CHAPTER 1

INTRODUCTION

1.1. The Definition of a Surface

Surface is defined generally as a boundary layer of one phase at its interface with another [1]. An interaction at surface is important because it is a key parameter that controls the property of the material and its responses to the environment. The depth of interaction at the surface depends particularly on the nature of the interaction involved. For example, surface bonding, catalysis, and wetability are phenomena associated with monolayers or less (i.e., a region with thickness less than 1 nm). Passive surface films, corrosion, and optical absorption are in the order of 500 nm. Thus, the distinction between a surface and a thin film becomes somewhat arbitrary. It depends on how one views the surface. Moreover, studying surface and its interfacial phenomena can be done with ease or with difficulty depending on the nature of the sample.

1.2. Surface Characterization of Polymer

Polymers have long been applied widely in numerous applications. This is because their varieties in both properties and appearances, which ranged from clear liquids to tough solids depending on their types and the processes from which they are produced. Many among their various useful applications involve directly with the surface property and also the surface characteristic of polymers. The acquisition of such a surface information is, therefore, the inevitable task for controlling and improving the quality of products. The examples of polymer industries and technologies making use of surface characterization are such as packaging, adhesives, composites, fibers and textiles, pharmaceuticals, optics, printing, coating and films, encapsulation, paints, and sensors. It is obvious that surface characterization of polymer has been of increasing importance for understanding basic interfacial phenomena and also for industrial purposes.

Since surface phenomena and processes occurring at interfaces have been a major focus of scientists and engineers, therefore, surface analysis technology has been continuously developed and modified. However, in general, the surface characterization is the use of vibrational, electron or ion spectroscopic and microscopic techniques for the study of material at the atomic level [1]. General procedure for spectroscopic measurements is that particles (e.g. electrons, atoms, ions) or photons (electromagnetic radiation: UV, X-ray, IR) are beamed at the surface of the sample as input sources, after which the particles or photons from the sample surface emerge with characteristics that provide the information about the surface. Such informations are:

- Geometrical structure of surface
- Chemical composition of surface
- Oxidation state of surface
- Energy state of surface species
- Chemical state of surface species
- Characteristic of surface site

etc.

For all these approaches to surface analysis, several issues are of particular practical interest: (1) whether there are any new chemically distinct structures on the surface in contrast to the bulk of the sample, (2) the concentration of the surface species and how it changes as one looks deeper into the surface, and (3) how to conduct nondestructive surface and interfacial measurements [2].

1.2.1. ATR FT-IR Spectroscopy

A number of different spectroscopic surface analysis techniques have the beam-in and beam-out combination [1] (see Figure 1.1). One of the most powerful surface characterization using electromagnetic radiation in the infrared region is attenuated total reflection Fourier transform infrared (ATR FT-IR) spectroscopy. When the incident radiation from a medium with high refractive index undergoes total internal reflection at the interface between two media of different refractive indices, the electric field penetrate from the interface into the medium with lower refractive index [3]. The electric field is strongest at the interface region and decays to zero within a few micrometers away from the interface. The field interacts with the material and give absorption spectrum which reveals surface characteristics of the material. The interaction between the beam and materials is quite complex since it depend on both material characteristics and experimental parameters.

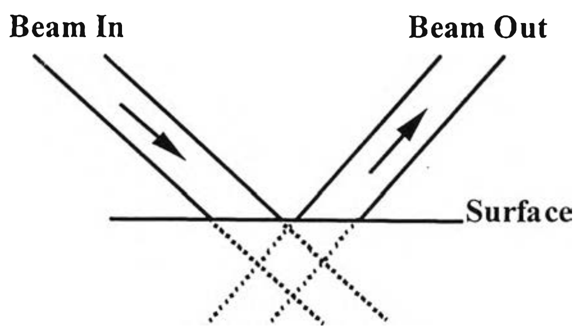

Figure 1.1 Arrangement of probe and analyzed beams in surface spectroscopy. Beams may be photons, electron, or ions.

ATR FT-IR spectroscopy is one of the powerful surface characterization techniques. It can be applied to any sample only if the sample can be put into contact with the internal reflection element (IRE). Due to high efficiency of today's computer, the application of optical theory for spectroscopic calculation has become routine. By varying experimental parameters and materials involve in ATR FT-IR spectroscopy, the information of materials at different depth can be obtained from ATR spectra. Since ATR technique is non-destructive, simple experimental set up, and information directly related to chemical composition of material is easily obtained, the technique become a routine surface characterization technique in most laboratories.

The basic theory for ATR FT-IR spectroscopy was first introduced by Fahrenfort and Harrick in 1960. For an internal reflection setup, an IRE is put into contact with the sample, when the angle of incidence is greater than the critical angle, all the energy is reflected back into the incident medium (see Figure 1.2). Although there is no light travels across the interface, there exists a strong electric field at the surface region of the sample. This electric field is greatest at the surface an exponentially decays as a function of depth from the surface of the sample. The nature of the electric field makes ATR technique a perfect candidate for surface characterization since it probes only at the surface region.

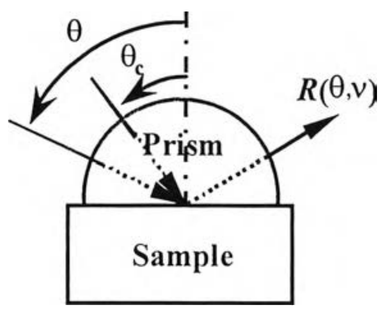

Figure 1.2 The simple optical and geometric arrangements of ATR measurements.

1.2.2. ATR Measurement: Advantages Over Transmission Measurement

Measurements conducted in transmission mode have certain limitations related to the lack of surface sensitivity. Because in transmission measurement, light propagates throughout a whole sample (see Figure 1.3), therefore, the information obtained is the average information coming from both the surface and the bulk of the sample. If there is any different characteristic between the surface and the bulk species, this difference will not be distinguished by the measurement conducted in transmission mode. This is due to the surface region is very thin compared to the bulk sample. The absorption contribution from the surface region is very small compared to that from the bulk. In many applications (for example, degradation studies, surface reactions and modifications, and forensic analysis) it is essential that the information coming from the bulk of the material be distinguished from that coming from the surface or interface. For that reason transmission spectroscopy may fail because, in addition to the fact that such measurements often require destructive sample preparations, the technique is not surface-sensitive; thus surface sensitivity is where ATR FT-IR spectroscopy surpasses other analytical methods. It is a convenient and surface-sensitive analytical tool. All the analysis requires are aligning an ATR attachment, pressing the sample against an ATR crystal, and collecting spectra, which carry the surface information of a sample.

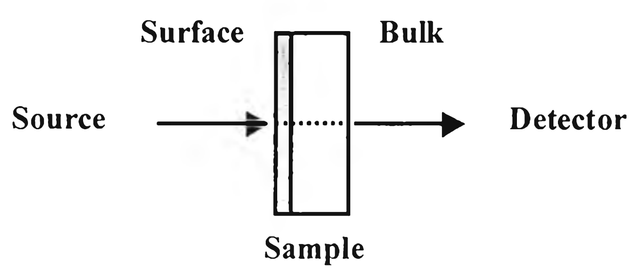

Figure 1.3 A simple geometrical arrangement of transmission measurement.

1.3. The Objective of This Research

Due to the nature of the electric field in ATR technique, the probing range is restricted to the surface region. However, the spectral intensity is greatly influenced by material characteristics and experimental condition. Furthermore, noise in the spectrum makes the absorption contribution at a greater depth from the surface less significant. The objective of this research is to determine the sampling depth in the surface characterization of polycarbonate by attenuated total reflection Fourier transform infrared (ATR FT-IR) spectroscopy.

1.4. Scope of This Research

1. Determine the effective number of reflections in an internal reflection element (IRE).

2. Determine the influence and necessity of having Optical contact in ATR experiment

3. Determine the sampling depth (i.e., depth from surface where chemical information is being probed) in ATR FT-IR spectroscopy from the observed spectrum.