SUPERCRITICAL FLUID POLYMER PROCESSING: A CONFOCAL RAMAN MICROSCOPIC INVESTIGATION

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Abstract: This study evaluates the dyeing of polymers under high-pressure and supercritical (sc) CO₂ conditions using confocal Raman microscopy. The effects of the dyeing conditions are evaluated in terms of morphological alterations to the host polymer matrix and the distribution of the impregnated dye as a function of depth.

The impregnation of polymers with doping solutes is performed in a ‘solvent-free’ manner with the use of scCO₂. The application of scCO₂ technology in polymer processing is an attractive alternative to conventional methods largely due to the ease of removal of CO₂ following processing. Of particular promise is the use scCO₂ to replace water in the industrial dyeing of textile fibres. The polymeric materials employed in the textile industry are generally polyesters and specifically poly(ethylene terephthalate) is widely used. Much information is needed regarding the effects of the processing conditions on polymer morphology and the dye distribution. Confocal Raman microscopy promises to be a premier tool to investigate the processed polymers and thus a tool to guide process optimisation.

Confocal Raman microscopy enables a material to be z-sectioned, whereby Raman spectra are acquired as a function of depth in a non-destructive manner. The Raman spectra of PET processed with scCO₂ are well characterised and the basis to determine CO₂-induced morphology and the presence of impregnated azo-dye has been assessed [1]. Confocal Raman microscopy has been used to study the change in dye concentration as a function of depth in PET dyed from a scCO₂ solution, revealing a significant dye concentration gradient along the line normal to the film surface [2]. In a separate study CO₂-induced morphological alterations in PET following exposure to scCO₂ has been studied as a function of depth [3,4]. That work revealed that CO₂-induced reorganisation does not occur uniformly through the thickness of the film but a region of semi-crystalline PET with a maximum degree of crystallinity at the surface is formed. This work combines the aspects of both aforementioned studies to evaluate the scCO₂ dyeing of PET with Disperse Red 1 in terms of the host polymer matrix morphology and the distribution of impregnated dye as a function of depth.

PET film samples have been dyed with Disperse Red 1 under high-pressure and scCO₂ conditions at different temperature, pressure, and exposure times. Depth profiles have been measured using a Renshaw 1000 system, utilising oil and dry objectives in confocal mode along the line normal to the film surface. Raman mapping was performed along the line normal to the film surface of the cross-sections of the same film samples and compared to the confocal data, demonstrating the ability to obtain accurate depth profiles with the oil immersion objective. The importance of the initial degree of crystallinity on the ability of the film to be dyed has also been investigated. Raman mapping data from a sample exposed to high-pressure CO₂ at 100 bar and 4.5°C for 24 hours is presented in Figure 1. The normalised intensity of the dye band along with the width of the carbonyl band (the narrowing of which is indicative of crystallinity) are plotted as a function of depth in Figure 2. In this manner our method of analysis enables us to correlate the observed dye distribution with the presence of CO₂-induced morphological changes.
Fig. 1. Raman spectra acquired by mapping across the surface of a PET film cross-section exposed at 100 bar and 4.5°C for 24 hours. Raman spectra were measured at 1µm increments along the line normal to the film surface demonstrating the distribution of dye (indicated by the band with the asteric) impregnated into the polymer as a function of depth.

Fig. 2. Normalised intensity of the band corresponding to DR1 and the width of the carbonyl band plotted as a function of distance from the film surface.

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References: