APPLICATIONS OF RAMAN SPECTROSCOPIC MAPPING FOR THE CHARACTERISATION OF HIGH PERFORMANCE POLYMERS

L. Rintoul¹, K. Thurecht², L. Chen², K. Goh², D.J.T. Hill² and A.K. Whittaker²

¹ School of Physical and Chemical Sciences, QUT, GPO Box 2434, Brisbane, 4001, Q. Australia. l.rintoul@qut.edu.au
² Centre for High Performance Polymers, Centre for Magnetic Resonance, The University of Queensland, St Lucia, Q 4067 Australia.

Keywords: Raman mapping, polymer characterisation, grafting, blending, composites.

Abstract: The importance of Raman spectroscopic mapping as tool for the characterisation of materials is illustrated by the following three examples: the determination of domain size in polymer blends; the component distribution in a wood polymer composite; and the penetration of a polystyrene graft.

Much research is directed towards the modification of polymers to enhance their primary properties by blending, grafting and forming composites. There is a great need to determine the spatial distribution of the components if the bulk properties of the new product are to be understood. Raman spectroscopic mapping of a polymer surface can provide chemical information to a lateral spatial resolution of 1 micron and requires little or no sample preparation, and therefore is an important tool for the characterisation of these new materials [1]. We present here three applications that arose from projects undertaken at the Centre for High Performance Polymers that illustrate the strength of Raman spectroscopic mapping as such a tool.

1. Characterisation of Polymer Blends Formed by Supercritical CO₂. (Kris Thurecht) [2] The aim of this project was to create polymer blends of two otherwise immiscible homopolymers, and hence form a material having unique properties. Supercritical carbon dioxide was used as a solvent and penetrant for styrene monomer into polyethylene. Upon penetration, the styrene was polymerised in supercritical CO₂ using a thermal initiator. For comparison, blends were also formed at standard temperature and pressure. Raman spectroscopic mapping was used to characterise the homogeneity of each blend. It showed the domain size was of the order of 5 microns at standard temperature and pressure whereas using supercritical carbon dioxide sub-micron domain at a higher concentration of polystyrene was achieved.

2. Determination of Polymer Distribution in a Wood-Polymer Composite. (Lan Chen). Impregnation of wood with polymer improves the properties of wood, such as hardness and compressive strength, resistance to abrasion, decay, weather and fire, and moisture exclusion. Flooring, sports equipment and musical instruments are just a few applications to take advantage of the favourable properties that impregnation with polymers confers. In this study two wood-polymer composites were formed by the impregnation of hoop pine with either methylmethacrylate (MMA) or 2-hydroxyethyl methacrylate (HEMA) monomer followed by in situ polymerisation.

Scanning electron micrographs indicated the

Fig. 1 Raman map of the mole fraction of HEMA in impregnated wood.
cell walls were swollen in the case of the HEMA composite, but chemical information was lacking as to whether the polymer had indeed penetrated the cell wall. Raman spectroscopic maps were recorded from a microtomed surface perpendicular to the timber grain. (Fig.1). The Raman signal from the polymer was not extinguished inside the cell wall in the case of HEMA, whereas no penetration was found for MMA.

3. Grafting of Polystyrene onto Kalrez® Fluoropolymer Elastomers. (Ken Goh) Perfluorinated polymers are inert materials that have excellent mechanical, thermal and electrical properties. Radiation grafting of styrene monomer greatly enhances the surface reactivity of the perfluorinated substrate and has found recent application in such diverse fields as medical implants for improving bio-compatibility and solid phase organic chemistry. However long-lived radicals generated during irradiation ultimately lead to degradation of the substrate. To circumvent this problem we have investigated various grades of a fluoroelastomer known as Kalrez®. This material is a copolymer of TFE and perfluorinated vinylmethyl ether (PFVME) and can contain various crosslink promoters such as nitrile. It was found that after radiation induced graft copolymerisation of styrene onto Kalrez® films, not only had the dimensions increased but the surface appearance and the shape of the substrate had dramatically altered. The exception was nitrile incorporated Kalrez®, which was able to retain its shape after styrene grafting. The penetration of styrene was studied by sectioning the film and recording a Raman line map across the sectioned surface. The relative mole fraction of styrene and fluoropolymer where calculated from the band areas of the benzene ring breathing mode of styrene at 1002 cm\(^{-1}\) and the C-C stretching mode of Kalrez® at 729 cm\(^{-1}\) in conjunction with estimates of their respective Raman scattering cross-sections. It was found that although “neat” Kalrez® had a lower percentage of graft, the styrene was able to penetrate deeper into the “nitrile” Kalrez®.

To conclude, Raman spectral mapping has proved a valuable tool for the characterisation of novel polymer materials, providing information on the distribution and domain size of the individual components in a blend, the degree of interaction between the matrix and the structural component of a composite, and the extent and intermixing between graft and substrate.

References: