THE ANALYSIS OF POLY(ANHYDRIDES) AND THEIR DEGRADATION BY NIR/FT RAMAN SPECTROSCOPY

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Langer et al (1985) have developed a series of poly(anhydride) polymers which degrade via the hydrolytic cleavage of the anhydride bonds to yield the associated low molecular weight, non-toxic acids. The rate of degradation is dictated by the length and nature of the hydrocarbon backbone chain. Aliphatic homo-poly(anhydrides) will erode faster than their aromatic contempories and the control of degradation can be altered further by forming copolymers of aliphatic and aromatic monomer units. In this paper, we demonstrate the potential NIR/FT Raman spectroscopy for the non-invasive solid state analysis of poly(anhydride) polymers and their subsequent degradation.
The poly(anhydrides) were synthesised as previously described (1), and Raman spectra collected on a converted series 1700 Perkin-Elmer FTIR with a Nd/YAG laser (1.064 um) as the irradiating source, the instrumental resolution was 6 cm^{-1}. The polymer powders (0.060g) were placed in a brass tube sample holder of bore 4 mm and sample depth of 3 mm and analysed at a laser power of 500 mw for 150 scans. The degradation studies were undertaken with poly(sebacic anhydride), PSA, rods (compressed 3 mm x 3 mm) stored in water for upto 15 days at 15 ^{o} C and were analysed at 700 mw for 50scans.
All anhydrides show a carbonyl band pair in the Raman spectra, which correspond to the symmetric and asymmetric stretches of the carbonyl groups about the intermediate oxygen atom, and approximately 50-70 cm^{-1} in separation. For the aliphatic polymer PSA these are at 1803 and 1739 cm^{-1} compared to the aromatic polymer poly[bis(p-carboxyphenoxy) propane)], PCPP, where the band pair is at 1764 and 1712 cm^{-1}. Therefore in a co-polymer of the two it is possible to differentiate between the two types of anhydride bond (Figure 1).

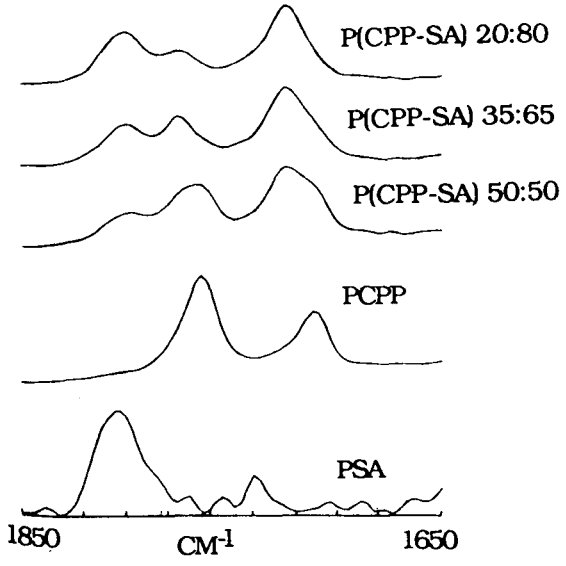
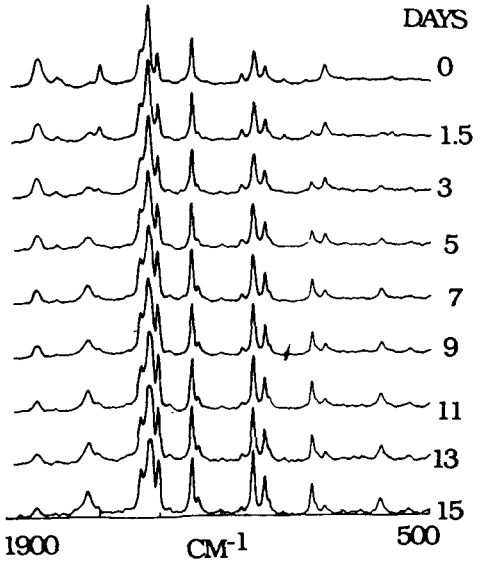


Figure 1. Comparison of the anhydride region of three co-poly(anhydride) mixtures.

Figure 2. The Raman spectra of the degradation of PSA over a 15 day period.



The degradation study shows the anhydride bond pair decreasing over the experimental period (Figure 2), with a complementary acid carbonyl band (1640 cm^{-1}) emerging, the spectra show no interference from water as this is the ideal Raman solvent. Our preliminary studies show that Raman spectroscopy is ideal for monitoring the hydrolytic degradation of these novel and dynamic polymers.

Domb . A and Langer . R . J. (1985) Polym. Sci., Chem. Ed. 23 : 453 - 470.