INVESTIGATION OF THE PHASE MORPHOLOGY IN PS/PMMA ULTRATHIN FILMS BY SERS

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Abstract: This contribution reports on experimental work of SERS effect on the phase analysis in PS/PMMA ultrathin films. Using SERS the Raman intensity of the thin films can be enhanced dramatically. It is demonstrated that SERS is a very promising and powerful technique for detailed characterisation of polymer blend thin films.

Bulk demixing of binary polymer mixtures have been studied extensively during the last decades and are reasonably well understood. [1] Near interfacial boundaries, however, surface effects may lead to physical properties that significantly differ from those in bulk. When polymers are used as functional materials, the surface characteristics play an important role and determine the functional performance. Examples are the contact angle with liquids, corrosion resistance, and frictional properties of the materials. In order to design the polymer surface with characteristic functionalities, it is necessary to control surface aggregation structure and surface orientation of polymeric chains as well as surface molecular motions. Molecular aggregation structure and molecular motions at the air-polymer interface are quite different from those in the bulk region due to the difference of free energy state between surface and bulk. This phenomenon has been attracting much interest from both theoretical and practical viewpoints. [2-5] The surface structure has been characterized by a number of techniques, each with its own inherent depth resolution, such as X-ray photoelectron spectroscopy (XPS), attenuated total reflection Fourier transform infra-red (ATR-FTIR) spectroscopy as well as the classical contact angle and surface tension measurements. Using SERS, G.Xue et al. [6] investigated the orientation of polymer chains on the surface of metals. It was found that different coating methods resulted different orientation of the sample molecules. Boerio et al. [7] studied the surface aggregation phenomenon in polystyrene (PS)/deteurated polystyrene (DPS) polymer blend during annealing above the upper critical solution temperature (UCST) by SERS.

In this study, The Raman spectra were obtained from a Renishaw (model RM2000) Raman spectrometer coupled with a Leica optical microscope. An exciting wavelength of 514.5nm was provided by an Ar laser source. The laser was focused to a 2um diameter spot on the sample using a 50× objective lens.

Two kinds of substrate were used in the experiment. One is the common glass substrate. And the other is prepared with a layer of fresh silver island film on the glass substrate as the method mentioned in [8]. Polystyrene/poly (methyl methacrylate) (PS/PMMA) was studied after thin films prepared on substrate by spin-coating from THF. The film thickness was controlled by varying the rotation speed. RAMAN spectroscopy combined with microscopy was used to obtain information on the morphology and structure of the thin films. From the relative intensities of the peaks around 1604cm^{-1}, 1585cm^{-1} due to stretching of benzene rings and 1728cm^{-1} due to stretching of C=O for PS and PMMA respectively [8], we can define the composition of the domains in the sea-island-like phase-separated structure in the microscopic image.

When the film thickness is thinner than 400nm, the Raman intensity of the films on glass substrate was almost equal with that of the noise. However, using SERS it can be enhanced dramatically. The spectra were shown in fig.1 and the comparison of the three different methods we used was listed in Table.1. It is demonstrated that SERS is a very promising and powerful technique for detailed characterisation of polymer blend thin films.

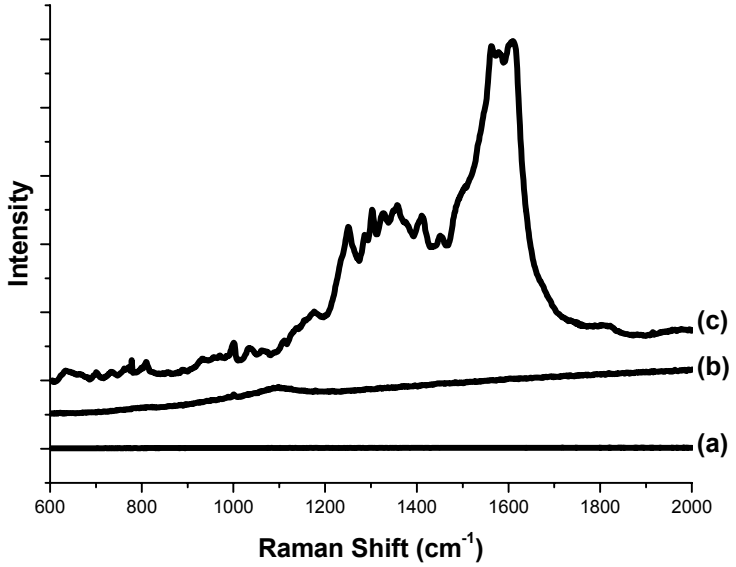

Fig.1 Raman spectra of PS/PMMA (50/50) blend thin films (a) on glass substrate, power 0.047mW (b) on glass substrate, power 0.47mW, (c) on silver/glass substrate, power 0.047mW.

Table 1 Comparison of the three Raman experiments on the PS/PMMA (50/50) blend thin films.

PS/PMMA (50/50) blend thin films (400nm)	Glass substrate	Power (mW)	Signal-to-Noise (S/N)
a	glass	0.047	Weak (~1)
b	glass	0.47	Weak (~5)
c	silver/glass	0.047	Strong (~120)

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