# Thermal degradation of polyurethane-backed poly(vinyl chloride) studied by Raman microline focus spectrometry

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Raman microline focus spectrometry has been utilized to record spatially resolved and spatially averaged Raman spectra from degraded poly(vinyl chloride) (PVC) sheet. Characteristics of simultaneous thermal and chemical degradation occurring in commercial polyurethane (PU)-foam-backed PVC sheet have been inferred from the observed Raman data. From a comparison of the data recorded across a section of the sheet, the presence of PU foam is shown to increase the degradation rate of PVC. In addition, higher concentrations, higher rates of formation and longer conjugation lengths of those polyenes formed during degradation are found at the PVC/PU contact interface. This is attributed to the extra chemical degradation occurring at the PVC/PU interface due to catalysis of dehydrochlorination by amine residues in the PU.

**(Keywords: microline focus spectrometry; poly(vinyl chloride); degradation)**

## INTRODUCTION

Poly(vinyl chloride) (PVC) is susceptible to thermal degradation through a process of dehydrochlorination. In this process, HCl is lost from the polymer backbone in sequential steps to yield long, conjugated polyenes. The formation, and subsequent cross-linkage, of these polyenes leads to a gross loss in the polymer's mechanical properties. In previous studies, the HCl has been found to be autocatalytic, accelerating the degradation[1]. In an earlier paper[2], using microline focus spectrometry (MiFS) we have shown how the presence of a polyurethane (PU) foam backing on one side of the PVC sheeting causes an increase in the extent of degradation at the PVC/PU interface. This phenomenon was attributed to an additional chemical degradation mechanism at work at that interface. Using MiFS instrumentation we now quantify various spectral parameters of the resonance Raman spectra from the degradation products and attempt to infer mechanistic and kinetic information from these data.

## THEORETICAL

The polyenes have strong u.v./visible absorption profiles (causing a colour change in the degraded polymer) which allows the resonance Raman condition to be met, leading to strongly enhanced Raman signals from the degradation products. The frequencies of the u.v./visible absorbance maxima from a degraded PVC sample are dependent on the distribution of the various conjugation sequence lengths ($n$) present in the sample[3]. The resonance Raman signal observed is thus highly dependent on the laser wavelength used to excite the spectra and the extent of overlap at that wavelength of the absorbance profiles of the various polyene sequence lengths present.

Previous studies have successfully used the Raman shift of the C=C symmetric stretch ($\nu_2$) band to monitor the polyene conjugation lengths that are formed in the degraded PVC. Raman shift data for the $\nu_2$ band of model polyene-containing molecules, such as *trans*-$\beta$-carotene (with $n=9$), have been correlated with the conjugation length[4] to provide an empirical formula used to estimate polyene conjugation lengths found in degraded PVC.

In any particular experiment, the Raman data obtained from a sample will be the concentration weighted sum of signals from those conjugation lengths being enhanced resonantly, and will also depend on the extent of resonance enhancement for any given value of $n$ at the exciting frequency.

Careful interpretation of Raman data yields an important insight into the presence and relative concentrations of different length polyenes. Furthermore, when a series of chemically indistinguishable polymers are degraded artificially for different time periods, a comparative study may be made of the changes that are occurring with time.

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## EXPERIMENTAL

Conventional microanalysis utilizes microscope optics to focus a spot of laser light (~1–2 μm diameter) on the sample and to collect the scattered light. In PVC analysis this leads to problems of sample heating and the possible occurrence of further degradation. Further problems arise when we consider the non-uniformity of the degradation across the polymer matrix, which results from the sequential conjugation of polymer units initiating at specific points in the polymer. This leads to variable Raman spectra from single-point analysis on a 5–10 μm scale. The MiFS instrument (*Figure 1*) overcomes this problem by focusing the exciting radiation onto the sample as a microline using cylindrical optics. A triple grating spectrometer is utilized for filtering the Rayleigh scattered and stray light and for dispersion of the Raman spectrum. The Raman scattered light is then detected using a sensitive two-dimensional (2D) CCD detector, and the resultant data consist of up to 250 spatially resolved Raman spectra originating from the focused line on the sample. The applications of this instrument have been described elsewhere[5–7]. The advantages of this technique are that the laser power density at the sample is significantly reduced, eliminating the problem of sample heating. On-chip electronics allow for spatial summation such that a representative one-dimensional (1D) spectrum may be produced which is spatially averaged over the length of the microline.

In this work, the 514.5 nm line from an argon-ion laser was used as a Raman exciting source, and a liquid-nitrogen-cooled, slow-scanned CCD detector (Wright Instruments) and associated software were used for data collection and manipulation.

The PVC sheeting (~0.8 mm thick) studied was prepared using PVC resin, plasticizer (di-octyl phthalate), lead phthalate and calcium stearate, in the ratio 100:60:3:2. Degradation was carried out by inserting a series of PU-foam-backed PVC sheets between glass plates, placing them in an oven at 120°C and removing samples at regular intervals. MiFS profiles were obtained across sections of the degraded PVC, using a laser power at the sample of ~10 mW through a 20× microscope objective with acquisition times of 300 s. Representative 1D spectra were obtained from three sampling sites on the PU contact surface and the air contact surfaces of each degraded PVC sample using a 30 s exposure. Summation of the 2D data from the detector produces a single 1D spectrum with spatial averaging over 270 μm on the surface of the sample, reducing any problems caused by inhomogeneity of the sample.

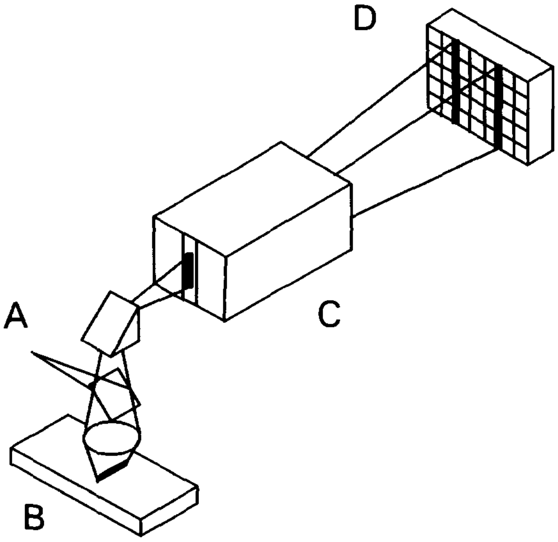

**Figure 1** Schematic of microline focus spectrometry apparatus: A, laser beam in; B, microline focused on sample; C, filter/spectrograph; D, CCD detector

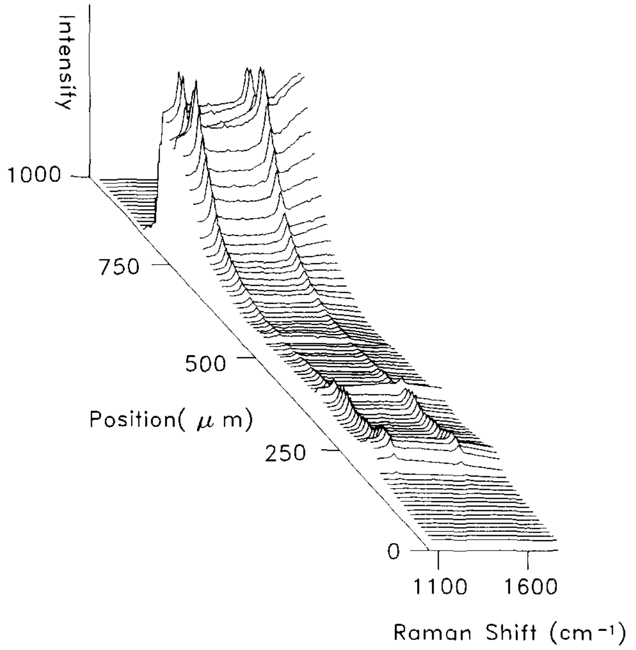

**Figure 2** Raman MiFS profile from a section through a PU-foam-backed PVC sheet. Sample degraded for 10 h at 120°C

## RESULTS

MiFS profiles reveal how the Raman spectrum of the degraded PVC sheeting changes as a function of distance across its section (from the PU contact side, ~950 μm, to what we have termed the air contact side, ~150 μm). *Figure 2* shows such a result for the PU-foam-backed PVC sample degraded for 10 h at 120°C. The spectrum covers the Raman shift region 1000–1800 cm$^{-1}$ and the resonantly enhanced peaks from the C–C stretch ($\nu_1$ at 1130 ± 1.5 cm$^{-1}$) and the C=C stretch ($\nu_2$ at 1500–1520 cm$^{-1}$) are clearly visible above the changing fluorescence background across the PVC section.

*Figure 2* also shows that the characteristics of the $\nu_2$ peaks are not uniform across the section. The variation is shown more clearly in *Figure 3*, which contains the same data for the $\nu_2$ peak, but with the fluorescence background subtracted. *Figure 4* shows the Raman shift variation of the $\nu_2$ band as a function of distance across the sample.

Other samples in the series were studied to determine the Raman shift and the intensity of the $\nu_2$ band as a function of degradation time between the two interfaces. In order to observe the differences between these parameters, a series of representative 1D spectra were recorded from the surface of each interface from all the samples. *Figure 5* shows how the values of the $\nu_2$ Raman shift measured from the air and PU interfaces change with degradation time.

As mentioned earlier, the $\nu_2$ peak intensities may be used as a comparative measure of the extent of

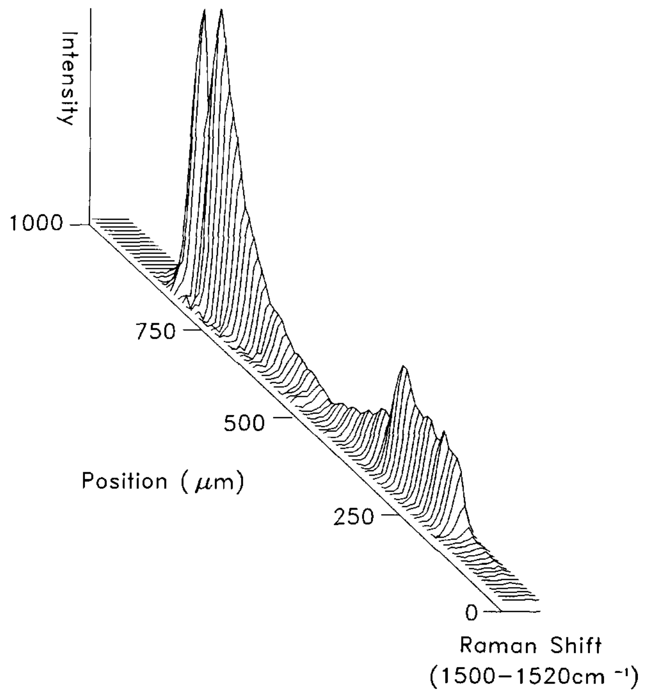

**Figure 3** MiFS profile of $\nu_2$ band data from *Figure 2* with background fluorescence subtracted

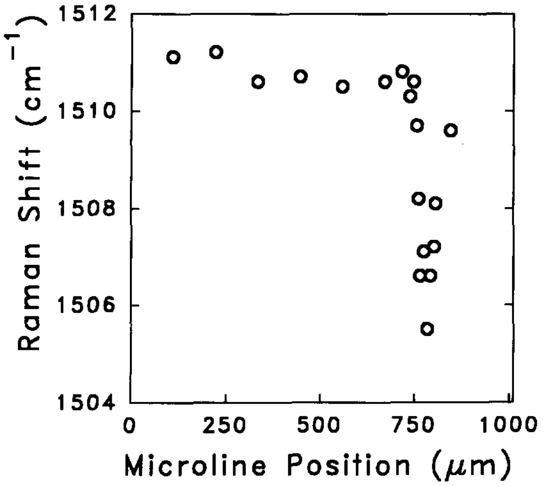

**Figure 4** Variations in $\nu_2$ Raman shift from *Figure 3* plotted as a function of sampling position

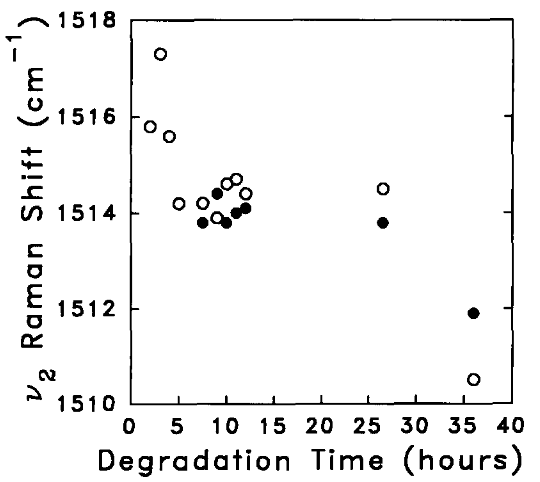

**Figure 5** Variations in $\nu_2$ Raman shift with contact interface (○, PU side; ●, air side) and degradation time, measured from Raman MiFS 1D spectra

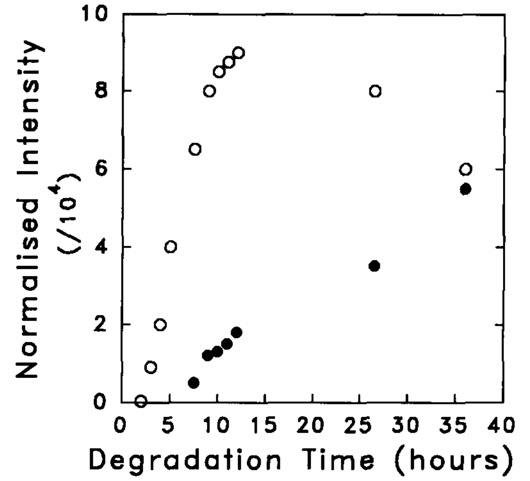

**Figure 6** Variations in $\nu_2$ Raman intensity with contact interface (○, PU side; ●, air side) and degradation time, measured from Raman MiFS 1D spectra

degradation; moreover, consideration of the trends in that variation with time enables the differences in relative degradation rates at each interface to be assessed. In order to correct for differing sample responses, all intensity data were normalized to a useful internal intensity standard, the PVC plasticizer spectral peak at 1600 cm$^{-1}$. Using this normalization technique, repeat data from a sample were found to be consistent to ±5%. *Figure 6* shows the variation of normalized $\nu_2$ peak intensity against time for each interface. The difference in extent of degradation between the two interfaces is most apparent in this figure.

## DISCUSSION

The MiFS profiles (*Figures 2* and *3*) show that gross variations in the extent of degradation occur across a section of the PVC matrix. There is a marked difference in the extent of degradation between the two interfaces. The PU contact side has degraded to a greater extent than the air contact side, the acceleration order being two to three times that of the air side. This, as we previously indicated[2], is a result of the amine catalyst residues from the PU foam diffusing onto the surface of the PVC and chemically initiating further degradation by assisting in the removal of protons during dehydrochlorination of the PVC at these elevated temperatures. As a consequence, more initiation sites form at the PU side, resulting, after propagation of polyenes and diffusion of the released HCl through the polymer matrix, in a greater extent and pattern of degradation being observed. The small increase in polyene signal close to the non-PU contact surface is due to a small leakage of HCl round to that interface during heating in the oven.

This mechanistic difference present during initiation also accounts for the Raman shift profile data presented in *Figure 4*. The polyene chain length formula, $\nu_2 = 1461 + 151e^{(-0.07808n)}$ (where $n$ = polyene chain length in C=C units[4]) may be used to correlate the shift data to conjugation length. It must be emphasized that the observed band shift is determined by the range of polyene sequence lengths present and their relative concentrations. Consequently, the large difference in the

Raman shift across the sample section is attributed to a much larger concentration of polyenes of $n = 14$–$16$ (i.e. $\nu_2 = 1505 \pm 1.5\,\mathrm{cm}^{-1}$) at the PU interface than at the air interface, where polyenes of lengths $n = 12$–$14$ (i.e. $\nu_2 = 1510 \pm 1.5\,\mathrm{cm}^{-1}$) are more abundant. The trends in these data are as expected, given the added chemical degradation. Longer conjugated polyenes are being observed at the PU interface and the highest levels of degradation are found here. At the extreme edge of the sample ($\sim 1000\,\mu$m), there is a sharp increase in the Raman shift and consequently a decrease in the average polyene length. This has been tentatively attributed to the onset of cross-linkage, which begins at higher concentration of long polyenes and yields a higher concentration of shorter residues.

The data from the spatially averaged 1D, MiFS spectra require careful interpretation. The $\nu_2$ Raman shift values at the PU interface and at the air interface (*Figure 5*) show a general downward change with degradation time. The data vary from $\nu_2 = 1518 \pm 1.5\mathrm{cm}^{-1}$ (i.e. $n = 10$–$12$) at 0–5 h, to $\nu_2 = 1510 \pm 1.5\,\mathrm{cm}^{-1}$ (i.e. $n = 12$–$14$) at 30+ h, which is indicative of a slow and consistent increase in concentration of longer polyene chain lengths. It is evident from the data that there is very little difference in the variation of average conjugated chain lengths between the two interfaces with degradation time. This suggests that the two degradation mechanisms that are dominant at the two interfaces have very similar propagation steps, and any differences that occur must happen before polyenes of conjugation length $n = 10$ are observed. As we have already seen in *Figure 4*, however, the value of $\nu_2$ changes considerably inside the matrix, so the trends observed here may be the sum of a number of factors.

The relative $\nu_2$ peak intensity data from the PU contact and air contact interfaces (*Figure 6*) are very different. Since the two sets of data for the two interfaces have been normalized by the same method they may be compared directly. The significance of the results lies in the fact that the data are consistent for all the samples, with the PU interface showing a greater extent of degradation. Initially, the rate of increase in polyene concentrations (as shown by the rate of increase in $\nu_2$ peak intensity) at the PU contact side is very fast (approximately six to eight times faster than at the air contact side). After 10 h, however, the rate of degradation decreases significantly. This may be due to two factors:

1. a steady-state situation is reached, where the initial fast build-up of polyenes $n = 8$–$18$, which are resonantly enhanced and thus 'observed' at 514.5 nm, is now equivalent to the propagation of these chains to longer lengths which are not resonance enhanced at this exciting frequency and thus not 'observed';
2. the level of degradation reaches a limit, i.e. the ionic polyene intermediate formed during polyene propagation is sufficiently stable that no further reaction occurs.

In contrast, *Figure 6* shows that at the air interface the extent of degradation is lower and linear with degradation time (constant rate). The data presented in *Figure 6* form a useful reference when using MiFS in the study of PVC degradation. The use of a standard data normalization procedure means that all further measurements on chemically similar samples, but with different degradation parameters, may be measured against this standard set. Future work will consider the effect of changing the Raman exciting source on the resonance Raman spectra from the samples, evaluation of spectra from non-PU-foam-backed PVC to determine the effects of purely thermal degradation, and eventually to determine the relative efficiency in degradation retardation of stabilized PU-backed PVC.

## CONCLUSION

The changes and trends in the Raman spectra excited by the 514.5 nm line of an argon ion laser of a reference set of thermally degraded PU-foam-backed PVC samples have been interpreted. The differences in extent of degradation at the two interfaces have been attributed to different degradation mechanisms being present.

The results suggest that the rate of dehydrochlorination of the PVC to those polyenes, which give resonance Raman spectra at the exciting frequency used, is different at the two interfaces. The significant difference is in the concentrations of polyenes present, observed through the polyene signal intensity. The PU contact interface shows a much greater extent of degradation with degradation time than the air interface. This suggests that there must have been more dehydrochlorination initiation sites formed at the PU interface. This implies that the amine catalyst residues from the PU foam have the effect of creating more dehydrochlorination initiation sites than random thermal initiation. The amines may also be involved in catalysing earlier stages of the 'unzipping' reaction at unsaturated structures already present in the PVC, the effects of which will not be seen at this exciting wavelength. Further investigation into the behaviour of other conjugation length polyenes in these samples at the two interfaces will provide an insight into the presence, relative concentrations and rates of formation of all the different length polyenes formed during the degradation reaction. Such a study should lead to a broader understanding of the mechanisms and processes involved in the thermal and chemical degradation of PVC.

## ACKNOWLEDGEMENT

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