CHAPTER I

INTRODUCTION

1.1 ATR FT-IR Spectroscopy

Infrared spectroscopy is a particularly useful analytical technique because of its enormous versatility. In general, infrared spectrum can be obtained nondestructively. To collect an infrared spectrum, various sampling technique can be employed such as transmission, reflection, reflection absorption, and attenuated total reflection techniques. The choice for sampling technique depends strongly on type of the sample (i.e., solid, liquid, or gas) and the required information. Attenuated total reflection Fourier transform infrared (ATR FT-IR) spectroscopy is one of the widely employed characterization technique in infrared spectroscopy. The phenomenon of total internal reflection in visible region was reported by Issac Newton [1]. The phenomenon remains unexplored until the early 1960s. It became a sampling technique for infrared spectroscopy with the pioneer efforts of Harrick and Fahrefort [2,3]. At the moment, ATR FT-IR technique has been used in a wide variety of applications including non-destructive technique, quantitative analysis [4,5], qualitative analysis [6,7], diffusion studies [8,9], surface characterizations [10,11], depth profiling [12], and environmental applications [13].

Attenuated total reflection (ATR) spectrometry is a well-known method. It is suitable for the analysis various types of samples such as highly absorbing materials, thin films deposited on a substrate, degradation studied, surface reaction, and interfacial reaction. ATR accessories employ an internal reflection element (IRE) or ATR crystal of high refractive index (i.e., Ge, Si, ZnSe, or diamond). The difference in refractive indices between the IRE and the sample causes the infrared energy to be totally internal reflected. At each reflection, the electric component of the beam penetrates into the sample by a short distance from the IRE/sample interface. Typically, the radiation penetrates the sample to a depth of only a few micrometers.

1.2 Limitation in ATR FT-IR Spectroscopy

Only the surface information is observed in ATR technique. The electric field is strongest at the IRE/sample interface and exponentially decays to zero as a function of depth within the interface region. According to the decay characteristic of the electric field, the contact between the sample and the IRE plays a major role on the spectral quality obtained from an ATR experiment. From physical characteristic of sample, liquid sample always wet the surface of IRE. As a result, a perfect contact (i.e., optical contact) between liquid sample and the IRE is always achieved. The solid sample, on the other hand, rarely has a good contact with the IRE especially the sample with rough surface. Although the solid sample with mirror-flat surface is employed, the optical contact between the sample and the IRE is difficult to obtain due to local irregularity of the surface. When the system does not have an optical contact, there is always an air gap between the sample and the IRE. The spectral intensity is decreased since the region near the surface of the IRE, where the electric field is strongest, is occupied by air gap. The larger the air gap is, the smaller the observed spectral intensity is. If an air gap is large enough, the spectrum cannot be obtained.

Solvent casting of polymer solution or hot pressing of polymer film onto the IRE has been employed in order to ensure optical contact at the interface. These approaches are, however, not applicable to various types of samples (i.e., surface treated polymers, polymer coatings, and insoluble polymers) since the required information may be destroyed during the sample preparation. In general practice, application of pressure to the solid sample against the IRE is employed for improving the contact between the IRE and the solid samples [5,6]. However, this approach is not generally applicable or not appropriate for soft IREs such as ZnSe and KRS-5 because excessive force may damage the surface of the IRE. A hard and rigid sample can also damage the surface of a hard IRE such as Ge when it is subjected to a high pressure.

For ATR experiment, optical contact between IRE and sample is necessary for obtaining a good spectrum. Pressure applicators are available for most commercial accessories. However their use is constrained by the material employed as the IRE (i.e., low mechanical strength). There are various types of materials that have been considered for using as IREs, and these are zinc selenide (ZnSe), Silicon (Si), Germanium (Ge), thallium iodide/thallium bromide (KRS-5), and diamond (C). In the past, diamond has been used as an infrared window in high-pressure cells [14,15] and for special ATR applications. The benefits of diamond are strength, hardness, its chemical resistance, and transparency throughout most of the mid-infrared region. Solid sample with an irregular surface require a method of providing intimate contact with the IRE. In the case of the diamond IRE, the small physical size of the diamond and its intrinsic hardness can help to obtain the optimal sampling condition via an applied pressure.

1.3 Diamond micro-ATR

In 1995, a new micro-ATR accessory was introduced (the DurasamplIR from SensIR Technologies, USA) [16]. In its standard form, this accessory features a diamond IRE sampling surface. All the practical benefits of diamond are retained: its strength and chemical inertness, and good optical performance with minimum interference in the region of the diamond absorption. This arrangement is made practically by a unique combination of a small, thin diamond element placed on top of a larger optical element made from a material of comparable refractive index, usually zinc selenide. The second, larger element acts as a mechanical support and as a focusing device for the infrared radiation entering and exiting the diamond IRE. However, on a larger optical element placed by thin diamond element has limitation of hardness. If high pressure is applied, it will break or crack. Moreover, the commercial DurasamplIR is expensive.

From the limitation of commercial diamond micro-ATR, this research is aimed to develop the homemade diamond micro-ATR sensor. The advantage of the homemade diamond micro-ATR sensor is to reduce the cost. In addition, the diamond micro-ATR sensor requires short acquisition time while sample preparation is not necessary. With a diamond micro-ATR sensor accessory, the user is provided with one of the most reproducible sampling methods available for sampling with optical contact problem in hard and rigid materials, rough surface, irregular shape samples, and sample with small sampling area. As long as the sample is under moderately applied pressure, good optical contact is achieved at the sample-sensing surface.

1.4 The objective of this research

The objective of this research is to develop the diamond micro-ATR sensor with two configuration of diamond tip (i.e., flat tip diamond and sharp tip diamond) for various types of sample analysis (soft polymers, hard and rigid polymers, coating polymer on metal, coating polymer on polymer, and sample with small sampling area). Spectra obtained via diamond micro-ATR sensor will be compared with those from a commercial ATR accessory. The experimental investigations of diamond micro-ATR sensor will be performed while its limitation will be explored.

1.5 Scope of this research

1. To fabricate homemade diamond micro-ATR sensor.
2. To investigate the efficiency of the diamond micro-ATR sensor for analyzing of soft polymers, hard and rigid polymers, thin film coated polymer on metal, coating polymer on polymer, and sample with small sampling area.
3. To compare infrared spectra observed by the diamond micro-ATR sensor with those observed by a commercial ATR accessory.