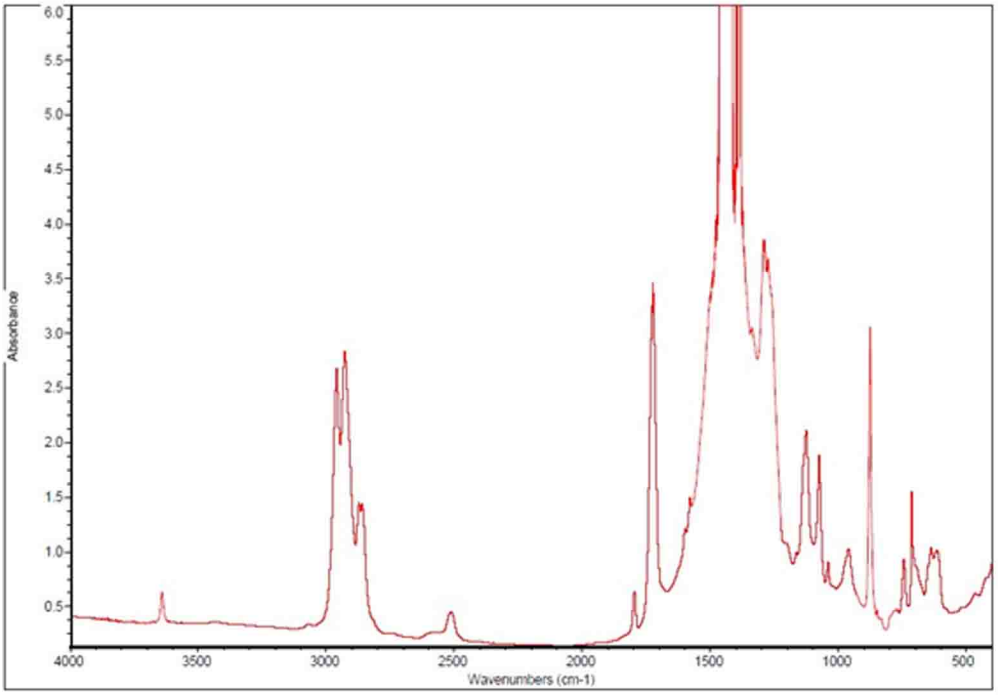
Filmsample8B

Filmsample9B

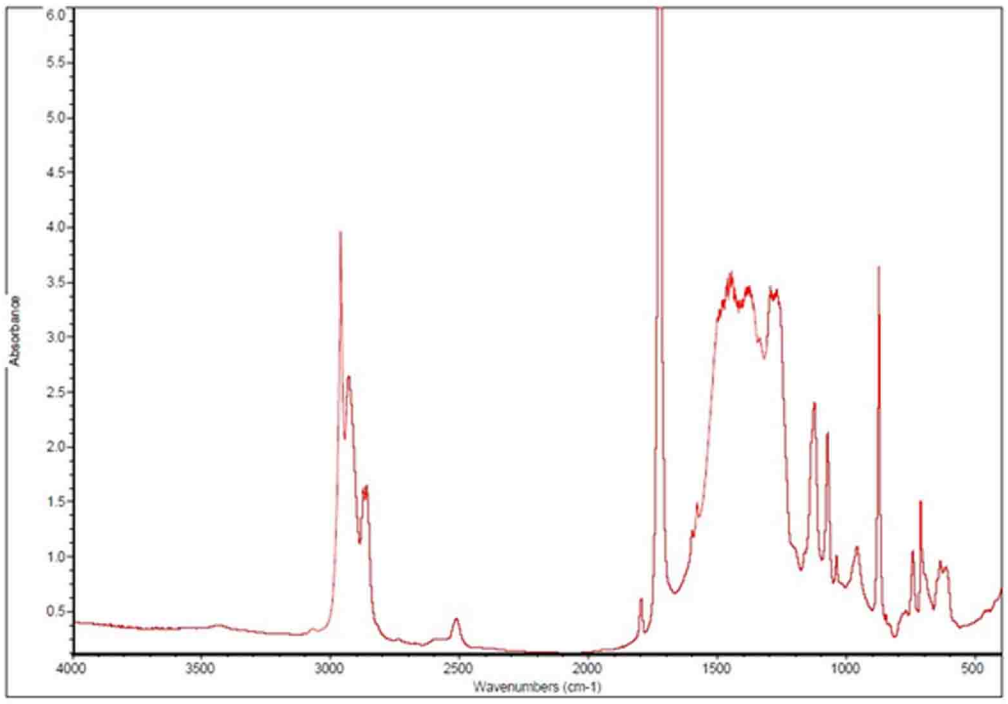


Filmsample12B

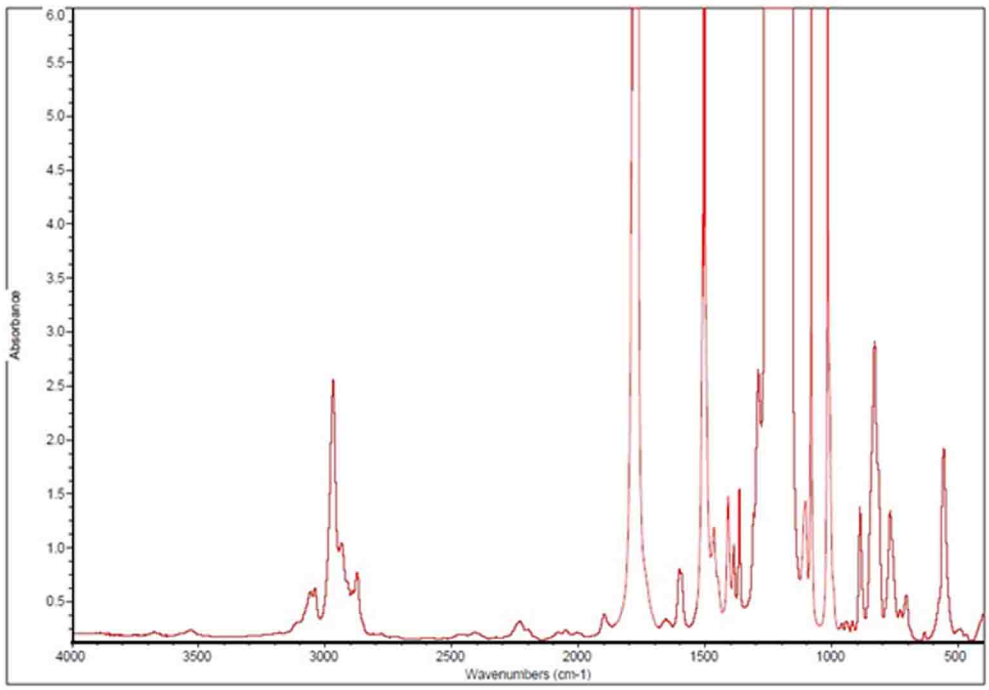
Filmsample13B



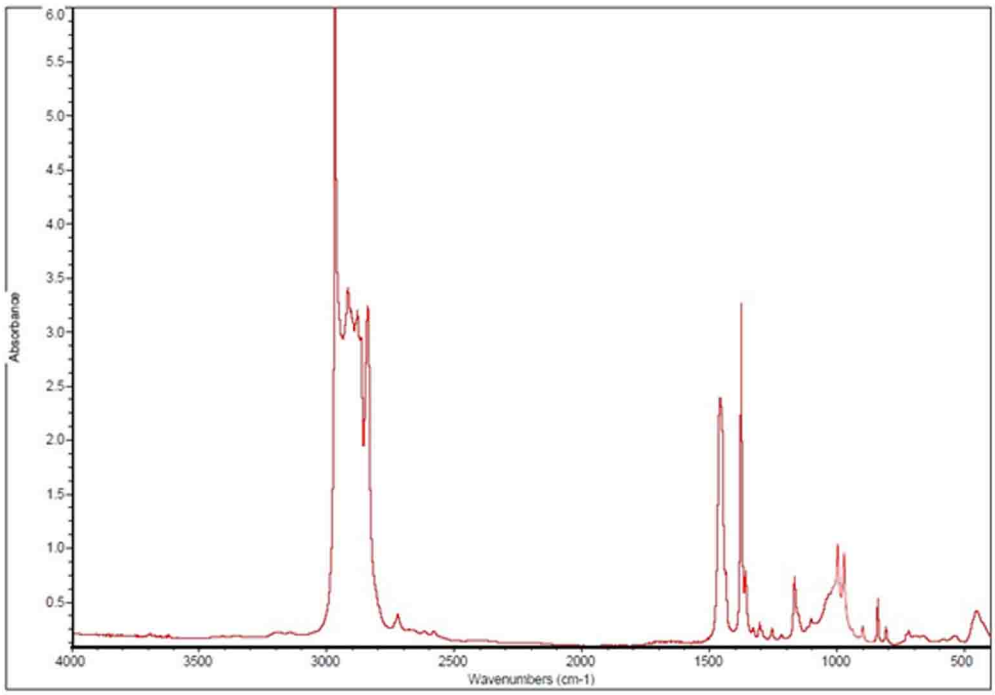

Sample 1 - Prepared as 50 micron thick film and run as Filmsample1B



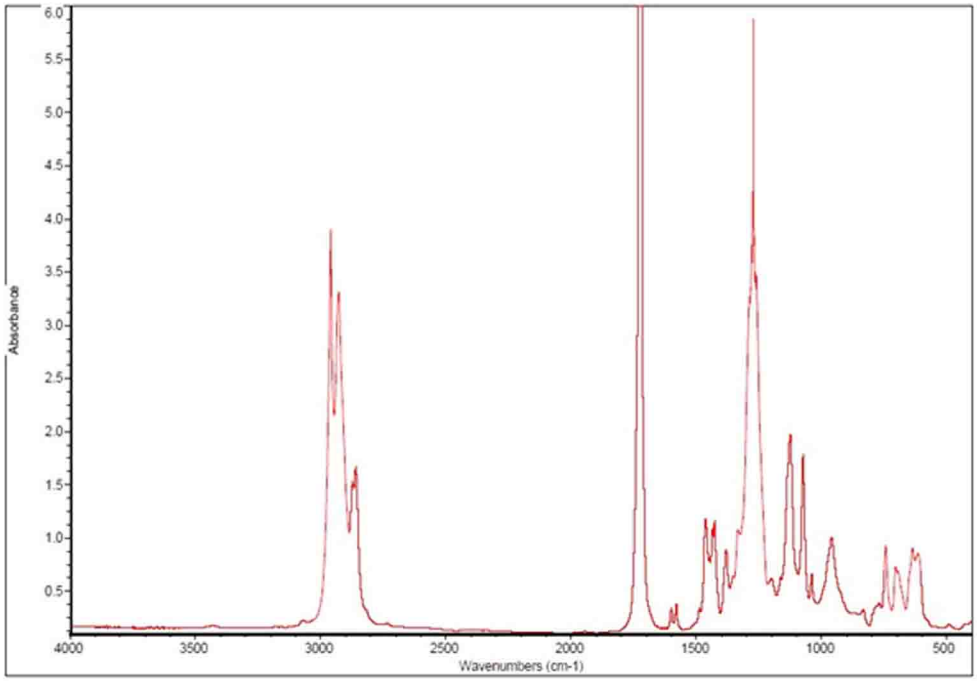

Sample 2 - Prepared as 50 micron thick film and run as Filmsample2B



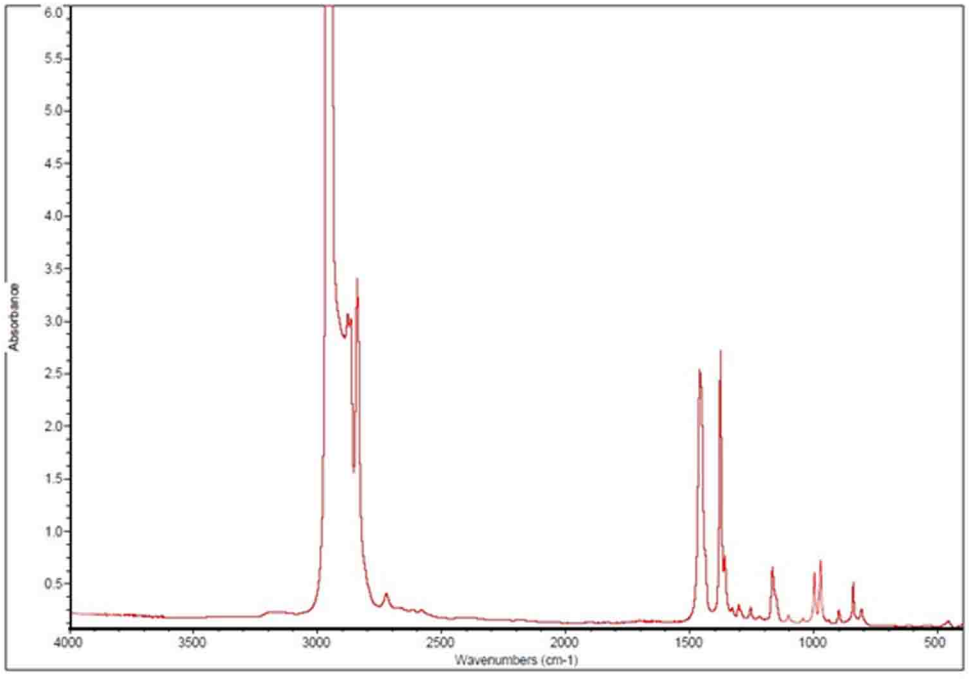

Sample 3 - Prepared as 50 micron thick film and run as Filmsample3B



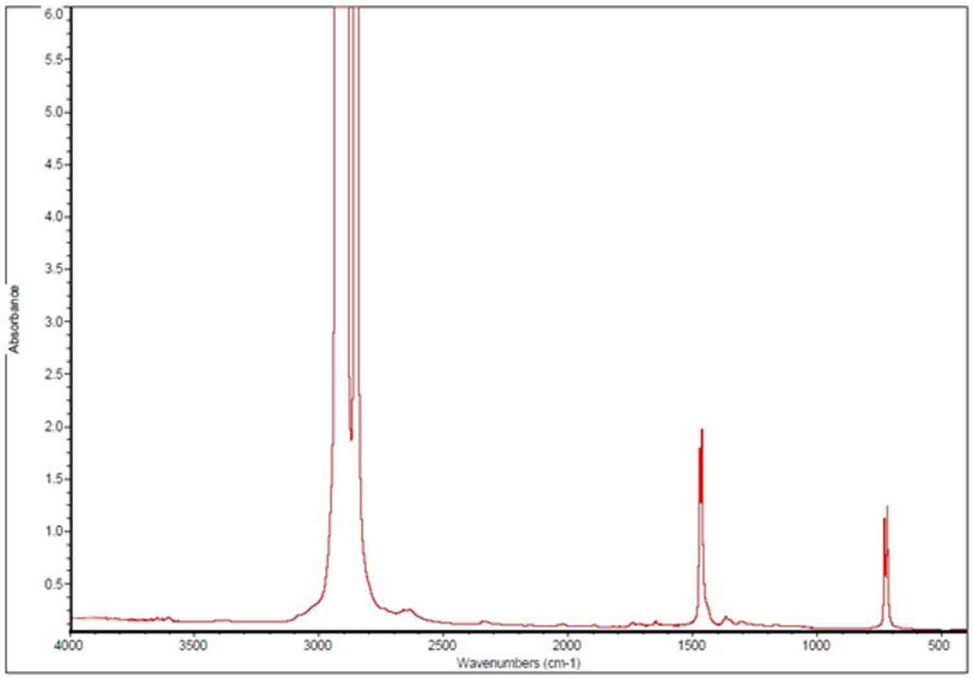

Sample 4 - Prepared as 50 micron thick film and run as Filmsample4B



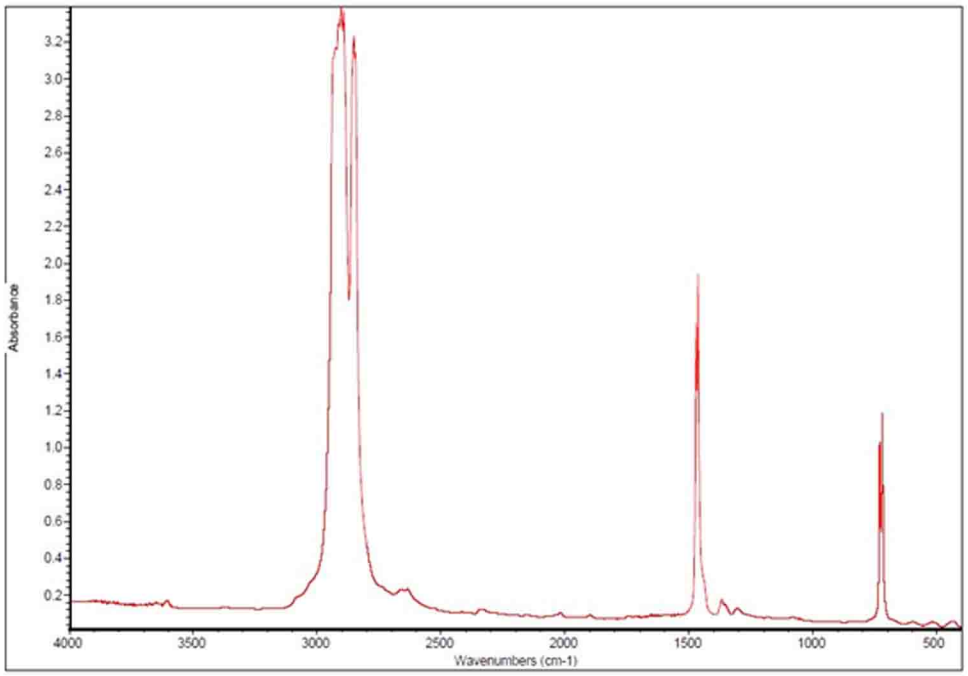

Sample 5 - Prepared as 50 micron thick film and run as Filmsample5B



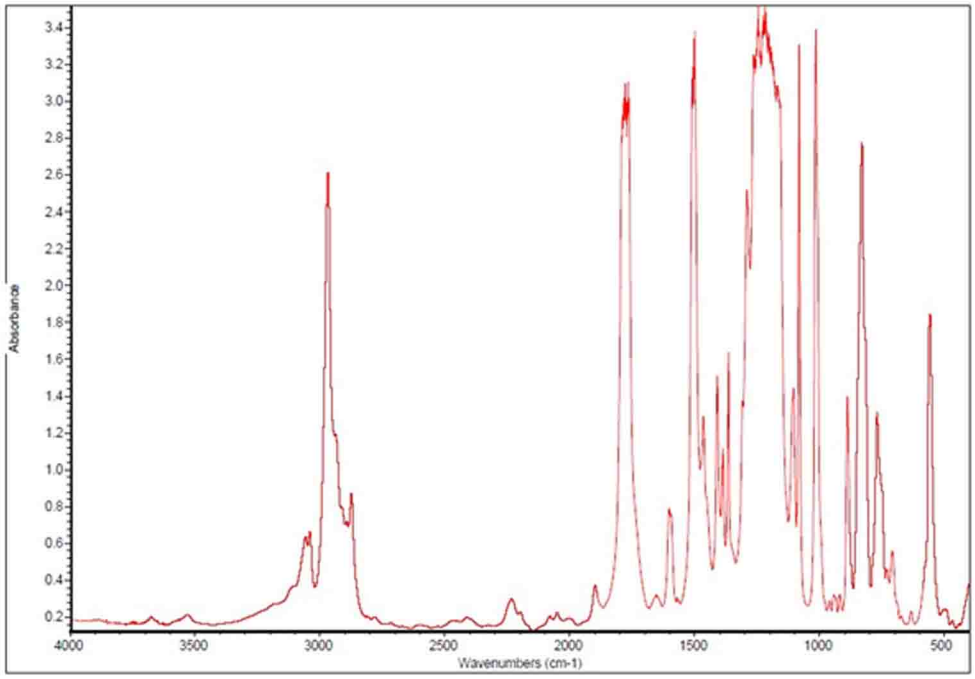

Sample 6 - Prepared as 50 micron thick film and run as Filmsample6B



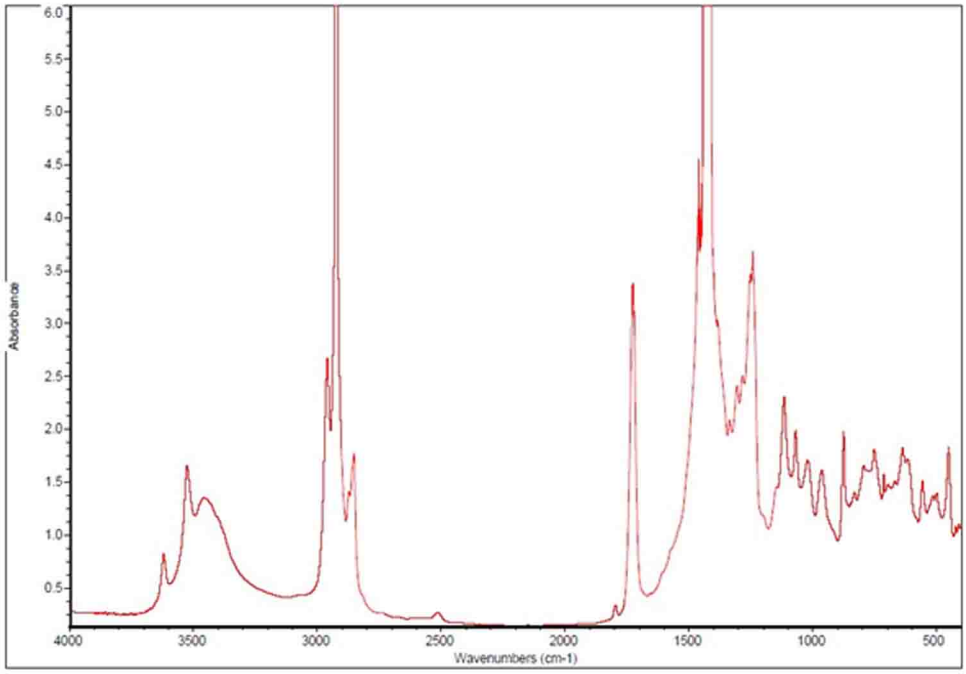

Sample 7 - Prepared as 50 micron thick film and run as Filmsample7B



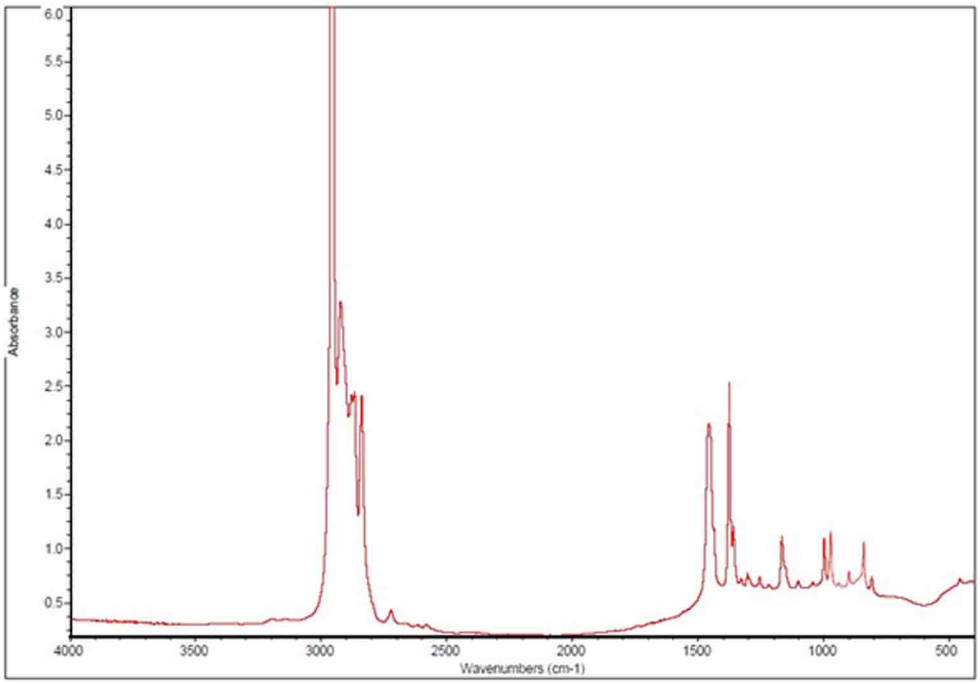

Sample 8 - Prepared as 50 micron thick film and run as Filmsample8B




Sample 9 - Prepared as 50 micron thick film and run as Filmsample9B




Sample 12 - Prepared as 50 micron thick film and run as Filmsample12B




Sample 13 - Prepared as 50 micron thick film and run as Filmsample13B

## Discussion

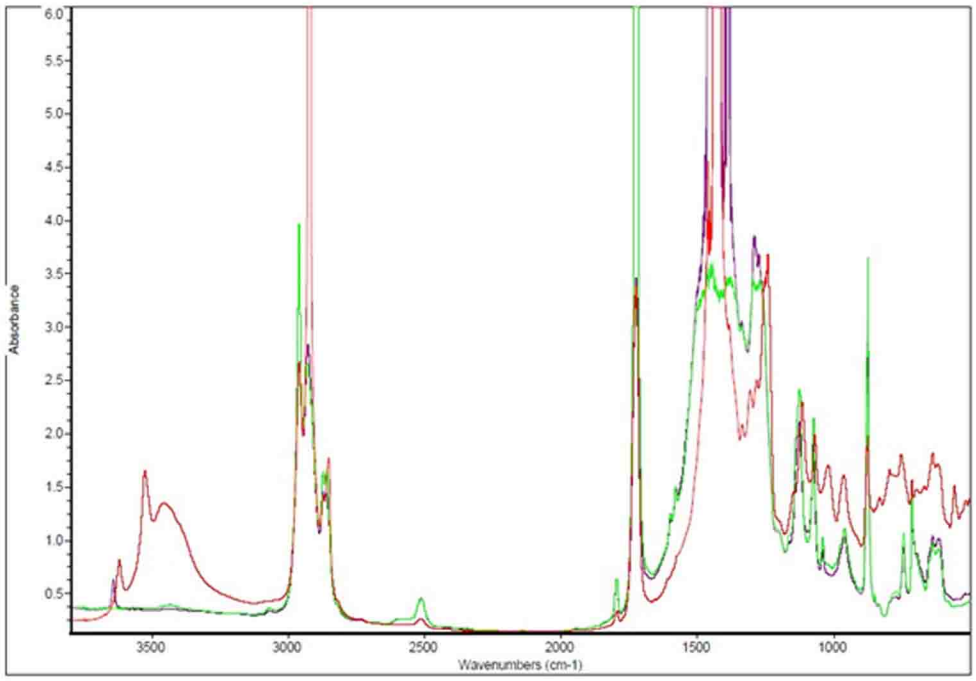
In general the actual thickness of the film measured by micrometer depth gauge agrees very well to the nominal thickness of a film that would be expected from a preparation using the 50 micron sizing ring.

The 11 individual transmission spectra collected for the plastic/polymer samples prepared as nominally 50 micron thick films are indicative of the family type of polymer material. The spectra representative of the same family type of polymer material show them to be similar, but there are some subtle features for each spectrum to enable the particular sample to be distinguishable from another sample type.

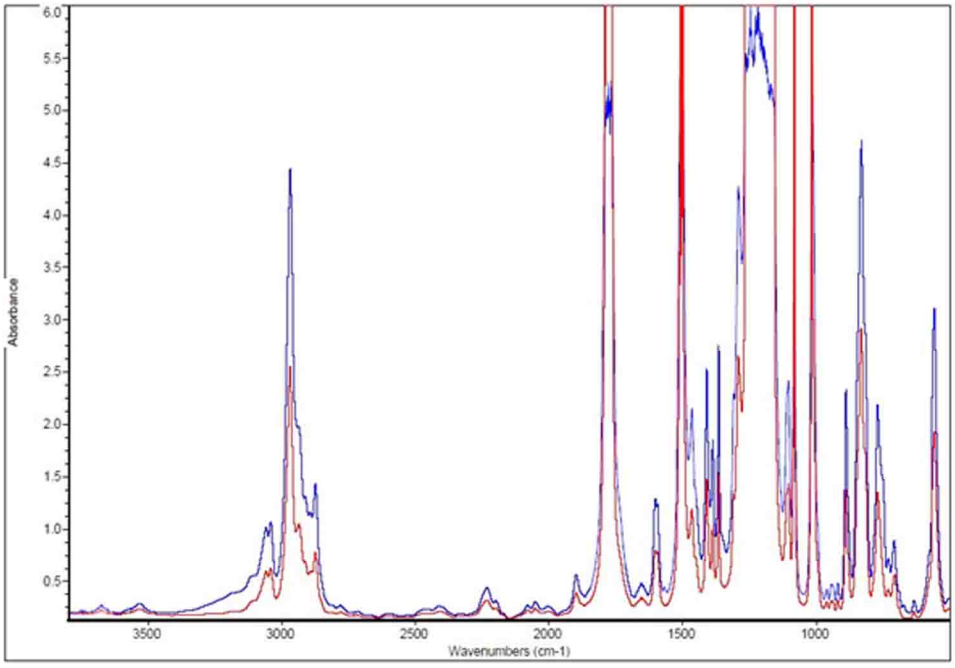
Of the 5 different polymer family sample types of spectra collected, 4 types can be compared from an overlay of their individual spectra. (Only one sample for a polyester family type of the examples taken was measured). The sample spectra compared for their overlays are:-

Samples 1, 2 and 12 for a PVC family type polymer material.
Samples 3 and 9 for a Polycarbonate family type polymer material.
Samples 4, 6 and 13 for a Polypropylene family type polymer material.
Samples 7 and 8 for a Polyethylene family type polymer material.

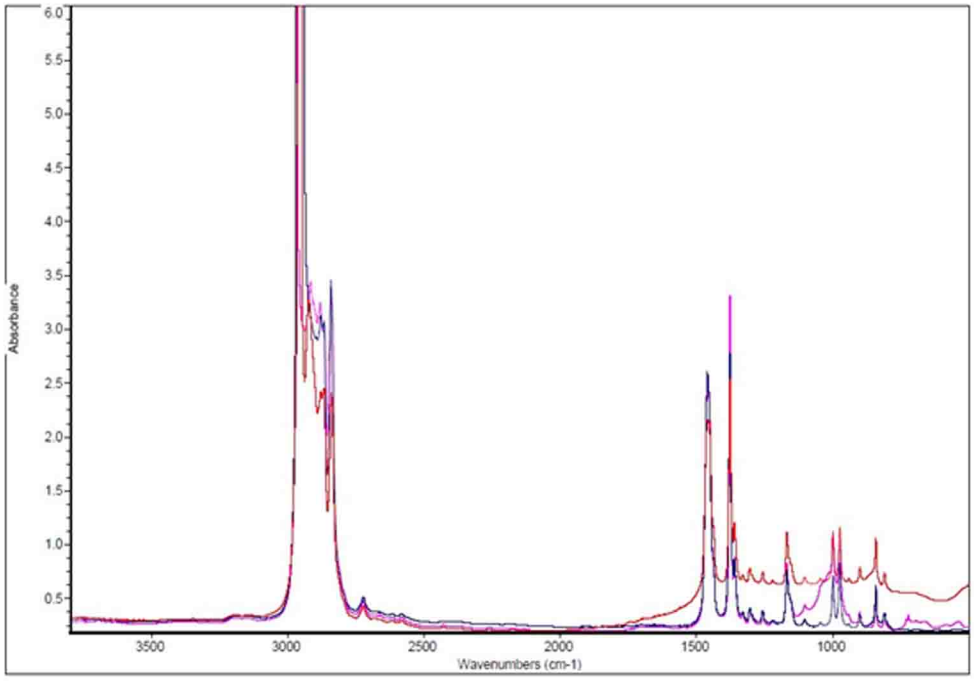
The overlaid spectra have been presented between 3800cm$^{-1}$ to 500cm$^{-1}$ and have all been fully scaled for the strongest absorbance peak in the spectrum.



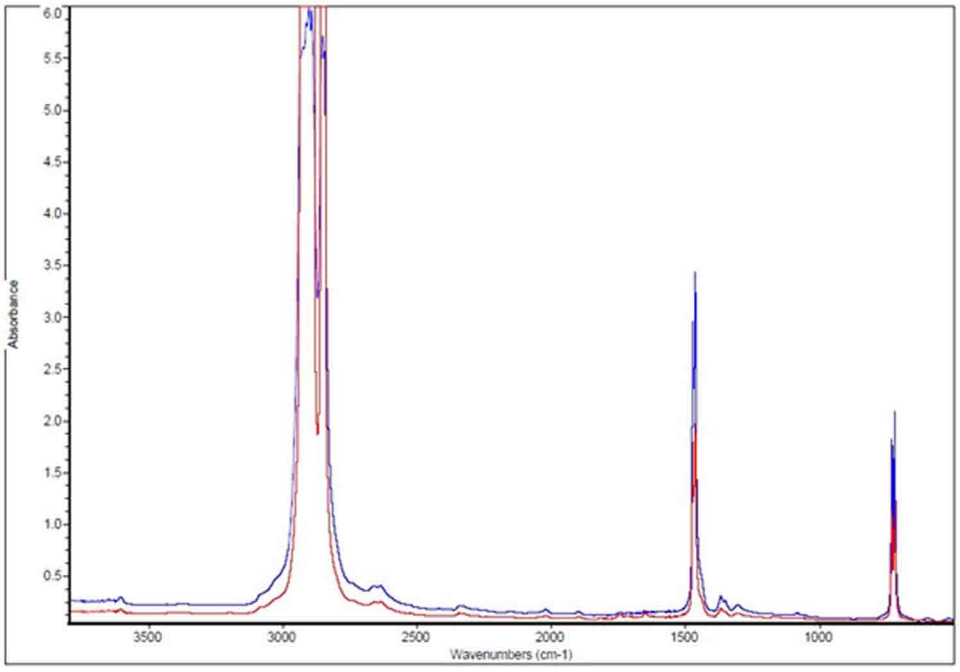

Sample 1 (blue), Sample 2 (green) and sample 12 (red) - Prepared as 50 micron thick films for comparison of PVC family type polymer material transmission spectra




Sample 3 (red) and sample 9 (blue) - Prepared as 50 micron thick films for comparison of polycarbonate family type polymer material transmission spectra




Sample 4 (purple), Sample 6 (blue) and sample 13 (red) - Prepared as 50 micron thick films for comparison of Polypropylene family type polymer material transmission spectra




Sample 7 (red) and sample 8 (blue) - Prepared as 50 micron thick films for comparison of polyethylene family type polymer material transmission spectra

## Conclusion

The Specac Mini-Film Maker Kit can be used to prepare thin films at 15mm diameter and thicknesses from nominally 15 microns to 500 microns for a variety of plastic/polymer materials, provided that the melting point of the polymer is below or does not exceed a temperature of 250°C.

The nominally 50 micron thick films prepared for the plastic/polymer type chosen, under a specific method and sample preparation step procedure, were subsequently analysed to produce an IR transmission spectrum which allows for the identification of the polymer material from a family type classification (e.g. a polycarbonate or a polypropylene material, etc.). There is good spectral agreement for peak positions regarding comparison of similar family type materials from an overlay of the individual spectra produced.

The nominal thickness of the films at 50 microns, that have been prepared using the 50 micron sizing ring, agree well for an actual depth gauge measurement of the film (within given tolerance limits), but for all the films, a pathlength of circa 50 microns for a transmission spectral measurement of the sample is exhibiting over absorption of the strongest bands/peaks in the spectrum. These very strong absorption bands/peaks cannot be resolved for determination of the molecular structure or specific chemical group species within the sample being studied under such conditions. For such polymeric sample types, full resolution of spectral peaks and measurable absorbance intensities (qualitative and quantitative data), may be achieved by use of the ATR technique rather than measurement by transmission. However, over-absorption of the strong bands in a transmission spectrum from the bulk of a polymeric material structure can be “sacrificed” for their confirmatory status if it allows for the weaker band absorption intensities from any low level constituents to be seen, should they be present at a measurable level from a corresponding pathlength increase. Therefore, it may be necessary to produce a consistent, uniform thin film from a plastic/polymeric sample for the determination of low level concentration constituents that cannot be reliably measured from a surface and short pathlength measurement technique and the Speac Mini-Film Maker Kit is ideal and easy to use for appropriate thin film production. (See Specac Application Note 44).

## Acknowledgement

The study was carried out by: C. Moss, Specac Limited, Orpington, Kent, UK.

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