

## CHAPTER III

### EXPERIMENTAL SECTION

The homemade  $\mu$ ATR accessory with a slide-on diamond  $\mu$ IRE and slide-on Ge  $\mu$ IRE were employed for surface characterization of polymer and polymer composites. Since spectral features (i.e., group frequency and peak position) of an infrared spectrum are unique to molecular structure of the material while the magnitude of absorption indicates concentration of the corresponding species, a collection of infrared spectra acquired at different position of the sample can be employed for the investigation of homogeneity of a specimen. To determine the homogeneity of polymer and polymer composites with ATR FT-IR microspectroscopy, the experiment was divided into two parts: surface characterization and depth dependent characterization. The specular reflection technique was also employed for the investigation of homogeneity in this study.

#### 3.1 Materials and Equipments

##### 3.1.1 Samples

###### 3.1.1.1 Homopolymers

- Polypropylene (PP)
- Poly(styrene-co-acrylonitrile)
- Polybenzoxazine (Ba-35x)

###### 3.1.1.2 Polymer composites

- Hydroxyapatite/polypropylene composites
- Polybenzoxazine/SiO<sub>2</sub> composites
- Polybenzoxazine/Al<sub>2</sub>O<sub>3</sub> composites
- Polybenzoxazine/SiC<sub>(particle)</sub> composites
- Polybenzoxazine/SiC<sub>(whisker)</sub> composites

### 3.1.2 Instruments

1. Nicolet 6700 FT-IR spectrometer equipped with a mercury-cadmium-telluride (MCT) detector.
2. Continuum infrared microscope with a built-in 15X Schwarzschild-Cassegrain infrared objective and a 10X glass objective.
3. Homemade slide-on diamond  $\mu$ ATR accessory with a gem-quality round brilliant cut diamond IRE (0.1005 ct type IaB natural diamond).
4. Homemade slide-on Ge  $\mu$ ATR accessory with a cone-shaped Ge IRE.

## 3.2 Default Spectral Acquisition

### Nicolet 6700 FT-IR Spectrometer

#### Instrumental Setup

Source	Standard Global <sup>TM</sup> Infrared Light Source
Detector	MCT/A
Beam splitter	Ge on KBr

#### Acquisition Parameters

Spectral resolution	4 $\text{cm}^{-1}$
Number of scans	64 scans
Spectral format	Absorbance

#### Advanced Parameters

Zero filing	none
Apodization	Happ-Genzel
Phase correction Standard	Mertz

### Continuum Infrared Microscope

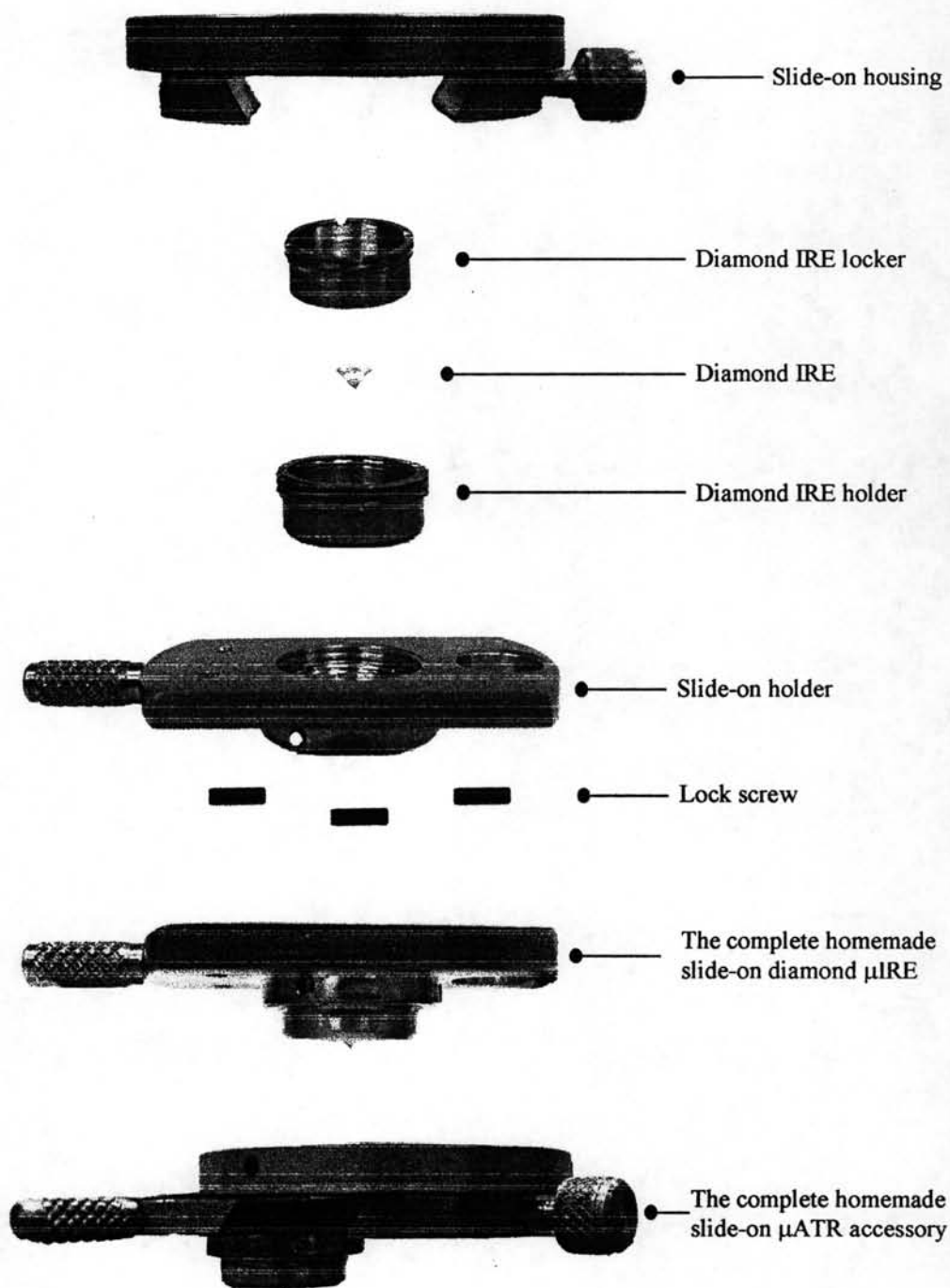
#### Instrumental Setup

Objective	15X Schwarzschild-Cassegrain
Aperture size	150 $\times$ 150 $\mu\text{m}$

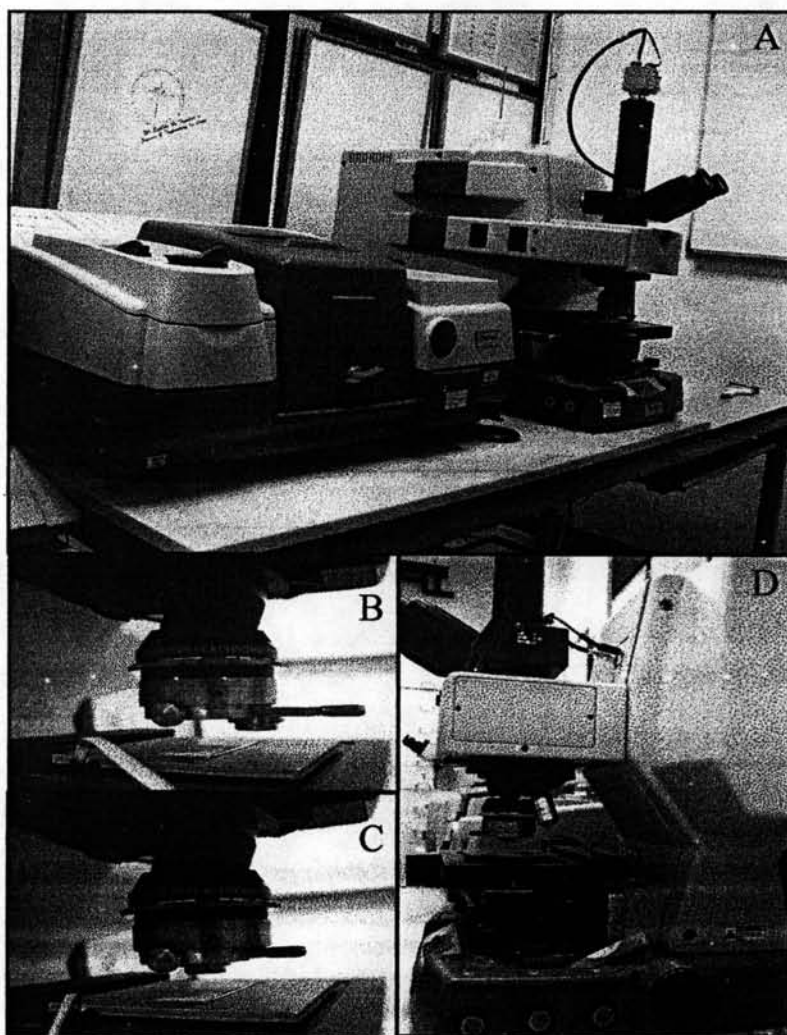
### 3.3 Homemade Slide-on Diamond $\mu$ ATR Accessory

The homemade slide-on diamond  $\mu$ ATR accessory consists of two components as shown in Figure 3.1. The first component is the slide-on housing. The metal housing was perforated and gouged out for placing the diamond slide-on  $\mu$ IRE. The second component was the slide-on IRE which designed for accommodating diamond alignment to achieve a maximum reflected energy. The slide-on IRE was slid into the position of slide-on housing that has been fixed on the objective of the Continuum infrared microscope. The complete set up of the slide-on  $\mu$ ATR accessory attached to the Nicolet 6700 FT-IR spectrometer was illustrated in Figure 3.2. The incident radiation from the infrared microscope was coupled into the table facet of the diamond and was underwent total internal reflection at the pavilion facet as shown in Figure 3.3. When obtaining the optimum position, the slide-on IRE was locked with a knob. The amount of light is controlled by the illuminating aperture of the microscope. The internal reflection of infrared radiation at the pavilion facet can be employed for ATR FT-IR spectral acquisition.

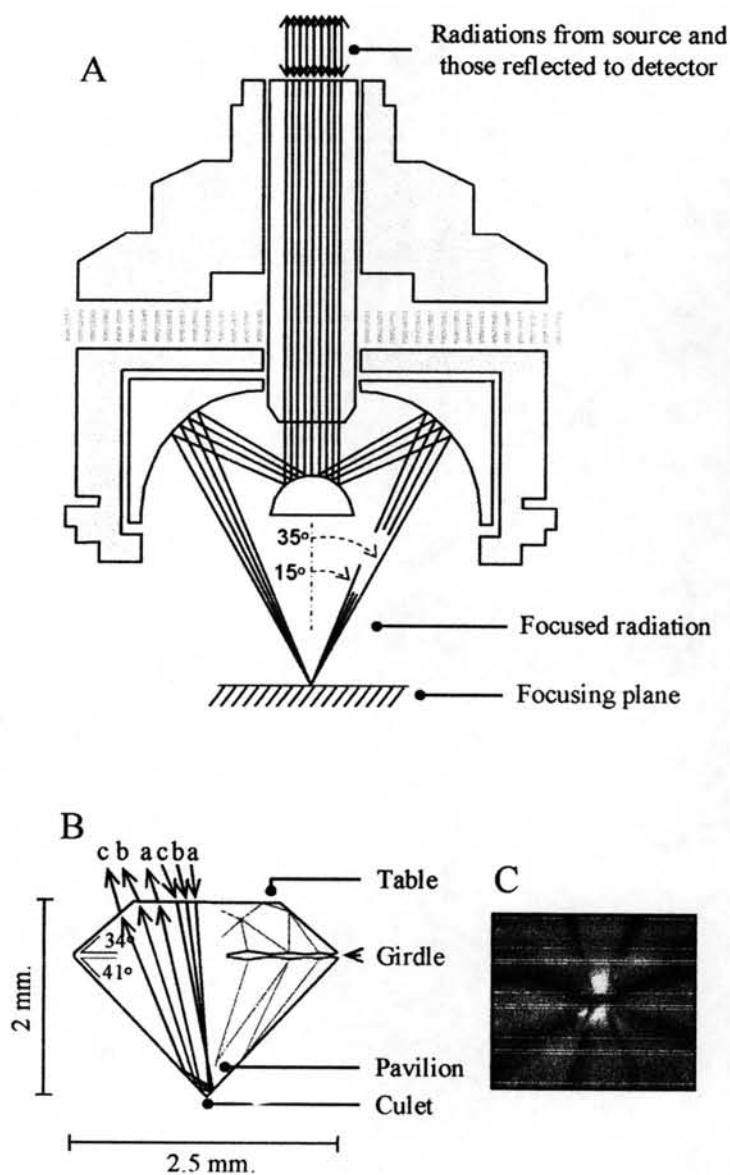
Since diamond  $\mu$ IRE has a small sampling (i.e., the contact area of near the culet) area (30  $\mu$ m in diameter), the molecular information within at small area can be acquired. Due to the small sampling area of each measurement, spectral variation over the surface of a sample can be measured while the chemical surface mapping of the surface can be generated from the absorption at a specific frequency. In this study, the surface mapping technique can be used to characterize the homogeneity of polymer and polymer composite by the slide-on diamond  $\mu$ IRE.



**Figure 3.1** Composition of the homemade slide-on diamond  $\mu$ IRE.



**Figure 3.2** Example of procedures for spectral acquisition (A) Continuum infrared microscope attached to the Nicolet 6700 FT-IR spectrometer, (B) slide-on diamond  $\mu$ IRE was slid into the position of slide-on housing on the 15X Schwarzschild-Cassegrain infrared objective, (C) slide-on diamond  $\mu$ IRE was fixed on the sampling position of the slide-on housing, and (D) the complete homemade  $\mu$ ATR accessory ready for a spectral acquisition.

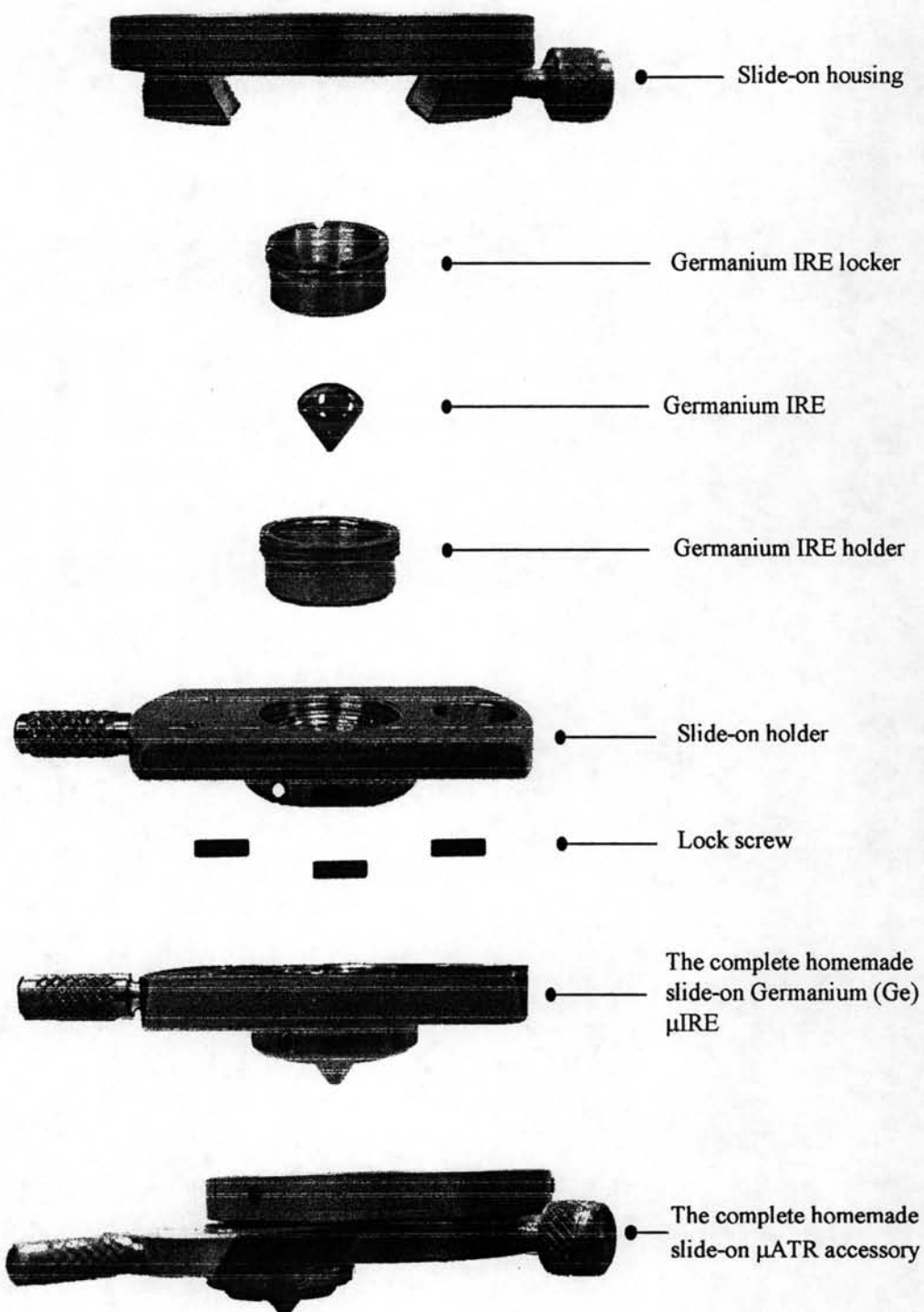


**Figure 3.3** Schematic illustration of ray tracing within the 15X Schwarzschild-Cassegrain infrared objective (A), focused radiation traveling within the diamond  $\mu$ IRE (B), and image of the tip of diamond  $\mu$ IRE under the visible light illumination.

### 3.4 Homemade Slide-on Ge $\mu$ ATR Accessory

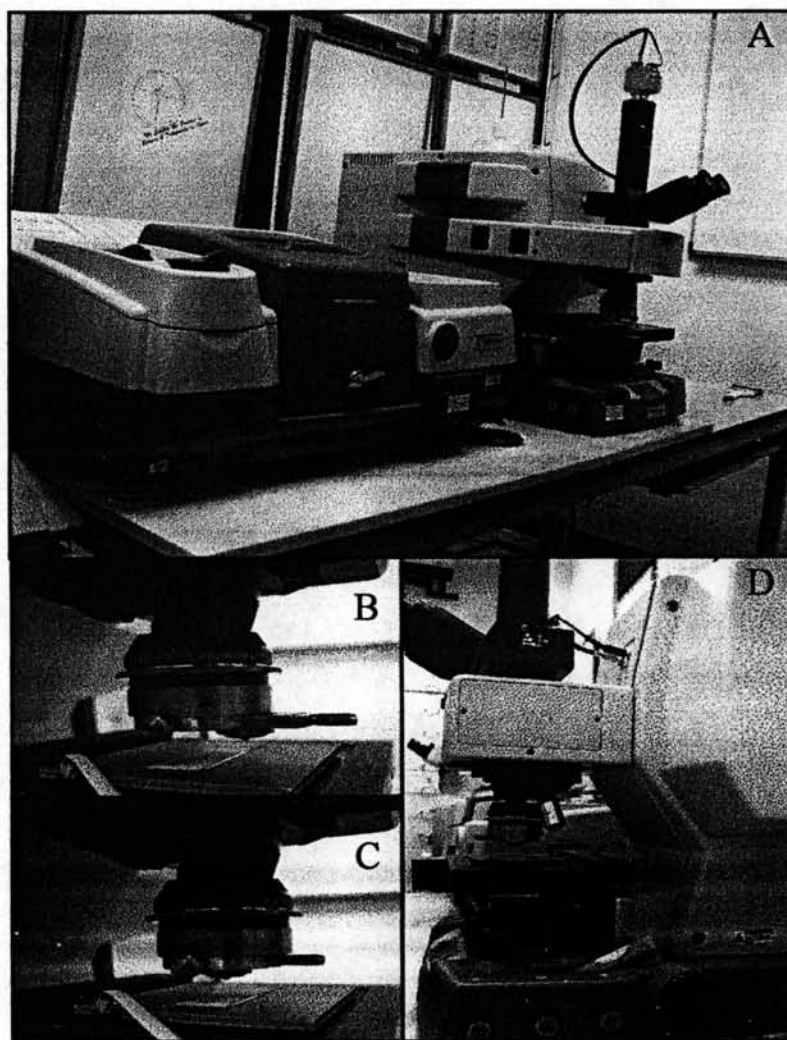
The slide-on Ge  $\mu$ IRE was developed from a commercial hemispherical Ge IRE. There are two main disadvantages of the commercial accessory. First, a large sampling area ( $5 \times 5 \text{ mm}^2$ ) of the hemispherical Ge IRE results in a poor optical contact between IRE and sample. Moreover, a large contact area also gives in an average molecular information over a large sampling area. Second, the sample holder is small and sample preparation is required. The Ge  $\mu$ IRE with small contact area (i.e.,  $100 \mu\text{m}$  in diameter) can acquire the molecular information of a small area. This study takes advantage of the small sampling area and exploiting it for homogeneity analysis of polymer and polymer composites. The surface mapping technique can be used to characterize the homogeneity of polymer and polymer composite by the slide-on Ge  $\mu$ IRE.

The homemade slide-on Ge  $\mu$ ATR accessory consists of two parts as shown in Figures 3.4. The first component is the slide-on housing. The metal housing was perforated and gouged out for placing the slide-on Ge  $\mu$ IRE. The second component is the slide-on IRE which designed for accommodating Ge alignment to achieve a maximum reflected energy. The slide-on IRE was slid into the position and securely locked with the objective (Figure 3.5). The incident radiation from the infrared microscope is coupled into the dome-shaped Ge  $\mu$ IRE (Figure 3.6). The amount of light entering into the IRE is controlled by the aperture of the microscope.

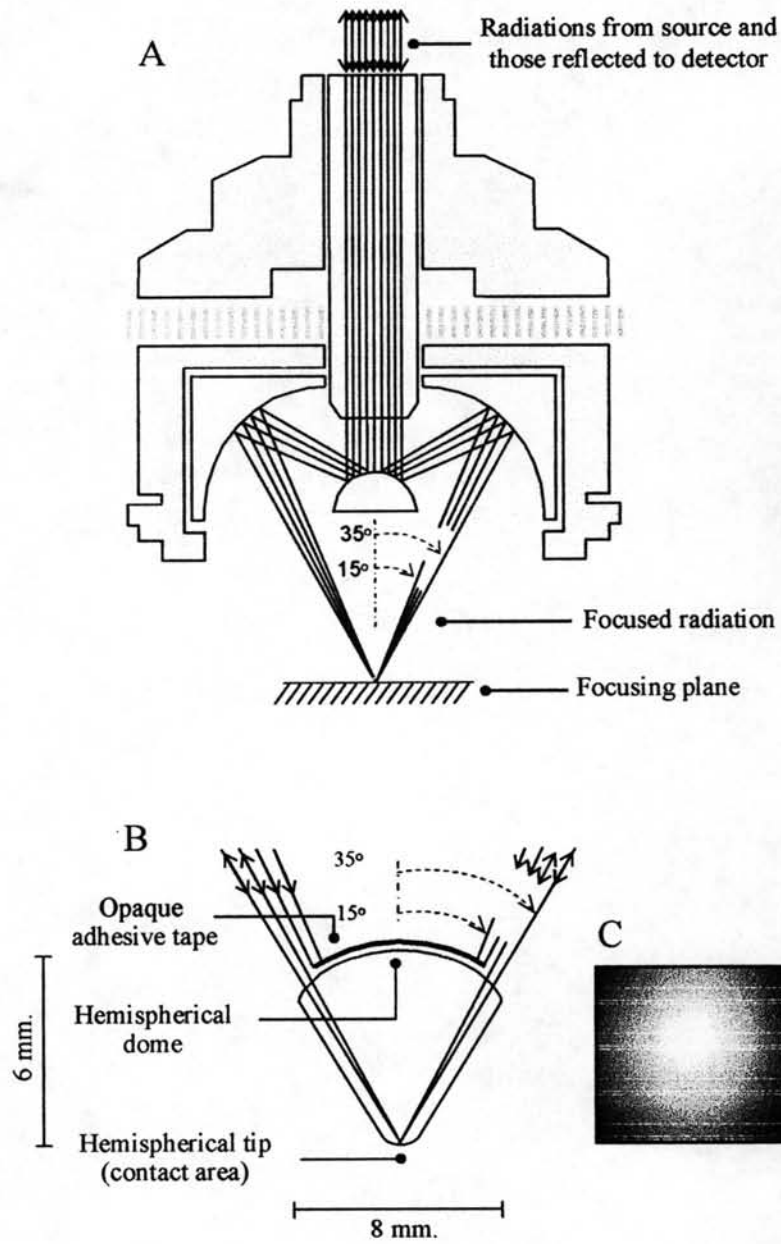


**Figure 3.4** Composition of the homemade slide-on miniature germanium (Ge) IRE.





**Figure 3.5** Example of procedures for spectral acquisition (A) Continuum infrared microscope attached to the Nicolet 6700 FT-IR spectrometer, (B) slide-on Ge  $\mu$ IRE was slid into the position of slide-on housing on the 15X Schwarzschild-Cassegrain infrared objective, (C) slide-on Ge  $\mu$ IRE was fixed on the position of slide-on housing, and (D) the complete homemade  $\mu$ ATR accessory ready for a spectral acquisition.



**Figure 3.6** Schematic illustration of ray tracing within the 15X Schwarzschild-Cassegrain infrared objective (A), focused radiation traveling within the Ge  $\mu$ IRE (B), and image of the tip of Ge  $\mu$ IRE under the visible light illumination (C).

### 3.5 Homogeneity of Polymer and Polymer Composites

#### 3.5.1 Surface Characterization by Area Mapping

##### 3.5.1.1 Surface Mapping by the Slide-on Diamond $\mu$ IRE

The slide-on diamond  $\mu$ IRE was employed for all ATR spectral acquisitions. A gem quality round brilliant cut type IaB natural diamond ( $\sim 0.1005$  ct) was mounted onto the slide-on holder. The slide-on IRE is slid into the position and fixed by the knob on the slide-on housing. The position was pre-aligned in order to achieved the maximum reflected energy with a highest aperture size ( $150 \times 150 \mu\text{m}^2$ ). The transmittance spectrum of the diamond was employed as a background for all ATR spectral acquisition.

To construct the surface mapping from the observed ATR FT-IR spectra, the sample (i.e., polypropylene, poly(styrene-co-acrylonitrile), hydroxyapatite/polypropylene composites) was mounted onto a glass slide and was placed on the microscope stage. A sampling area of the map was selected through the built-in infrared objective. The spectral point-by-point mapping was done in a grid pattern. The spectral acquisitions at the defined positions were automatically controlled by the OMNIC<sup>TM</sup> and At $\mu$ s software packages. Under the mapping algorithm, the microscope stage was automatically raised until the solid sample contacted the tip of a miniature-IRE. The degree of contact was controlled by the contact alert sensor plate installed on the microscope stage. When a force exerted on the sensor plate (i.e., as the stage was raised against the IRE) reached a set value, the stage was stopped and a spectrum acquisition started. After the acquisition finished, the stage was retreated and was driven to the next position by the automatic x-y controller with a step-size of  $200 \mu\text{m}$ . The stage was then automatically raised and a new spectral acquisition started. ATR FT-IR spectra along the grid were employed for the construction of the chemical image of functional groups on the surface. Variation of absorption band unique to a chemical species indicated the changes of the concentration across the measured area. As a result, the homogeneity or uniformity of a composite can be determined from the chemical image constructed from an absorption band unique to the polymer matrix or the filler.

### **3.5.1.2 Surface Mapping by the Slide-on Ge $\mu$ IRE**

The cone-shaped Ge as IRE was employed in the slide-on Ge  $\mu$ ATR accessory. It was mounted onto the slide-on and was aligned to achieve a maximum reflected energy. The IRE was slid into the position of the slide-on housing at the objective of the infrared microscope and locked with a knob when the maximum reflected energy was achieved. The single beam from the Ge  $\mu$ IRE without a sample was employed as a background for all ATR spectral acquisition. Spectral acquisition algorithm was the same as that of section 3.5.1.1.

## **3.5.2 The Depth Profiling via Line Mapping**

### **3.5.2.1 Experimental Procedure for the Slide-on Diamond $\mu$ IRE**

The natural diamond round brilliant cut type IaB (0.1005 ct) was employed as the IRE for the slide-on diamond  $\mu$ IRE. Slide-on IRE is slid into the position of Continuum infrared microscope and locks with knobs of slide-on housing on microscope when the maximum reflected energy is achieved with a highest aperture size ( $150 \times 150 \mu\text{m}^2$ ). The transmittance spectrum of the diamond was employed as a background for all ATR spectral acquisitions. To collect the cross-section surface line mapping of ATR FT-IR spectra with slide-on diamond  $\mu$ IRE, the analyzed sample (i.e., polypropylene, hydroxylapatite/polypropylene composites) was mounted onto the glass slide. It was razorblade-cut with an oblique angle in order to increase the distance along the cross-section surface. To make sure that the cross-section surface is smooth, the sample is re-polished with a sand paper.

To construct a surface map ATR FT-IR of the analyzed sample, a sampling line map was selected through the built-in infrared objective. The spectral point-by-point mapping was done in a grid pattern. The spectral acquisitions at the defined positions were automatically controlled by the OMNIC<sup>TM</sup> and Atlus software packages. Under the mapping algorithm, the microscope stage was automatically raised until the solid sample contacted the tip of a miniature IRE. The degree of contact was controlled by the contact alert sensor plate installed on the microscope stage. When a force exerted

on the sensor plate (i.e., as the stage was raised against the IRE) reached a set value, the stage was stopped and a spectrum acquisition started. After the acquisition finished, the stage was retreated and was driven to the next position by the automatic x-y stage controller with a step-size of 100  $\mu\text{m}$ . The stage was then automatically raised and a new spectral acquisition started. ATR FT-IR spectra along the grid were employed for constructing of the chemical image of chemical species on the surface. Variation of absorption band unique to a chemical species indicated the change of the concentration across the measured line. As a result, the homogeneity or uniformity of a composite can be determined from the chemical image constructed from an absorption band as unique to the polymer matrix or the filler.

### **3.5.2.2 Experimental Procedure for the Slide-on Ge $\mu\text{IRE}$**

The cone-shaped Ge as IRE was employed for slide-on Ge  $\mu\text{IRE}$ . It was mounted onto the slide-on holder and was aligned to achieve a maximum reflected energy. The slide-on is slid into the position of Continuum infrared microscope and locks with knobs of slide-on housing on microscope when the maximum reflected energy with a highest aperture size was achieved. The ATR spectrum of the Ge  $\mu\text{IRE}$  without a sample was employed as a background for all ATR spectral acquisitions. Condition of all spectral acquisition in this section is the same as that of section 3.5.2.1.

## **3.6 Surface Characterization of Homogeneity by Specular Reflection Technique**

The specular spectrum of polymer and polymer composites were performed by a Continuum infrared microscope. The microscope was operated in the reflection mode. Reflection with a normal incidence from gold mirror was employed as a background spectrum. To construct the surface mapping, the analyzed sample (i.e., polypropylene, hydroxyapatite/polypropylene composites) was mounted onto the glass slide and was placed on the microscope stage. A sampling area of mapping was selected through the built-in infrared objective. The spectral point-by-point mapping of the sample was done in a grid pattern. The spectral acquisitions at the defined

positions were automatically controlled by the OMNIC<sup>TM</sup> and AtI $\mu$ s software packages. Under the mapping algorithm, the microscope state was automatically raised until focus on the surface of specimen was achieved. The stage was stopped and a spectrum acquisition started. After the acquisition finished, the stage was driven to the next position by the automatic x-y stage controller with a step-size of 200  $\mu$ m. The aperture size was set as 150 $\times$ 150  $\mu$ m<sup>2</sup>.