SAMPLE PREPARATION EQUIPMENT

Comparison of Thin Films from 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).

Application

This is an expansion of the study from Specac Application Note 43 (Thin Film Production of Plastic / Polymer Materials Using the Mini-Film Maker Accessory).

5 (five) specific samples were chosen from an original set of 13 plastic/polymer samples (and from which 11 samples had been made into nominal 50 micron thick films), to form into nominal 15 and 25 micron thick films along with their 50 micron thick films at a 15mm diameter, to be compared from their resultant IR transmission spectra of the specific polymer family type.

Equipment and Method

The thinner films are made using the two thinnest sizing rings available for use with the Mini-Film Maker Kit (p/n GS03970), nominally at 15 microns and 25 microns for the film thicknesses.

Note:
15 and 25 micron thick sizing rings are also offered for use with the Specac Film-Makers (p/n GS15640 and GS15800), which in turn must be used in the larger sized Manual Hydraulic Presses. It is possible that what works as a method procedure with the Mini-Film Maker Kit (p/n GS03970) for specific sample preparation and film thickness production can be applied and adapted for use with these other, larger film making accessories (the films formed are 29mm in diameter).

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

From the 11 plastic/polymer samples used for Application Note 43 (50 micron thick film production), the 5 samples chosen that were melted and pressed to form nominal 15, 25 and 50 micron thick films are shown in table 1 (15 spectra obtained).

Table 1

Sample Number	Polymer Family Type	Sizing Ring Used (Actual Thickness of Film)	Film Spectrum
3	Polycarbonate	15 microns - (30 microns)	Filmsample3C
4	Polypropylene	15 microns - (22 microns)	Filmsample4C
5	Polyester	15 microns - (22 microns)	Filmsample5C
8	Polyethylene	15 microns - (23 microns)	Filmsample8C
12	Polyvinylchloride (PVC)	15 microns - (27 microns)	Filmsample12C
3	Polycarbonate	25 microns - (42 microns)	Filmsample3A
4	Polypropylene	25 microns - (32 microns)	Filmsample4A
5	Polyester	25 microns - (31 microns)	Filmsample5A
8	Polyethylene	25 microns - (30 microns)	Filmsample8A
12	Polyvinylchloride (PVC)	25 microns - (36 microns)	Filmsample12A
3	Polycarbonate	50 microns - (52 microns)	Filmsample3B
4	Polypropylene	50 microns - (49 microns)	Filmsample4B
5	Polyester	50 microns - (46 microns)	Filmsample5B
8	Polyethylene	50 microns - (42 microns)	Filmsample8B
12	Polyvinylchloride (PVC)	50 microns - (50 microns)	Filmsample12B

The 5 plastic/polymer sample types chosen are shown below for their original form and as the nominal 50 micron thick films prepared as mounted in a Specacard.

Sample 3

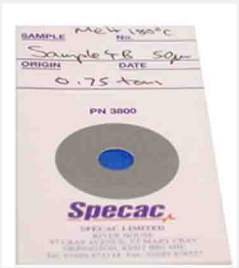
Sample 4

Sample 5

Sample 8

Sample 12

Sample 3



Sample 4

Sample 5

Sample 8

Sample 12

Table 2

Sample Number	Melting Point	Sizing Ring Choice	Sample Size	Load Applied	Load Duration	Cooling Down Stage (*)
3	200°C	15, 25 and 50 microns	One pellet	0.75 Tons	20 seconds	Film Assembly Placed on Cooling Block
4	180°C	15, 25 and 50 microns	Small fragment	0.75 Tons	20 seconds	Film Assembly Placed on Cooling Block
5	180°C	15, 25 and 50 microns	One bead	0.75 Tons	20 seconds	Film Assembly Placed on Cooling Block
8	200°C	15, 25 and 50 microns	Small fragment	0.75 Tons	20 seconds	Film Assembly Placed on Cooling Block
12	180°C	15, 25 and 50 microns	Sliced section	0.75 Tons	20 seconds	Film Assembly Placed on Cooling Block

The polymer sample types for Cellophane (Sample 10) and Polystyrene (Sample 11) of the original 13 polymer sample types could not be used in comparison for these varying thickness film preparations as it is not possible to form any thickness of film from their original expanded form. Only ATR spectra have been obtained for the polymer types as Samples 10 and 11. Examples of the ATR spectra for all of the original 13 plastic/polymer samples are to be found from Specac Application Note 42.

Transmission spectra over the spectral range between 4000cm^{-1} to 400cm^{-1} for the prepared nominally thick 15 micron, 25 micron and 50 micron films 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.

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.

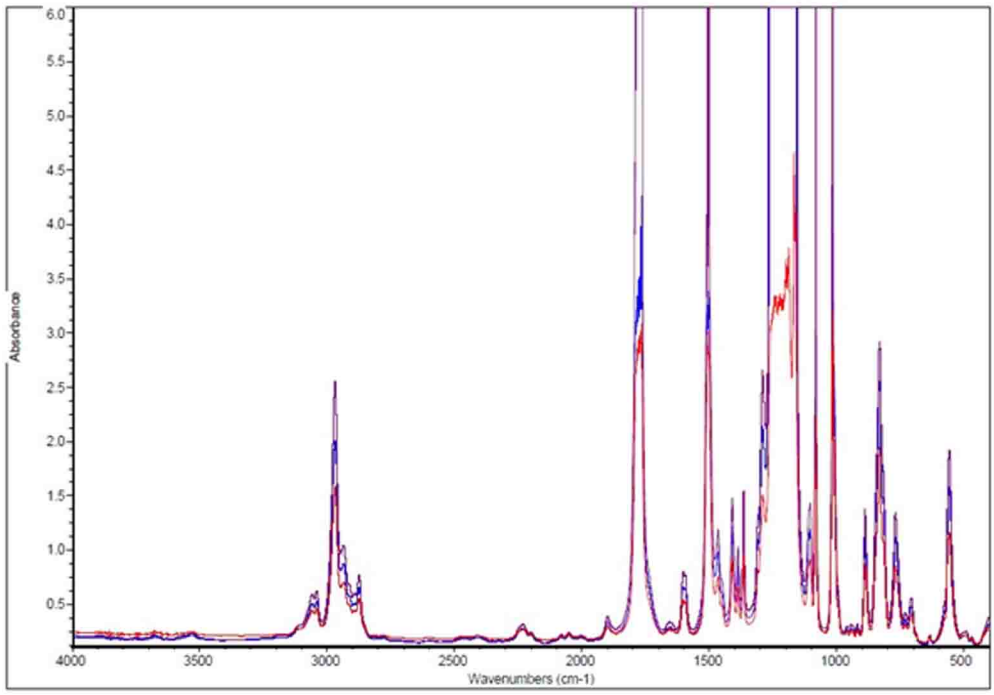
(*) For the Cooling Down Stage step, specifically, when the 0.75 tons load bring applied from the press was released at the melting point temperature, the film maker assembly of parts was removed from the press whilst hot and placed on the black coloured cooling block disc of the kit of parts. Access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

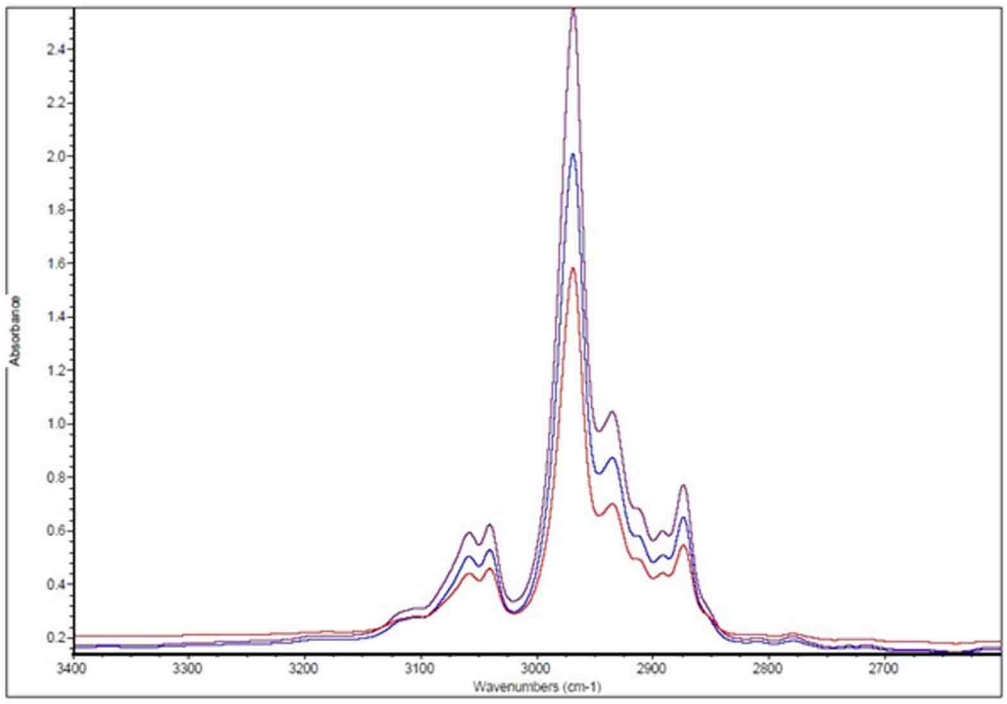
As a cross check for the actual film thickness prepared from use of each thickness of sizing ring, each film when mounted in a Specacard was measured for its thickness using a digital micrometer depth gauge. The actual film thicknesses measured for each sample against the specific sizing rings used are shown (between brackets) in table 1.

Spectral Data

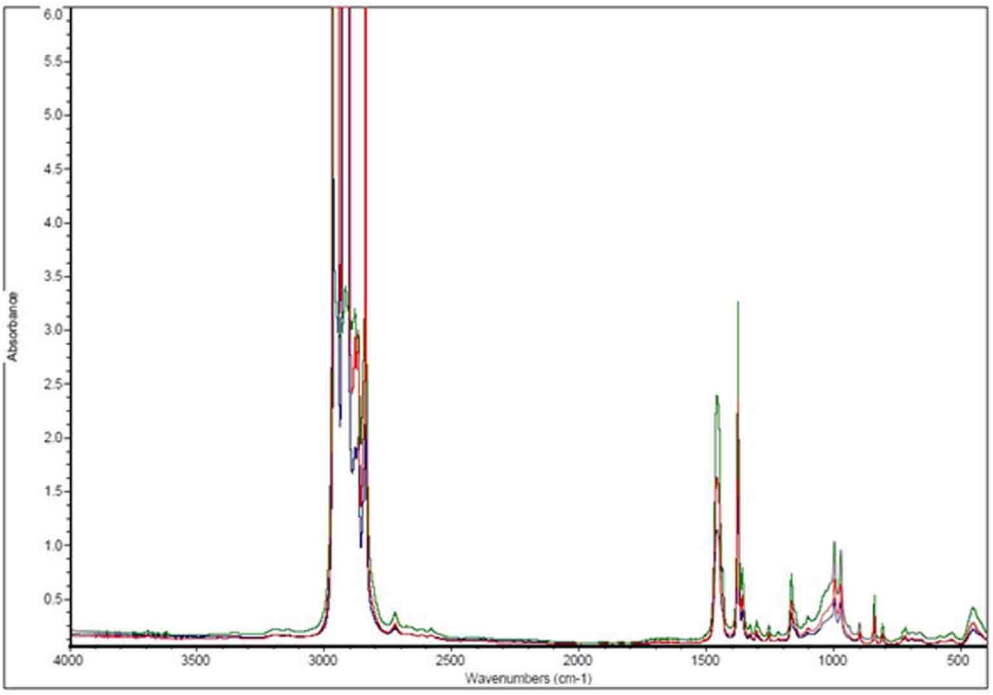
The transmission spectra collected for the 15 film samples prepared using the 15, 25 and 50 micron thick sizing rings under the specific method and sample preparation procedural steps are presented as follows.



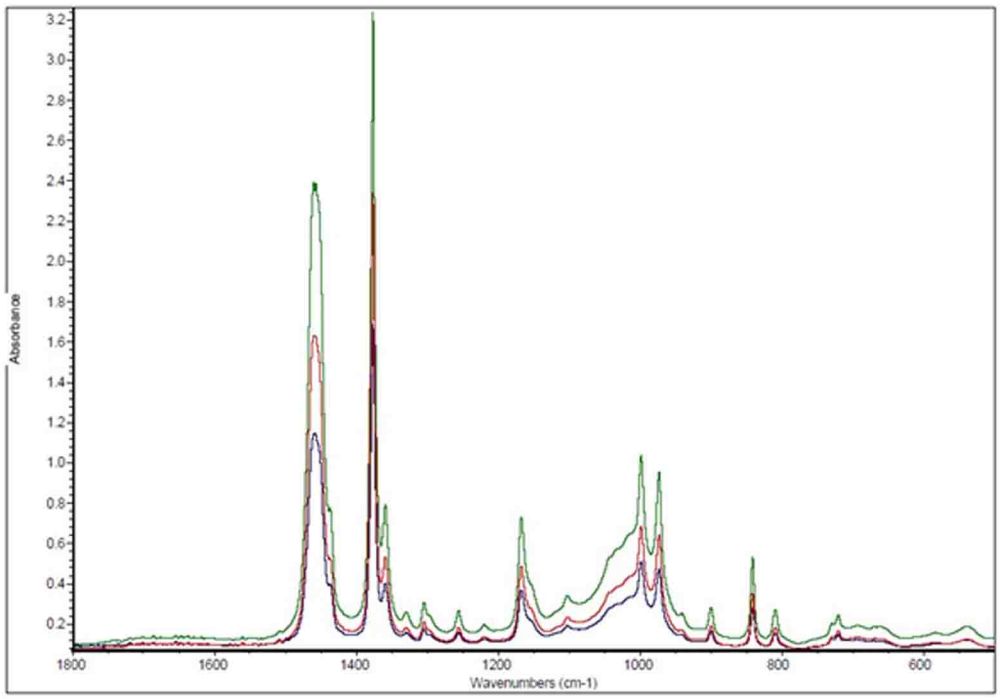
Sample 3 - 15 micron 3C (red), 25 micron 3A (blue) and 50 micron 3B (purple) thick films
Overlaid spectra from 4000cm^{-1} to 400cm^{-1} for a common absorbance scale



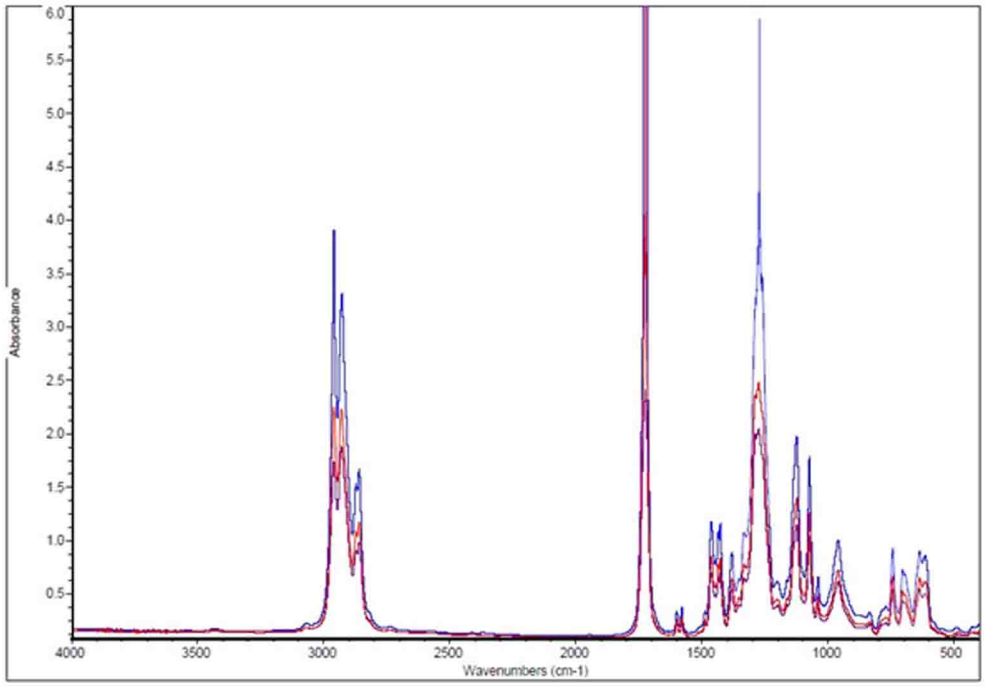
Sample 3 - 15 micron 3C (red), 25 micron 3A (blue) and 50 micron 3B (purple) thick films
Overlaid spectra from 3400cm^{-1} to 2600cm^{-1} for a common absorbance scale



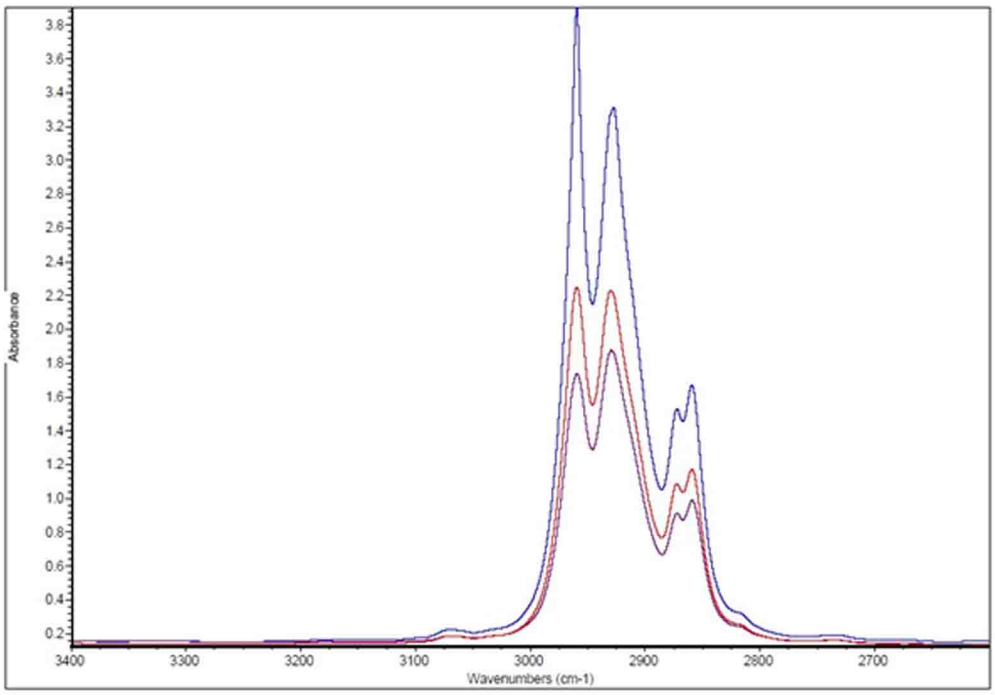
Sample 4 - 15 micron 4C (blue), 25 micron 4A (red) and 50 micron 4B (green) thick films
Overlaid spectra from 4000cm^{-1} to 400cm^{-1} for a common absorbance scale



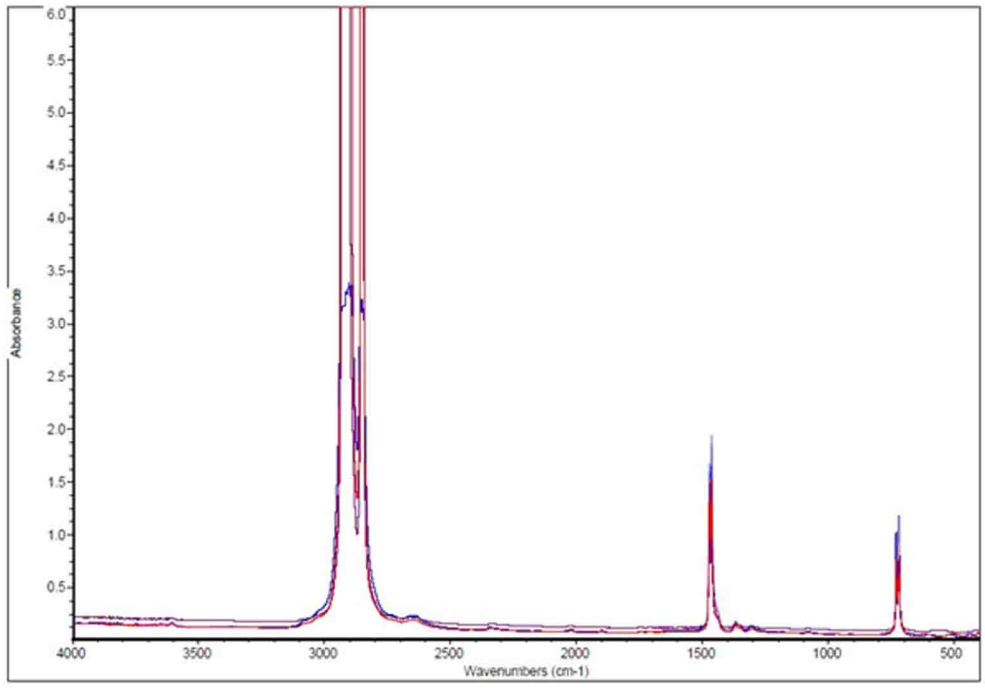
Sample 4 - 15 micron 4C (blue), 25 micron 4A (red) and 50 micron 4B (green) thick films
Overlaid spectra from 1800cm^{-1} to 500cm^{-1} for a common absorbance scale



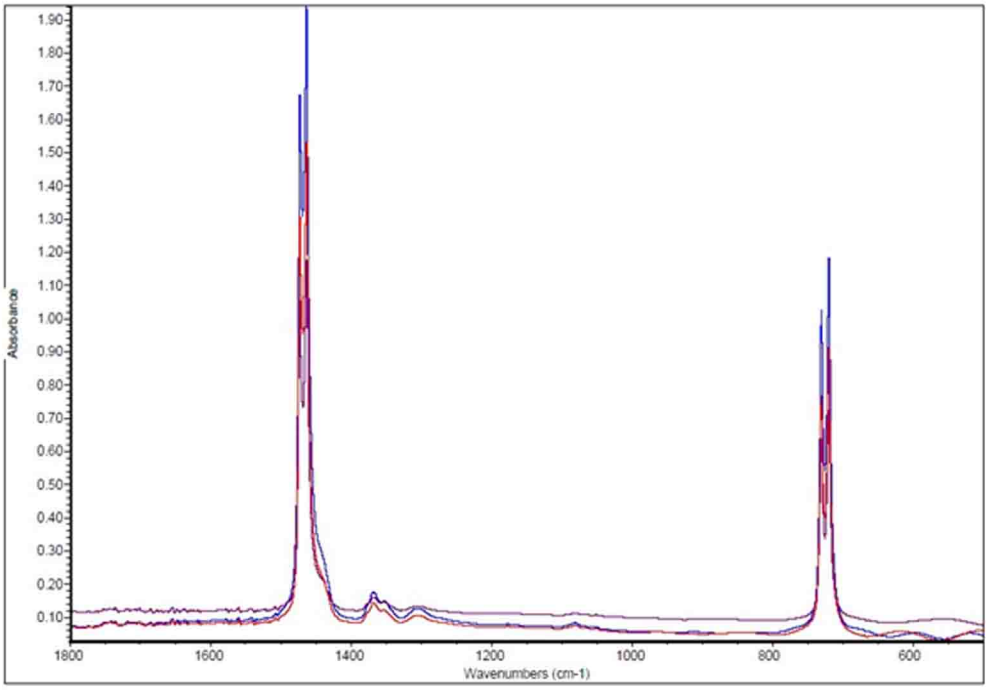
Sample 5 - 15 micron 5C (purple), 25 micron 5A (red) and 50 micron 5B (blue) thick films
Overlaid spectra from 4000cm^{-1} to 400cm^{-1} for a common absorbance scale



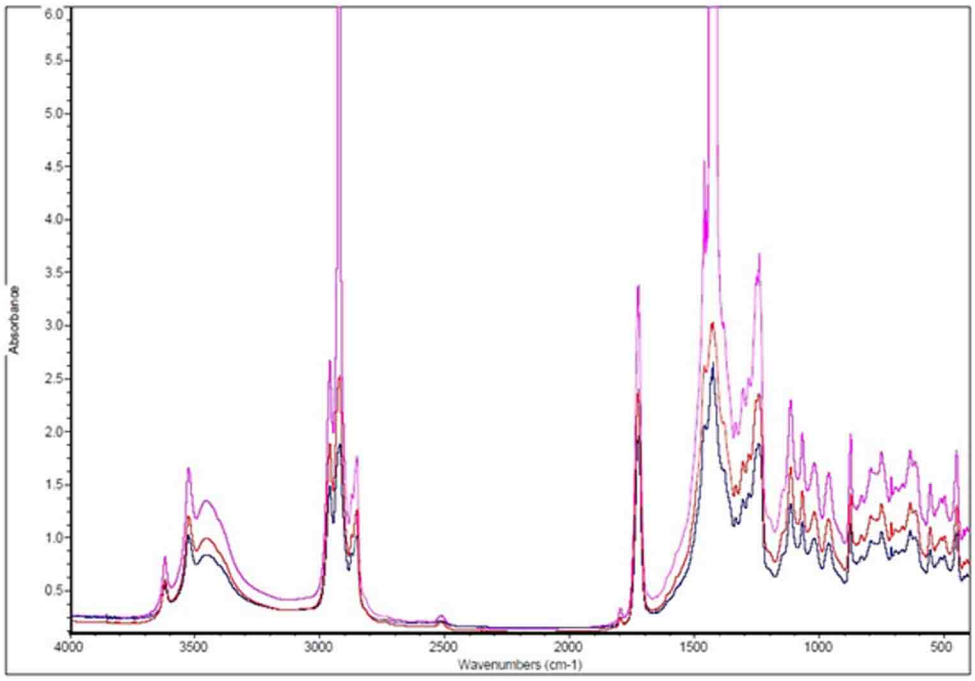
Sample 5 - 15 micron 5C (purple), 25 micron 5A (red) and 50 micron 5B (blue) thick films
Overlaid spectra from 3400cm^{-1} to 2600cm^{-1} for a common absorbance scale



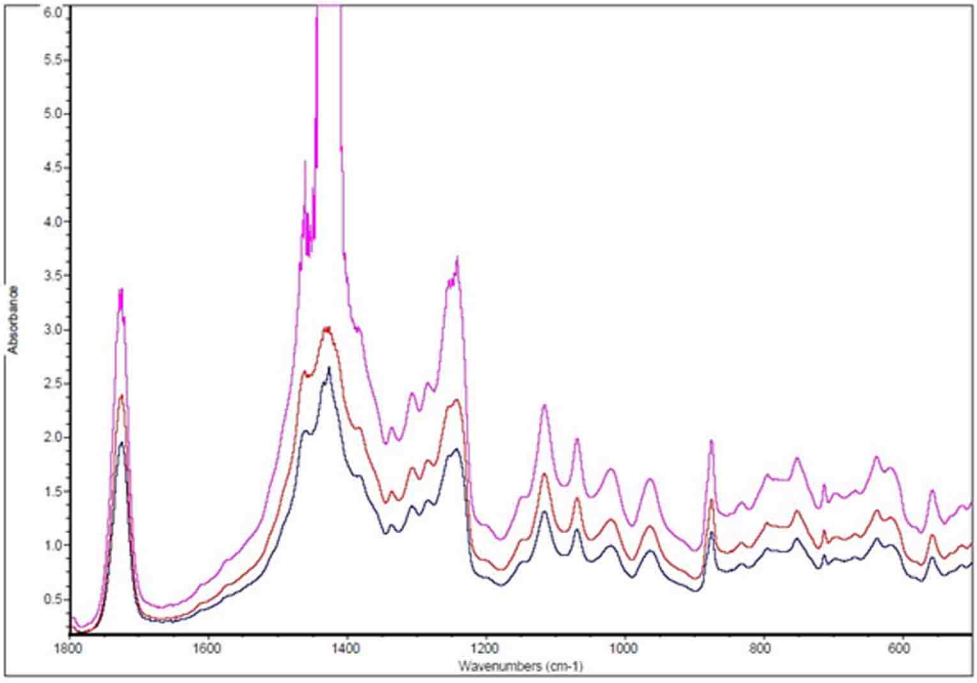
Sample 8 - 15 micron 8C (red), 25 micron 8A (blue) and 50 micron 8B (purple) thick films
Overlaid spectra from 4000cm^{-1} to 400cm^{-1} for a common absorbance scale



Sample 8 - 15 micron 8C (red), 25 micron 8A (blue) and 50 micron 8B (purple) thick film
Overlaid spectra from 1800cm^{-1} to 500cm^{-1} for a common absorbance scale



Sample 12 - 15 micron 12C (blue), 25 micron 12A (red) and 50 micron 12B (purple) thick films
Overlaid spectra from 4000cm^{-1} to 400cm^{-1} for a common absorbance scale



Sample 12 - 15 micron 12C (blue), 25 micron 12A (red) and 50 micron 12B (purple) thick films
Overlaid spectra from 1800cm^{-1} to 500cm^{-1} for a common absorbance scale

Table 3

Sample Number	Polymer Family Type	Film Spectrum	Measured Thickness of Film (T)	Abs Value (A) at Peak Position	Comparison Factor (T/A)
3	Polycarbonate	Filmsample3A	42 microns	2.01 at 2970cm^{-1}	20.90
3	Polycarbonate	Filmsample3B	52 microns	2.55 at 2970cm^{-1}	20.40
3	Polycarbonate	Filmsample3C	30 microns	1.58 at 2970cm^{-1}	20.00
4	Polypropylene	Filmsample4A	32 microns	2.35 at 1376cm^{-1}	13.62
4	Polypropylene	Filmsample4B	49 microns	3.26 at 1376cm^{-1}	15.03
4	Polypropylene	Filmsample4C	22 microns	1.70 at 1376cm^{-1}	12.94
5	Polyester	Filmsample5A	31 microns	2.25 at 2959cm^{-1}	13.78
5	Polyester	Filmsample5B	46 microns	3.90 at 2959cm^{-1}	11.80
5	Polyester	Filmsample5C	22 microns	1.74 at 2959cm^{-1}	12.64
8	Polyethylene	Filmsample8A	30 microns	1.53 at 1463cm^{-1}	19.61
8	Polyethylene	Filmsample8B	42 microns	1.94 at 1463cm^{-1}	21.65
8	Polyethylene	Filmsample8C	23 microns	1.18 at 1463cm^{-1}	19.49
12	PVC	Filmsample12A	36 microns	1.66 at 1116cm^{-1}	21.69
12	PVC	Filmsample12B	50 microns	2.30 at 1116cm^{-1}	21.74
12	PVC	Filmsample12C	27 microns	1.31 at 1116cm^{-1}	20.61

Discussion

The 3 individual transmission spectra collected for the 5 different plastic/polymer samples prepared as nominally 15, 25 and 50 micron thick films are indicative of the family type of polymer material. 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 film preparation procedure using the 15, 25 and 50 micron sizing ring.

From comparison of the overlaid spectra for each film thickness, there is a corresponding increase in the spectral peak band intensities with an increasing thickness for the film. A “comparison factor” can be calculated for a consistency of film preparation using a particular sizing ring, from the measured “actual” thickness of the film (T) against the maximum absorbance intensity value (A) from a particular resolvable peak position from the IR transmission spectrum produced for each film. This is shown in table 3 for all 15 films prepared.

The comparison factor calculated for each sizing ring used can be considered as the theoretical pathlength of film needed to be prepared that would produce an absorbance intensity of 1.00AU for each sample type. For each sample type the comparison factor is broadly in agreement for an actual particular film thickness measured spectroscopically from the different sizing ring option used. Cross-referencing with the micrometer depth gauge device used for measurement of the prepared films for their actual thicknesses, the comparison factors for each sample type lie within the accepted tolerance limits of such measurements at +/- 2 microns.

Taking the polycarbonate sample (Number 3) as an example, for the spectral peak at 2970cm^{-1} and for a 52 micron thick film sample using the 50 micron sizing ring (as measured by the digital depth gauge), the absorbance intensity is 2.55AU (absorbance units). Using the comparison factor calculated for this sample type from the nominal 50 micron sizing ring (20.40), a reading of 1.58AU for a similar family sample type at this peak position in the spectrum would theoretically determine that the film pathlength is circa 32 microns. The measured film thickness for the sample using the nominal 25 micron sizing ring is at 30 microns, and so falls within expectations of a consistent film thickness that can be prepared using the most appropriate nominal thickness sizing ring.

Similarly, taking the polyester sample (Number 5) as an example, for the spectral peak at 2959cm^{-1} and for a 46 micron thick film sample using the 50 micron sizing ring (as measured by the digital depth gauge),

the absorbance intensity is 3.90AU (absorbance units). Using the comparison factor calculated for this sample type from the nominal 50 micron sizing ring (11.80), a reading of 1.74AU for a similar family sample type at this peak position in the spectrum would theoretically determine that the film pathlength is circa 21 microns. The measured film thickness for the sample using the nominal 25 micron sizing ring is at 22 microns, and so falls within expectations of a consistent film thickness that can be prepared using the most appropriate nominal thickness sizing ring.

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 nominal 15, 25 and 50 micron thick films prepared for the plastic/polymer types chosen for this study, under specific, defined 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 polypropylene material, etc.). There is a good spectral agreement for peak positions regarding comparison of similar family type materials from an overlay of individual spectra produced for the different film thicknesses.

The absorbance intensity for the vibrational band features resolvable in a transmission spectrum for particular film thicknesses are shown to vary in direct and corresponding accordance with the film thickness prepared. Depending upon the sample type chosen and specific methodology of sample preparation for production of a thin film, it may not be possible to obtain an exact match for a thickness of film corresponding to the nominal sizing ring thickness chosen, e.g. 50 microns using the 50 microns sizing ring. However, any film thickness produced corresponds directly to a consistent and proportional increase or decrease in spectral peak position intensity from a transmission spectral measurement, dependent upon the nominal thickness sizing ring used.

A consistent methodology of sample preparation procedure should be adopted for such factors as melting points, sample size, load application and duration and sample cooling and duration stages. When established for such sample preparation steps, reproducible and consistent film thicknesses can be prepared from a choice and changing of a nominal thickness sizing ring alone, in use of the Specac Mini-Film Maker Kit (p/n GS03970). If larger diameter films at 29mm are to be prepared, then a similar methodology for the film preparation may be used with the Specac Film Makers (p/n's GS15640 and GS15800). Possibly the only factor to change to obtain a consistent set of film thicknesses if both 15mm and 29mm diameter films are to be prepared, would be a requirement for using a larger amount of sample to melt because of the increased sample surface area of 29mm diameter film compared to the 15mm diameter films as formed using the Mini-Film Maker Kit.

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

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