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Use of micro-ATR/FTIR imaging to study heterogeneous polymer oxidation by direct solvent casting onto the ATR IRE

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Abstract

A technique is described whereby micro-ATR/FTIR imaging can be used to follow polymer degradation reactions in situ in real time. The internal reflection element (IRE) assembly is removed from the ATR objective and polymer is solvent cast directly onto the IRE surface. The polymer is then subjected to degradation conditions and molecular structural changes monitored by periodically replacing the IRE assembly back in the ATR objective and collecting spectra which can be used to construct images. This approach has the benefit that the same part of the sample is always studied, and that contact by pressure which might damage the polymer surface is not required. The technique is demonstrated using the polymer Topas which was degraded by exposure to UVC light in air.

Keywords: imaging FTIR, ATR, polymer degradation

1. Introduction

Attenuated Total Reflectance FTIR (ATR/FTIR) is a mid-IR spectroscopic technique that measures the near surface layer [1], and has demonstrated suitability for the investigation of a wide range of sample types. The phenomenon under investigation in this article is the degradation of polyolefin films, which is commonly studied by ATR/FTIR spectroscopy [2-4]. A comparison of the vibrational spectroscopic techniques transmission IR, emission IR and ATR/FTIR by Delor et al [5] concluded that ATR/FTIR spectroscopy is a reliable method for the study of the evolution of degradation products of elastomers by infrared spectroscopy.

ATR/FTIR spectroscopy is commonly performed at a single point on the sample surface that is determined to be representative of the sample being examined. There are many situations however, where spectral information may be desired in a lateral context. Although this is often referred to as *spatially resolved* spectroscopy, it is more correctly termed *laterally resolved* spectroscopy, as the information acquired is in 2 dimensions. Examples of some subjects where lateral information is desired might include polymer blend surfaces, layer interfaces, biological samples, etc.

When lateral information is required micro-ATR/FTIR spectroscopy may be used [6]. This involves an IR microscope fitted with an ATR objective and a mercury-cadmium-telluride (MCT) detector to record spectra. An aperture can be adjusted on a micro-ATR/FTIR spectrometer to measure an area on the sample smaller than the size of the contact surface. Thus micro-ATR/FTIR spectroscopy allows for improved lateral resolution, but at the cost of signal/noise ratio, as there is less reflected light received by the detector. Micro-ATR/FTIR spectroscopy is often used in mapping mode to characterize surfaces.

Do et al [7] deduced an optimum aperture size for the measurement of some carbon-filled polymeric materials. It was found that the minimum aperture setting, which allowed for a best possible compromise between signal/noise ratio and collection time, was 40 μm . The authors then added that the actual lateral resolution being achieved when using micro-ATR/FTIR spectroscopy can be determined by dividing the aperture size by the refractive index of the internal reflection element (IRE). In this case it was found to be around 12 μm , which is close to the diffraction limit of infrared radiation.

The main drawback of micro-ATR/FTIR spectroscopy is that good contact with the sample is required so that for each point the sample must be brought into contact with the IRE of the ATR objective. This is time-consuming and, because the ATR contact area is very small, may lead to sample damage. There is also the possibility of transferring material from one point on the surface to another.

An alternative approach is to use imaging ATR/FTIR, a relatively recent mid-IR spectroscopic technique that is able to acquire multiple, laterally resolved spectra simultaneously by the use of a focal plane array (FPA) MCT detector. Images can be created

in a number of different ways including band area or intensity, ratios of band areas or intensities, and more complex methods such as principal component analysis. The pixels are assigned a colour on an arbitrary colour scale according to the numerical value of the image creation method. The benefits of this approach are much improved speed, as well as lateral resolution.

In recent times, the use of micro-ATR/FTIR imaging has introduced some significant improvements to the achievable lateral resolution of IR imaging spectrometers [8-11]. Chan and Kazarian published new findings in 2003, reporting the achievement of lateral resolution of 3-4 μm using micro-ATR/FTIR with a Ge IRE.

As part of a larger project studying the heterogeneous oxidation of certain polymers [12,13], we required a technique to monitor the polymer surface during degradation. Transmission-mode IR spectroscopy is generally unsuitable due to sample thickness, interference fringes in films and poor lateral resolution. Difficulties arise when seeking to monitor the development of oxidation using ATR/FTIR spectroscopy because it requires the sample to be in optical contact with the IRE. This is most commonly achieved by the application of controlled pressure. However the IRE cannot remain in constant contact with the sample during oxidation, as the sample must be subjected to accelerated oxidation conditions between spectra acquisition.

This introduces two hindrances to the study of oxidation. Firstly, the identical spot on the sample surface must be found repeatedly during accelerated oxidation to study changes in the surface chemistry. Secondly, ATR measurements on an identical location require repeated application of pressure to obtain spectra which may damage the surface and/or change the degradation chemistry.

This paper describes a different approach to the problem by solvent casting the polymer directly onto the IRE surface. This was made easier by the fact that in the instrument that we used the IRE is attached to a metal assembly which is readily removed from the ATR objective. The method circumvents the need to continually return to the identical location on the polymer surface, and ATR pressure is not applied as the material is in good optical contact with the IRE from the start. A similar approach has previously been used by Kuimova et al who studied live liver cells deposited on a layer of poly-L-lysine on the surface of an

IRE. [14] The development of oxidation can then be easily studied as the IRE assembly can be removed from the ATR objective and the polymer under test can be subjected periodically to oxidation conditions such as heat, oxygen, UV light etc. Degradation can then be monitored by replacing the IRE in the ATR objective and collecting ATR spectra and images. The approach is demonstrated by the use of a model polymer, Topas®, which was treated with titania to promote oxidation.

2. Experimental

Spectral data were collected using a Varian FTIR imaging system. The system consists of a rapid scan Varian 3100 FT-IR spectrometer, a Varian 600 UMA FT-IR microscope equipped with an ATR objective, and a 32 x 32 liquid nitrogen cooled mercury cadmium telluride (MCT) focal plane array detector. A Ge slide-on IRE was used in the ATR objective. Spectra were processed and images created using Varian Resolution Pro software. The normal field of view of the IR microscope is 175 μm x 175 μm . When the ATR objective with the Ge IRE is used this reduces to 44 μm x 44 μm because of the effect of the refractive index of the Ge which is 4. Hence, each pixel in the image represents, nominally, a section of the sample about 1.4 μm square.

Topas® an ethylene/norbornene copolymer (see Figure 1 for structure) was used as the model polymeric material for solvent casting degradation experiments. Topas (5 g) was dissolved in 50 mL of cyclohexane on a hot plate stirrer set to 40 °C and left to dissolve overnight with stirring. 2.5 μL of the solution was deposited onto the surface of the slide-out Ge IRE of the ATR/FTIR objective, using a micro-pipette. Degussa P25 titania was deposited onto the wet surface, and the slide-out IRE assembly with the solvent-cast polymer was left to dry under vacuum at about 80 °C overnight. The assembly was then irradiated with UVC, and images collected every hour, up to 8 hours of irradiation. Spectra were acquired at 16 cm^{-1} resolution with 1064 scans co-added, over a range of 4000–850 cm^{-1} .

3. Results and Discussion

Images were constructed based on a carbonyl index calculated by taking the area ratio of the carbonyl stretching band around 1715 cm^{-1} to that of the C-H deformation band near 1465

cm^{-1} using the integration limits 1705 cm^{-1} to 1725 cm^{-1} , and 1460 cm^{-1} to 1475 cm^{-1} , respectively. Some typical spectra showing points with high, medium and low carbonyl index are shown in Figure 2. A carbonyl index, derived from an area ratio of two bands was used in preference to a single band area or intensity, to allow for any variation in absorbance which might occur, for example because of variations in the optical quality of the contact between the IRE and the sample. The images, presented in Figure 3, immediately begin to show an increase in the amount of light blue (indicating an increase in carbonyl absorption) after 1 hour of irradiation in air, and after 5 hours there appears to be a significant concentration of oxidation products that register 0.05 on the carbonyl index scale. By 6 hours the degradation begins to occur more rapidly, and after 8 hours of irradiation the oxidation is quite extensive. The oxidation process occurring is clearly heterogeneous, as Figure 3H contains pixels ranging in colour from green to red, covering 0.05 to 0.15 on the carbonyl index. These images demonstrate the applicability of imaging ATR/FTIR to the investigation of the heterogeneous oxidation of polymers.

Figure 4 is a schematic representing the Topas film containing titania particles cast onto the IRE surface. The Harrick equation [15] can be used to estimate the depth of penetration (d_p) of the IR radiation into the Topas film, which at 1700 cm^{-1} , close to the carbonyl stretching region, is about 510 nm using a nominal angle of incidence of 40° [16] and a refractive index of 1.5 for Topas [17].

In order to examine the images to determine the spread of oxidation, carbonyl index values were calculated for the spectra that fell across a line map drawn through the 4th pixel of each row for each of the images shown in Figure 3. The relative rates of oxidation can be obtained by plotting the carbonyl index for each pixel against time. Points corresponding to regions of high (row 29) and low (row 7) carbonyl index have been plotted, along with the average of all points for comparison (Figure 5).

It can be seen in Figure 3 that the carbonyl absorption is the most intense in the upper part of the images. It is likely that this region contained a higher concentration of titania particles, and that the polymer has been photosensitised. This explains the more rapid formation of oxidation products during UV irradiation, and the overall greater carbonyl absorption intensity in this region. After 8 hours of irradiation the Topas from the lower part of the

image (row 7) shows less carbonyl formation compared to the upper edge of the image (row 29).

There is also a clear induction period during which little or no carbonyl containing degradation products are formed, however the length of this induction period is about 1 hour longer at the point corresponding to row 7. At row 29, where there is a high probability of a titania particle in the immediate environment, the induction period only lasts 2 hours. Once the induction period has ended the polymer appears to degrade at a rate apparently independent of titania photosensitisation effects.

This micro-ATR/FTIR spectroscopic experiment seems useful for the study of heterogeneously oxidising polymers using infrared spectroscopy, for the following reasons:

- It provides an advantage over other laterally-resolved techniques, such as chemiluminescence imaging, by supplying chemical information contained within the mid-IR spectra. This can be used to trace the degradation pathway of materials, examine different oxidation products and identify domains of varying sensitivity to oxidation that might correspond to different concentrations of components in a polymer blend.
- Polymer oxidation can be studied in real time, and as data are collected from the same area of polymer, the effect of impurities such as catalyst residues can be monitored.
- Samples are not subjected to pressure from the IRE, avoiding sample damage and removing the influence of mechanical stress on the oxidation process.
- Imaging ATR/FTIR spectroscopy with an IRE of high refractive index achieves a lateral resolution of around 3-4 μm , which is a significant improvement on the resolution obtainable by transmission spectroscopy. [9,18] This also allows for the collection of a large amount of data on a small sampling area, dependent on the number of individual detector elements in the FPA.

There are however some technical issues regarding polymeric materials that need to be addressed before this technique can be used for routine analysis of heterogeneously degrading polymers. These include:

- Polymers need to be dissolved in a solvent. The chosen solvent is required to be volatile and non-aggressive to the adhesive holding the IRE into the ATR assembly. For certain polymers, such as high molecular weight polyethylene, finding the appropriate solvent could prove to be quite difficult. If elevated temperature is used then dissolution must be under non-oxidising conditions.
- Certain polymers have a tendency to shrink due to crosslinking when oxidising, and lift off the IRE surface. Additionally, polymers sometimes lift off the IRE surface during solvent volatilisation.
- It is difficult to determine the imaging location on the IRE surface. This might affect heterogeneous polymers with a low concentration of a secondary component, such as catalyst particles, as there is a reduced likelihood that imaged area will contain a particle.
- There is no clear method for determining the thickness of the polymer film once it has been solvent cast
- For studies of polymer oxidation the measurement is taking place at the interface between the polymer and the IRE which means that oxygen must pass through the thin layer of polymer material. Hence the technique tends to measure the degradation of the bulk material rather than the material close to the surface in direct contact with the atmosphere.
- The technique works well with the particular instrumentation described because the IRE is on a metal bar which can be easily removed from the ATR objective. For other ATR objective designs the IRE is not easily removed making the procedure more difficult because the entire ATR objective would have to be removed from the microscope

4. Conclusions

A novel experiment based on imaging ATR/FTIR spectroscopy in which a model polymer system containing titania was photooxidised and imaged in real time has demonstrated the heterogeneous development of oxidised domains in the polymer Topas. It is thought that these domains of higher carbonyl product concentration are most likely due to an increase in the rate of degradation caused by a higher concentration of titania particles in the immediate vicinity.

The technique presented may be generally useful in imaging ATR/FTIR spectroscopy, and has allowed the acquisition of previously unobtainable data in real-time. In particular the ability to acquire laterally-resolved chemical data without the need to force IRE contact or relocate a position on the sample surface is advantageous. While it holds great potential for the study of heterogeneous systems, there are a number of technical and instrumental issues that need to be addressed before this can become a routine technique.

Acknowledgements

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Figure Captions

Figure 1. Molecular structure of Topas®.

Figure 2. Typical individual spectra from various points on the irradiated Topas film showing polymer with (A) low carbonyl index (B) medium carbonyl index and (C) high carbonyl index.

Figure 3. Images taken of Topas containing TiO₂ and irradiated with UVC. Each figure is labelled with the cumulative irradiation time. The numbers on the *x* and *y* axes represent the number of pixels. The image has been smoothed.

Figure 4. Schematic showing Topas film incorporating titania cast onto the IRE surface. The estimated extent and depth of penetration of the ATR/FTIR technique is shown by the box labelled “imaged area”. The titania particle locations are hypothetical and the diagram is not to scale.

Figure 5. Rates of degradation for pixels in row 7 and 29, and the average of all pixels.

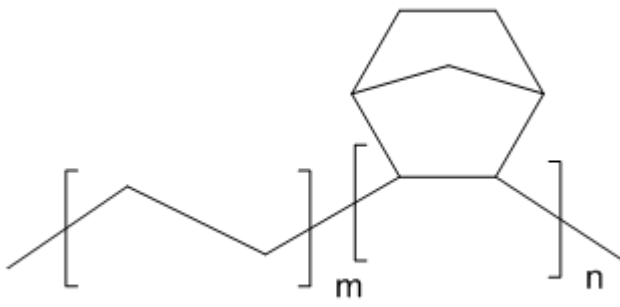


Figure 1

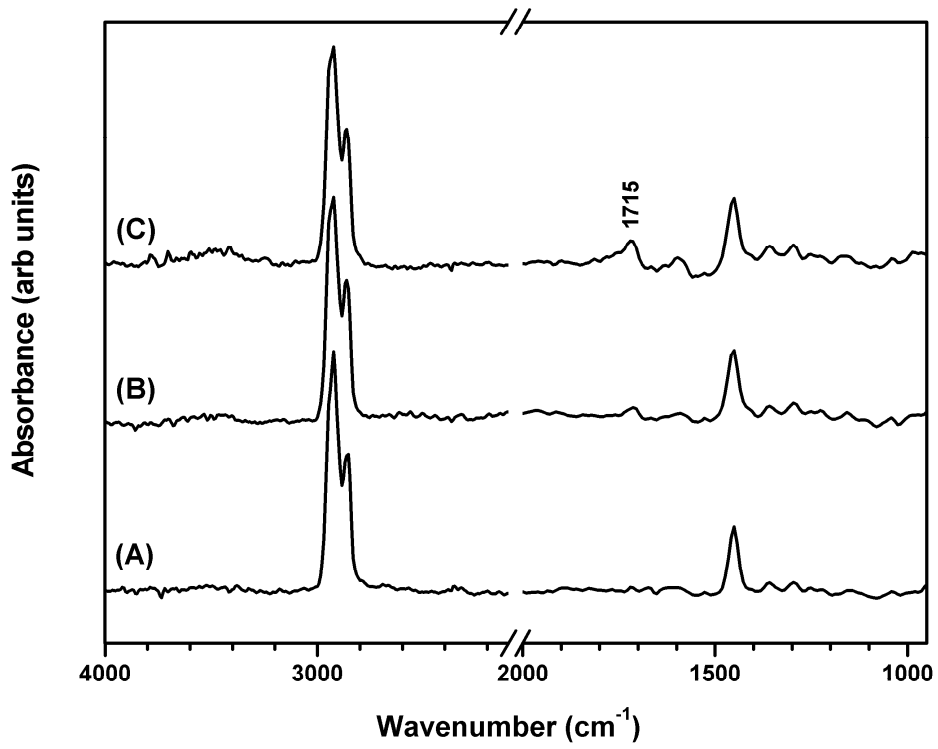
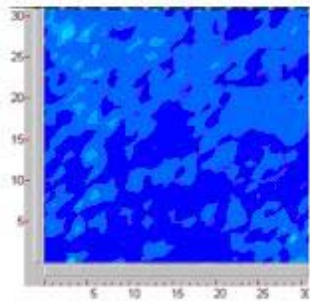
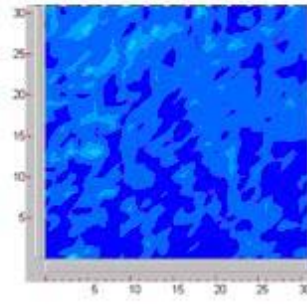


Figure 2

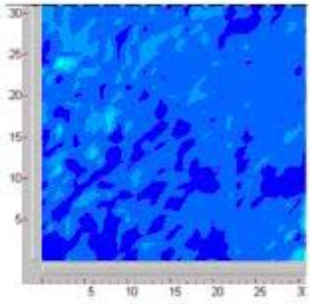
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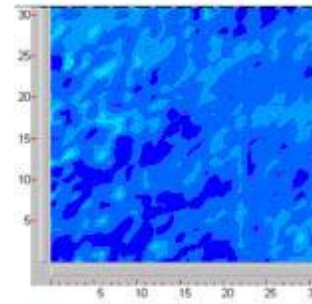
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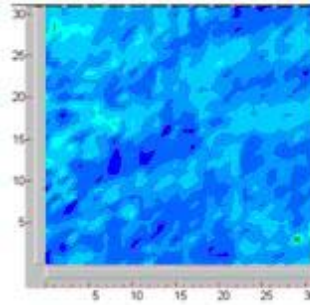
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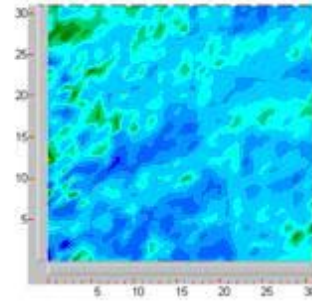
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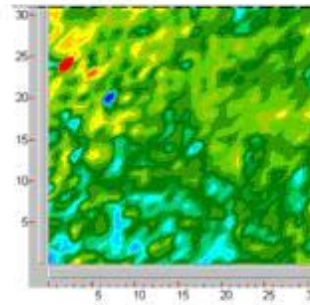
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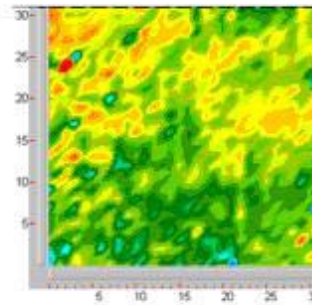
F 5 hours



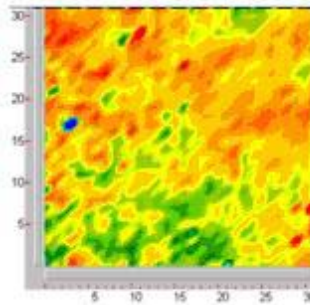
G 6 hours



H 7 hours



I 8 hours



Colour scale showing carbonyl index

Figure 3

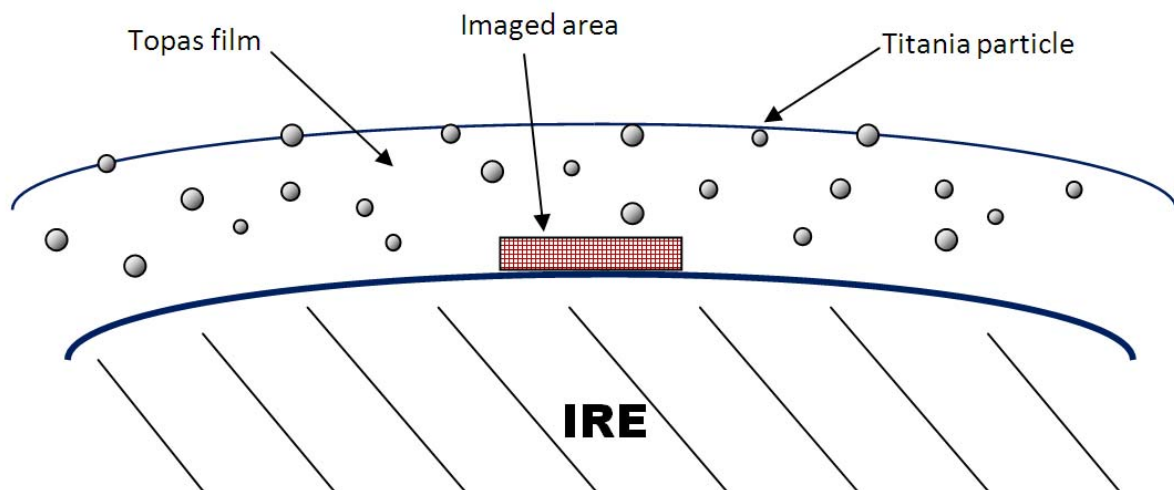


Figure 4

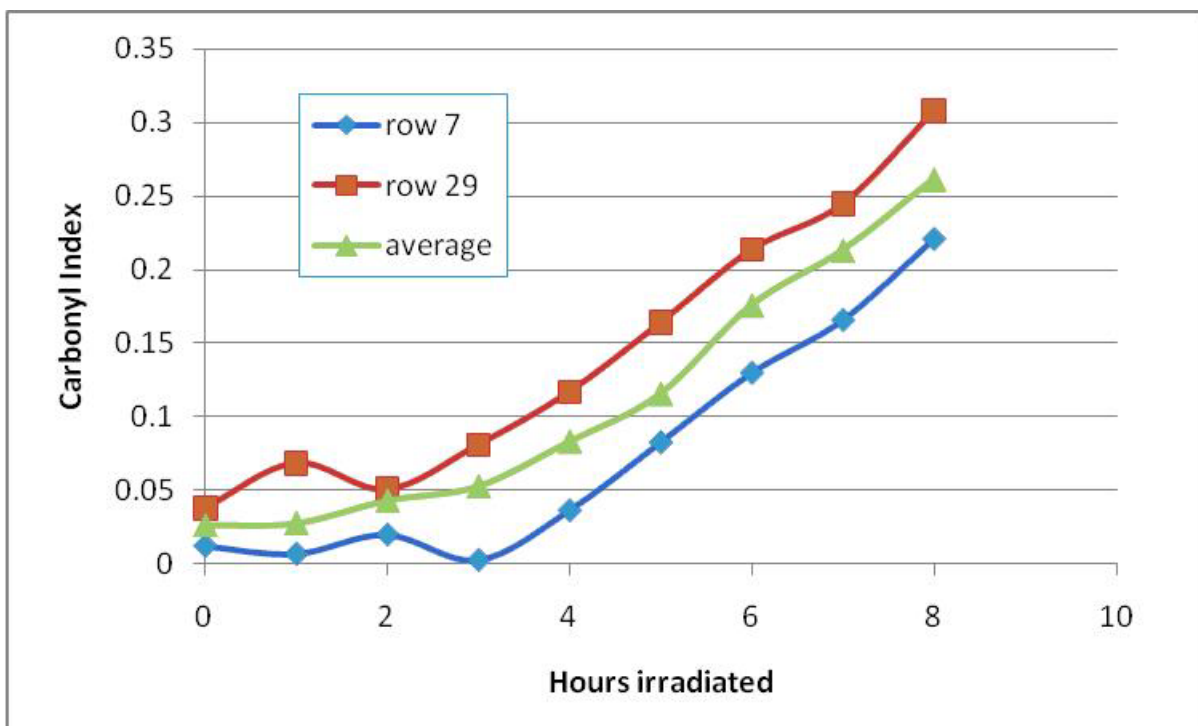


Figure 5