Deposition of polymer bilayer configuration by pulsed laser ablation and its use for study of polymer–polymer interface

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MS received 12 May 1993

Abstract. Thin films of polyphenylene sulphide (PPS) and polyethylene (PE) polymers have been deposited in a bilayer configuration using pulsed excimer laser ablation. Such bilayer specimens have been annealed at different temperatures, up to a maximum of 120°C, and for different time intervals, up to a maximum of 110 min, to investigate the evolution of the interface. By employing the technique of spectroscopic ellipsometry, the nature and the degree of thermally induced polymeric transport across the interface are brought out.

Keywords. Bilayer configuration; interfacial thickness; infrared; PPS; PE.

1. Introduction

In recent times, polymers and polymer based materials have found an important place in science and technology in view of a unique set of properties exhibited by these carbon based long chain molecular systems. Polymers in their basic forms, as well as their blends and alloys, have already found immense applications in industry. Most of these applications have been based on bulk forms (Gilmore et al 1980; Wu et al 1986; Composto et al 1988; Jordon et al 1988; Rafailovich et al 1988; Witlow and Wool 1989) of such materials and it is only recently that emphasis has been laid on the development of polymer thin film based technologies. Thin film configurations offer some obvious and specific advantages over bulk forms such as large surface to volume ratio leading to accessibility of the material for external influences to be sensed, ability to control the microconstitution of the material synthesized and thereby creation of material forms with novel structure–property relationships, ease of post-synthesis processing and patterning for possible integration with other compatible technologies, etc. Moreover, the thin film configuration and the interfaces therein being accessible to a variety of characterization techniques, study of such configurations can be of vital importance and interest in the context of the development of an understanding regarding the corresponding processes occurring in the related bulk situations. For instance, these studies can provide information about interdiffusion and reactions across the interfaces of specific polymer pairs and invite discussion on the applicability criteria and limits in the case of polymer blends.

Pulsed ultraviolet (UV) laser ablation has proven very useful in two types of material processing applications in the field of polymers: material removal leading to controlled etching and material deposition in the form of thin films (Ready 1963; Srinivasan and Leigh 1982; Dijkkamp et al 1988; Hansen and Robitaille 1988; Malshe et al 1989). Polymers being delicate materials, any attempt to form thin films from an already formed polymer can, in general, crack the polymer, leading to carboniferous deposits. However, a window of parameter space exists for the interaction of short UV laser pulses with the polymers which can lead to deposition of high quality
polymeric forms. In this work, we have deposited thin films of polyphenylene sulphide (PPS) and polyethylene (PE) using pulsed excimer laser ablation technique. Bilayer configurations involving these two polymers have also been formed and subjected to different thermal treatments to study interface diffusion and reaction (if present). Polyethylene has a unique combination of good properties, such as wear and abrasion resistance, impact resistance, etc which makes it a good candidate for many different applications such as gears, sprockets, liners for conveyers and ball mills, etc. PE is also used as a piezoresistive material and hence it can be used as a pressure sensor. PPS is usually used in application areas wherein high thermal stability is required. The combination of PPS and PE offers a unique opportunity for experimentation: first, because PPS and PE have different glass transition temperatures ($T_g = -120^\circ$C for PE) and ($T_g = 88^\circ$C for PPS). Thus as there is a mismatch in the mobility factors, at 90$^\circ$C, PE will diffuse more in PPS. Further, for temperatures well below 90$^\circ$C and temperatures well above 90$^\circ$C, there can be a difference in the mobility of individual polymers and hence a difference in diffusion coefficients can be expected. Secondly, the combination is an immiscible combination due to which there can be no reaction chemically, but diffusion of PE in PPS can take place. Thirdly, the difference in refractive index between the two polymers is large enough ($n_2 - n_1 > 0.02$) for ellipsometric analysis.

2. Experimental

In our experiments, pressed pellets of polyphenylene sulphide and polyethylene were used as targets for pulsed laser ablation. A single such pellet was mounted in a deposition chamber which could be evacuated to a base pressure of 1 × 10$^{-7}$ torr (Varian diffstack). A KrF excimer laser (wavelength 248 nm, pulse width 20 ns) was focussed onto the target at an angle of 45°. The target was rotated during irradiation at 10 rpm. The substrates were mounted at a distance of 5 cm from the target surface. The deposition of polyphenylene sulphide was carried out at 90$^\circ$C and at an energy density of 0.4 J/cm$^2$ (Kale et al 1992). The deposition of polyethylene was carried out at room temperature and at an energy density of 1 J/cm$^2$. The substrate used for the deposition of PPS was single crystal (100) silicon, and on the layer of PPS, PE was deposited. The results reported here are for 6000 Å thick PPS film and 3000 Å thick PE film. Thickness measurements were performed on a Tally step (Taylor Hobson) system. The deposition of PPS was carried out at 90$^\circ$C by considering the glass transition temperature of PPS. The glass transition temperature being 88$^\circ$C, at 90$^\circ$C the chain structure is expected to rearrange itself, reducing the voids, if any. For polyethylene, the glass transition temperature being very low ($-120^\circ$C), the deposition was done at room temperature. The deposited individual films on silicon and bilayer films were characterized using infrared (IR) transmission and spectroscopic ellipsometry technique. Further, the interface study was also done using spectroscopic ellipsometry (McCraikin and Colson 1964).

3. Results and discussion

Figure 1 shows the IR transmission spectra of PPS pellet (figure 1a) used for laser ablation and PPS film (figure 1b) so obtained. Firstly, it can be observed that there
are striking similarities in both the spectra, indicating that the major IR active groups which constitute the polymer configuration are present in the polymer film. The 1,2,4-trisubstitution peak which appears at 860–900 cm\(^{-1}\) is seen in both the spectra. Similarly, the C–H bending peak which appears at 800 cm\(^{-1}\) is seen in both the spectra. Figure 2 shows the IR transmission spectra of the bulk PE pellet (figure 2a) and the laser ablated PE film (figure 2b). The C–H stretching band of alkane group which appears at 2960 cm\(^{-1}\) and two bands of C–H stretching which appear at 2800 cm\(^{-1}\) and 2900 cm\(^{-1}\) are seen in both the spectra. Thus from both the figures it can be seen that although the polymer chains may have cracked into smaller chains,
they still retain the basic polymeric form. Figure 3a shows the refractive index of PE film deposited on silicon substrate and figure 3b shows the refractive index of PPS film deposited on the silicon substrate. These spectroscopic ellipsometry data agree well with the reported values of these polymers (Bueche 1962).

A bilayer specimen of such well characterized films was prepared with 3000 Å PE film on 6000 Å PPS film. This bilayer was formed on the silicon substrate. This specimen was annealed at different temperatures, viz. 45°C, 90°C and 120°C, and for

![Figure 3. Spectroscopic ellipsometry data of a. PE film and b. PPS film.](image)

![Figure 4. Infrared transmission spectra of (PPS + PE) film deposited a. at room temperature, b. and annealed at 90°C for 30 min, c. and annealed at 90°C for 60 min and d. and annealed at 90°C for 110 min.](image)
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various time intervals from 30 min to 110 min. Figure 4 shows the IR of bilayer samples (PPS + PE) annealed at 90°C for various time intervals. These spectra basically show the peaks of both PE and PPS with no significant change in the peak intensity due to the annealing effect. This shows that there is no chemical reaction between the two polymers, which is quite obvious since the two polymers are chemically immiscible. Further, the nature of the peaks does not change with the temperature of treatment, which is also because of the immiscible nature of the two polymers (figure not shown). The interface analysis was carried out using spectroscopic ellipsometry technique. The rotating polariser ellipsometer (SOPRA, France, Model ES2G) was used for the analysis.

The PPS film was treated as a substrate with PE film as a layer over it. The change in the overlapped film due to the formation of an interface with subsequent heat treatment was studied using ellipsometry technique. A one-layer model was utilized for PE on PPS substrate using experimental data of PPS and PE independent films. This model was tailored with the actual bilayer film. The graphs of standard deviation between the simulated model and the experimental bilayer specimen for the films treated at different temperatures (viz. 45°C, 90°C and 120°C) and for different times (viz. 10 min, 30 min and 60 min) were plotted. The analysis of these graphs showed a gradual increase in standard deviation as the time increases, at a particular temperature. This increase is high for a film treated at 120°C and is low for a film treated at 45°C. Further, in the simulated model, one layer was introduced whose thickness was varied and refractive index was kept constant. It was found that the

![Graph of treatment time (t) vs interfacial thickness for film annealed at different temperatures: a. 45°C, b. 90°C and c. 120°C.](image)

Figure 5. Graph of treatment time (t) vs interfacial thickness for film annealed at different temperatures: a. 45°C, b. 90°C and c. 120°C.
thickness of the film to be introduced in between was minimum (10 Å) for a film treated at 45°C (for 1 h) and was maximum (100 Å) for a film treated at 120°C (for 1 h). Now, using the same thickness of the interface but varying the refractive index, similar graphs were plotted. The variation of refractive index was done in the range $n_1$ to $n_2$. However, it was found that the simulated model, having interface with refractive index equal to 1.8, was the best fit with the experimental specimen. Figure 5 shows the variation of interfacial thickness with time ($t$)^1/3 for different temperatures.

4. Conclusion

The diffusion coefficient of PE into PPS at 90°C is thus \(0.1225 \times 10^{-16}\) cm²/s, while at 45°C it is \(0.064 \times 10^{-16}\) cm²/s and that for 120°C is \(0.7 \times 10^{-16}\) cm²/s.

Acknowledgements

The authors deeply acknowledge the guidance of Prof. S B Ogale for carrying out this work. The authors are grateful to the Department of Atomic Energy, Government of India, for financial support.

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