

Microscopic Structural Studies on Polymer Surfaces using FT-Raman and FT-IR

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KEYWORDS

FT-Raman, FT-IR, microscopy/polymers, plastics/polyvinyl chloride (PVC)/MicroRaman, Nic-Plan, attenuated total reflectance (ATR)/depth profiling

INTRODUCTION

FT-Raman microscopy can measure spectra from a range of thermoplastics. This note is an indepth study of the use of FT-Raman to provide depth profiling information of samples of UV treated polyvinyl chloride (PVC). FT-Raman proved very sensitive to the formation of carbon double bonds in the structure due to the formation of polyene breakdown products which occur in the weathering process. Analysis of Raman bands at 1493 cm^{-1} (-C=C-) and at 1126 cm^{-1} (=C-C=) in a linear microscope map, suggest the depth to which the UV radiation penetrates.

We also studied the surface of these samples using attenuated total reflectance (ATR) on an infrared microscope. Deconvolution of weak, overlapping bands around 1740 cm^{-1} provided information on the level of oxidation produced.

Polyvinyl chloride is a very widely used and versatile polymer due to its flexibility in sheets and toughness in bulk. Products utilizing PVC include pipes, seat covers, cable insulation and floppy disk covers. In addition, its desirable physical qualities mean that PVC is often used as a component in co-polymers.

The main disadvantage of PVC is that it weathers easily with exposure to heat

and/or UV radiation present in sunlight. Weathering effects manifest as a surface discoloration and loss of flexibility and eventually lead to increased brittleness and cracking. In chemical terms, the degradation causes the generation of a wide range of break down products due to dehydration, oxidation and the formation of carbonic acids and carbonyl groups.

These deficiencies mean that PVC is seldom used in products which will be used outdoors since prolonged exposure will lead to the degradation. In situations where the properties of PVC are desirable in an unsuitable environment, the product can be coated with a protective outer layer. However, the added expense often means that different materials are chosen.

FT-Raman¹ is a relatively new analytical technique compared to FT-IR. However, FT-Raman has many unique advantages that lead to the technique quickly growing in popularity within both industrial and academic environments. Raman has been a useful tool in the analysis of polymers for many years and polymer chemists developed the use of Fourier transform techniques to extend the range of samples which could be studied using Raman. FT-Raman is a non-destructive technique which can be used with no sample preparation for both qualitative and quantitative measurements² FT-Raman yields fundamental vibrational information in the same way that FT-IR does. In addition, Raman data is complimentary to IR data since many of the molecular structures which IR is insensitive to are very strong in a Raman spectrum.

Figure 1 shows MircoRaman spectra of some common thermoplastic materials – acrylic (polymethylmethacrylate); polysulfone; polystyrene G.P.; and cellulose acetate. Each spectrum was measured in less than 1 minute from a $20\text{ }\mu\text{m}$ diameter sample area. These data illustrate the FT-Raman technique's ability to offer easy data collection and well defined, sharp spectral bands.

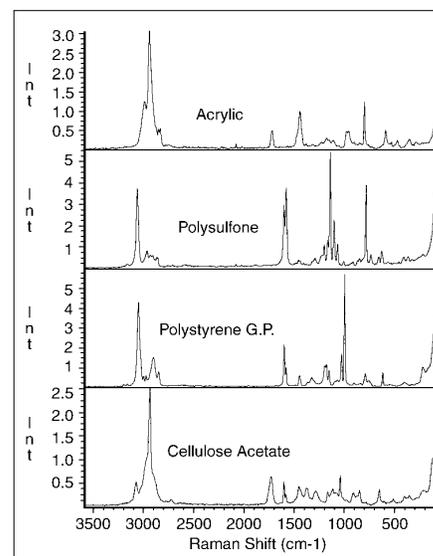


Figure 1: Spectra of some common thermoplastics by FT-Raman

Infrared absorption is a well established technique for studying polymers and related materials. Attenuated total reflection (ATR)³ allows the study of the surface of bulk materials where good contact can be made between the ATR crystal and the sample surface. The development of micro-ATR tools has expanded the usefulness of the technique⁴ by allowing not only the study of small samples but also samples with rough surfaces. This is possible since a

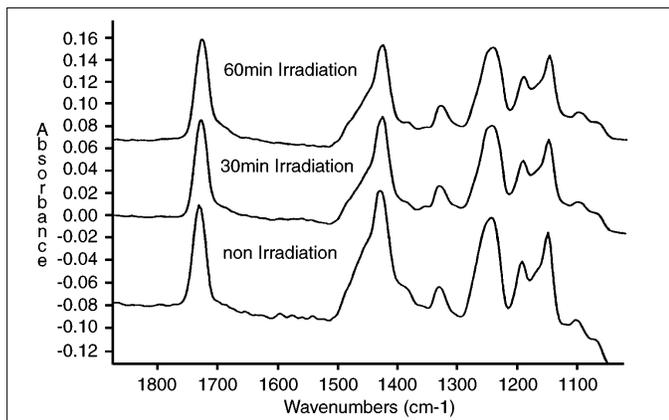


Figure 2: ATR spectra of weathered PVC

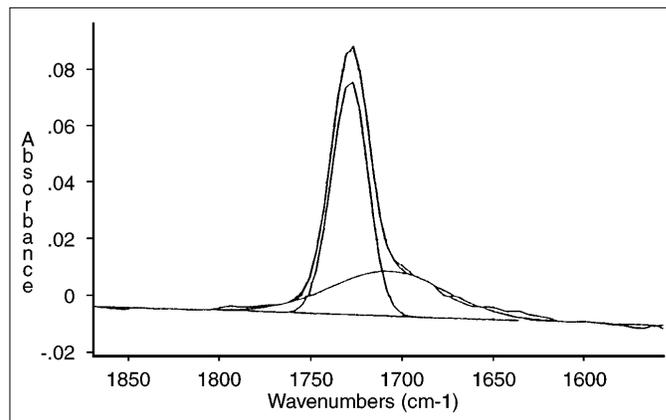


Figure 3: Curvefitting to analyze subtle changes in the FT-IR spectrum

much smaller “flat” area is needed to make sample contact. In addition, small surface areas can be studied with each measurement to cover a range of 15 to 150 μm diameter. These studies utilize a micro-ATR objective with a diamond crystal and measured an area of 30 μm diameter. The nature of ATR is that absorption occurs in a thin layer close to the sample surface – while this is sample dependent the penetration depth for PVC is approximately 3 μm .

INSTRUMENTATION

These FT-IR measurements were made with a Magna-IR[®] 750 equipped with a Nic-Plan[™] microscope and diamond crystal ATR objective. FT-IR data was accumulated for 128 seconds at 8 cm^{-1} resolution. Sample contact with the ATR objective is achieved by simply raising the microscope stage until the crystal makes contact with the sample.

FT-Raman data was measured using a Raman 950 spectrometer with the MicroRaman microprobe. The microprobe was operated in 180° reflectance mode, with a cooled Germanium detector and near infrared laser excitation at 1064 nm. Raman data was accumulated for 256 s at 8 cm^{-1} resolution. The microscope allowed a depth profile to be generated by sectioning the sample and collecting spectra in successive steps of 50 μm steps from the surface to the center of the material. The clear advantage of using excitation around 1 μm in an FT-Raman measurement is avoiding fluorescence – a strong, broad emission which can otherwise swamp the Raman signal.*

RESULTS

The attenuated total reflectance measurements show the spectra of raw PVC and PVC after 30 and 60 minutes of exposure to UV radiation. Each of these spectra appear to be very similar. The fingerprint region of these spectra can be seen in Figure 2. Closer inspection reveals that there are small changes in the small band at 1700 cm^{-1} . This band can be attributed to the presence of carbonic acid and its presence is an indication of the build up of this break down product.

Analysis of this component is complicated by the presence of a strong absorption at 1740 cm^{-1} . This derives from an additive in the PVC product and strongly overlaps with the band of interest. In this study we chose to use curve fitting to approximate the two band shapes and thereby separate the two overlapping regions. An example is shown in Figure 3. Curve fitting allows us to track the size of the carbonic acid peak – independent of the overlapping additive spectrum – and associate it with a relative concentration increase with increasing exposure.

Figure 4 shows the FT-Raman spectra measured from the surface of the PVC after 0, 30 and 60 minutes of exposure to the UV radiation. Changes in the Raman spectra are far more dramatic than those in the IR and are therefore much simpler to analyze. The most noticeable effect is an increased background in the spectra as the exposure time is increased. This may be attributed to the fact that among the many break-down products present in the sample, some components are fluorescent. Using 1.064 nm laser excitation and FT-Raman detection

this fluorescence remains relatively small and a simple baseline correction can be applied from within the OMNIC software to remove this interference. It is interesting to note that with conventional dispersive Raman, even at 780 nm, this fluorescence is so large that it prevents useful data from being collected.

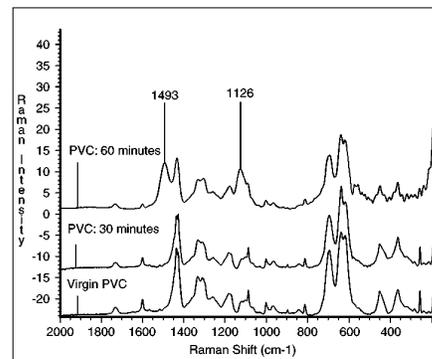


Figure 4: FT-Raman spectra taken from the surface of weathered PVC samples

The biggest spectral change in the FT-Raman data is the appearance of bands at 1493 cm^{-1} and 1126 cm^{-1} . These can be attributed to the presence of $-\text{C}=\text{C}-$ and $=\text{C}-\text{C}=\text{C}$ bonds in polyene breakdown products. IR measurements are not sensitive to these vibrations since they are symmetric vibrations which therefore generally have no permanent dipole. In the Raman these bands are strong and relatively broad and this can tell us several things about the break down products. The intensity of the bands indicates that the polyenes are present in significant concentrations. Tracking the intensity of these peaks will relate directly to the concentration of the breakdown products. Comparing intensities with depth or exposure information can lead to conclusions about weathering rates and penetration.

The broad band widths indicate that the double bonds appear at different locations along a relatively long polymer “backbone chain.” For a given polymer chain, a double bond at each possible position along the chain – from the ends to the middle – will have a subtly different vibrational frequency. In a study such as this we are measuring the cumulative effects of many C=C bonds in every possible position along chains of various lengths. The resulting Raman emission is therefore averaged or “blurred” into a relatively broad band.

The FT-Raman microprobe is capable of looking at spots as small as 6-10 microns and is therefore an ideal tool for mapping the microscopic effects such as non-uniform degradation of the polymer over the surface area. In this study we were interested in the depth to which degradation occurs when the polymer surface is exposed to UV radiation. We can study this easily by taking a piece of the PVC and sectioning it such that the cut side exposes the depth from the surface. Under the microprobe we then measured FT-Raman spectra in 50 μm steps starting at the weathered surface and continuing down into the bulk. The results of these measurements are shown in Figure 5: the first spectrum (top) is at the surface of the PVC and the subsequent spectra represent 50 μm steps down into the interior. The emissions at 1493 cm^{-1} and 1126 cm^{-1} which arise with the presence of breakdown products can be seen to decrease with sample depth from the irradiated surface.

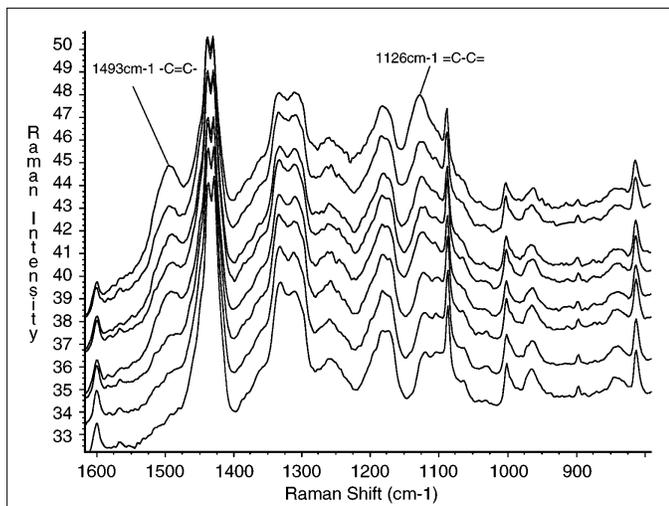


Figure 5: FT-Raman microprobe spectra of depth profiling weathered PVC samples. The “top” spectrum represents the surface of the sample

The magnitude of spectral bands arising from both the -C=C- and =C-C= bonds is largest at the surface and falls to the level of untreated PVC after approximately 500 μm . This indicates that 500 μm is approximately the depth to which the UV light can penetrate with enough intensity to cause significant degradation.

CONCLUSIONS

FT-IR and FT-Raman microscopy are powerful tools in the study of polymer materials. For these samples both FT-Raman and FT-IR gave information on the degradation of PVC materials. In FT-IR, attenuated total reflectance represents a useful technique since it avoids the normal sample preparation associated with infrared absorption measurements and when combined with microscope technology allows a small sample area to be studied. However the infrared spectra suffered from overlapping bands arising from additives in the polymer. Changes occurring in the IR spectra and curve fitting was required for interpretation.

FT-Raman intrinsically avoids the need for sample preparation and in this case provides data more easily and with less need for manipulation than FT-IR. The ability to utilize microscopy techniques with the Raman has proved to be very powerful since it allows us to study these small effects in highly regionalized areas of the sample. This can be very important for example when looking at depth of penetration.

While the IR is sensitive to the highly polar bonds in the molecules such as the carboxylic acid -COOH, the Raman is more sensitive to the symmetric vibrations commonly associated with the polymer “backbone” (in this case -C=C- and =C-C= bonds) and inter-chain reactions. FT-Raman measurements are also sensitive to the molecular environment of these bonds with broad bands indicating a range of molecular chain lengths and chain positions for the C=C bonds.

A summary of PVC break-down products is shown in Figure 6.

Break-down route	polyene chains (-C=C- and =C-C= bonds)
Product	FT-Raman at 1.064 μm 1491 cm^{-1} and 1126 cm^{-1} Oxidation
Detection technique	Carboxylic acids (-COOH)
Removal of hydrochlorides	FT-IR/ATR spectra 1700 cm^{-1}

Figure 6: Table summarizing the Reaction process and detection techniques for the degradation products of PVC exposed to UV radiation

Employing FT-Raman and near infrared laser excitation avoids most of the fluorescence problems which were seen with conventional Raman measurements⁵. FT-Raman microscopy is shown to be a very useful technique in analyzing the depth from the exposed surface to which reaction has occurred.

REFERENCES

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In addition, Raman has long been a useful tool for the analysis of polymer samples. There are several useful reviews of synthetic polymer studies. For example – JK Agbenyaga, G Ellis, PJ Hendra, WF Maddams, C Passingham, HA Willis, *Spectrochim. Acta*, **46A**, 197 (1990)

Notes

* Recent surveys suggest that in dispersive Raman studies of “real world” samples about 90% suffer fluorescence problems in the visible and UV. This falls to about 30% in the red at around 750 nm but is very low with NIR at 1064 nm.

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