polymer communications

Improved technique for cross-sectional imaging of thin polymer films by transmission electron microscopy

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An improved method for obtaining cross-sectional images of thin polymer films by transmission electron microscopy is described. Two examples are described in order to demonstrate the simplicity and flexibility of the technique. In the first example, the structure of a highly ordered block copolymer on a solid surface is examined. In the second example, the behaviour of colloidal gold particles at the interface between immiscible polymers is considered.

(Keywords: transmission electron microscopy; cross section; interface structure; thin film morphology; block copolymers)

Introduction

The overall properties of a large sample of material are generally dominated by the bulk properties. The influence of the sample surface on these properties can be neglected when the ratio of volume to surface is very high. However, as the sample size decreases the influence of the surface on the properties of the material becomes more pronounced. One example of this phenomenon is the tremendous decrease in the melting temperature of gold crystals with decreasing crystal size: the melting temperature of a 1 nm crystallite is reduced to half the value for bulk gold[1]. Similar effects, although on different length scales and on properties other than the melting point, are observed for very thin polymer films and for polymers at interfaces. In the case of polymers, the presence of the surface may change the structure and morphology of the film, thereby changing the properties dramatically. These effects are particularly important when polymers are used as surface coatings, compatibilizers or adhesives. In order to better understand the surface or interface properties of thin films it is important to know their structure and how the structure is influenced by the nature of the substrate.

Thin polymer films of submicrometre thickness are quite fragile and almost always have to be investigated on a substrate. Surface-sensitive techniques are therefore employed so that the substrate does not interfere with the measurement. Examples include X-ray photoelectron spectroscopy[2,3], Rutherford backscattering spectrometry[4,5], forward recoil spectrometry[6], secondary ion mass spectrometry[7,8] and X-ray and neutron reflectivity[9]. All these methods have a disadvantage in that they average over sample areas that are much larger than potentially important microscopic structures. Therefore they are incapable of determining the size of those structures or of detecting any defects, which are often of vital importance for understanding the behaviour and properties of thin films. Only in highly ordered and properly oriented systems can structural details, such as concentration profiles along the depth direction, be obtained.

Transmission electron microscopy (TEM) can be used to study polymer films, provided that there is suitable contrast between the features of interest (obtained, for example, by staining) and that the sample is resistant to damage induced by the incident electron beam. These limitations can often be circumvented, making TEM an excellent technique for studying the structure of thin polymer films. Defects, fine structures and non-ordered morphologies can be resolved over a wide range of length scales from the atomic level to several micrometres. Thin films can easily be imaged directly by TEM in a 'top view' mode by mounting them onto the conventionally used copper grids, which may be coated with an additional thin film as a support[10]. Cross-sectional views can only be obtained by microtoming the specimens, which is impossible for free-standing films owing to their fragility. One approach for obtaining sectionable samples is to embed the thin films in epoxies or other embedding materials[11-14]. These materials consist of monomers that are polymerized and crosslinked by different curing procedures. The drawbacks of this method are obvious in that the monomers and the curing conditions can lead to severe changes of the structure or even dissolution of the film. In this communication we report an easy and fast preparation technique that allows cross-sectional TEM to be performed on very thin films of most polymers and circumvents the disadvantages of embedding.

Experimental

Thin polymer films were spun-cast directly onto clean Ultem (trademark of General Electric) sheets (20 mm × 20 mm × 1.5 mm), some of which were coated with a uniform layer of evaporated gold. These composite samples were subjected to various thermal and chemical treatments and were then microtomed at room temperature using a Reichert-Jung Ultracut E ultramicrotome (Leica) equipped with a diamond knife. Sections with thicknesses of 50–100 nm were floated onto the water bath of the knife upon sectioning and were

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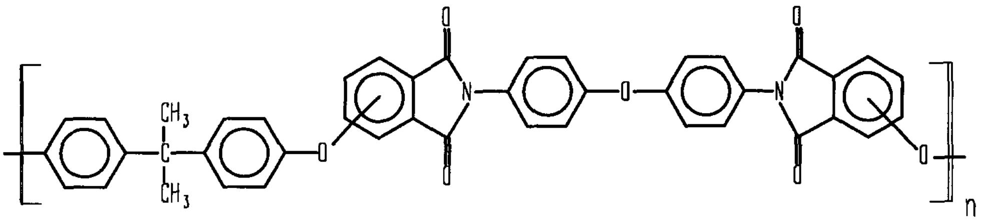

Figure 1 Chemical structure of Ultem

subsequently picked up onto conventional copper grids for TEM studies. Electron micrographs were recorded on Kodak SO 163 film using a Philips 400T electron microscope operated at 100 kV.

As a first example, a symmetric polystyrene–poly(methylmethacrylate) (PS–PMMA) diblock copolymer (M_w = 100 000; $M_w/M_n = 1.07$; PS volume fraction 50%) was investigated. The second example consisted of a layer of 20 nm colloidal gold particles (Polysciences) sandwiched between thin films of poly(2-vinylpyridine) (PVP; $M_w \approx 100\,000$; $M_w/M_n \approx 1.2$) and PS ($M_w = 293\,000$; $M_w/M_n = 1.06$). A detailed description of the sample preparation for the two examples is given below.

Results and discussion

It is clear that a support for the thin films is necessary in order to obtain cross-sections. This support material must meet several criteria. First, it must be sectionable and yet be mechanically stable. Metals, glass or other hard materials that would destroy the sectioning knife cannot be used. The support should also provide good adhesion for the polymer film and not react with the polymer or change its structure. It should be insoluble in a wide range of solvents and have a high glass transition temperature to permit thermal treatment of the specimen. Finally, the surface of the substrate should be smooth and the substrate should be transparent and stable in the electron beam. One material which meets all these criteria is Ultem, a polyetherimide. The chemical structure of Ultem is shown in *Figure 1*. Ultem has a T_g of 226°C (ref. 15), is inexpensive, is commercially available in sheet form, has excellent thermal and mechanical properties and is insoluble in apolar solvents.

A typical procedure consists of the following steps. First the Ultem sheets are cleaned by rinsing them with acetone. After drying the polymer film is applied. This can be done by directly spin-casting the polymer solution onto the Ultem sheet or by floating an already dry film onto the substrate. In order to create multiple layers this step can be repeated and various treatments such as annealing and staining can be applied. Cross-sectional microtomy is then performed in a region of interest. After drying and (if necessary) staining, the sections are investigated by TEM. Here we describe two different samples which illustrate the simplicity and flexibility of the preparation technique.

The first example shows that surface interactions have a strong influence on the morphology of a symmetric diblock copolymer of PS and PMMA. It also demonstrates the great flexibility of the technique in that even metal/polymer composites can be studied. For this experiment a thin, continuous layer of gold, about 140 nm thick, was evaporated onto the clean Ultem sheet. On top of this a film of the copolymer, 250 nm thick, was spun-cast from dilute toluene solution. The composite was then annealed in vacuum at 170°C for 240 h. Additional staining was not necessary because the contrast between PS and PMMA is large enough to exhibit the lamellar structure.

The micrograph of the Ultem/gold/PS–PMMA block copolymer composite (*Figure 2*), shows the substrate at the bottom covered with a very dark layer of gold. On top of the gold layer is a highly ordered lamellar structure consisting of alternating PS and PMMA domains. The PS domains appear dark due to a higher mass thickness and electron density. The bright PMMA domains are much thinner (7.6 nm) than the PS domains (20 nm) even though the volume fractions of the PS and PMMA components in the block copolymer are equal. According to neutron reflectivity measurements the thicknesses of the PS and the PMMA microdomains are 21 nm and 18.8 nm, respectively[16]. Obviously the PS domains are well preserved whereas the thickness of the PMMA domains is substantially reduced. Shrinking of the PMMA phase can be attributed to degradation of the polymer in the electron beam[17,18]. Degradation also thins the sample in the direction parallel to the electron beam, further enhancing the contrast between PS and PMMA domains.

There are two major points to focus on in this case. First, PS is present at the free surface and at the polymer/gold interface, and the thickness of these PS layers is half the thickness of the PS domains in the middle of the film. These results can be explained easily by the lower surface tension of PS and the lower interfacial energy for PS/Au as opposed to PMMA/Au. Second, the degree of order is extremely high. Grain boundaries between regions of different lamellar orientations, always present in bulk samples, were not observed. The presence of two interfaces close to each other forces the polymer domains to orient parallel to the substrate surface and is the reason for the extremely high degree of orientational ordering. This result has been obtained from previous experiments[16], but the perfection of the lamellar ordering has not been directly observed until this time.

This example shows that with the preparation method presented here it is easy to obtain information about the structure of very thin polymer films in cross-sectional view without resorting to the more commonly used embedding techniques[12,13]. It also suggests other advantages of this preparation method, namely the small amount of polymer needed and the short time spent in collecting the morphological data. The conventional methods would require preparing a bulk sample by melt pressing or by slow solvent evaporation[19–25]. In either case much more time and material would be required. Our new preparation technique allows not only for the 'edge view' investigation of very thin films, which up to this point has not been easily accessible, but also offers

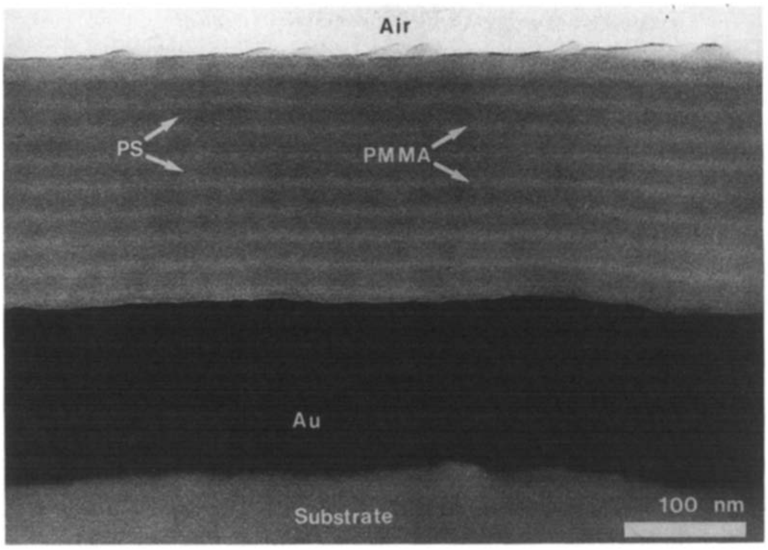

Figure 2 Cross-sectional TEM micrograph of a very thin PS-*b*-PMMA film on gold

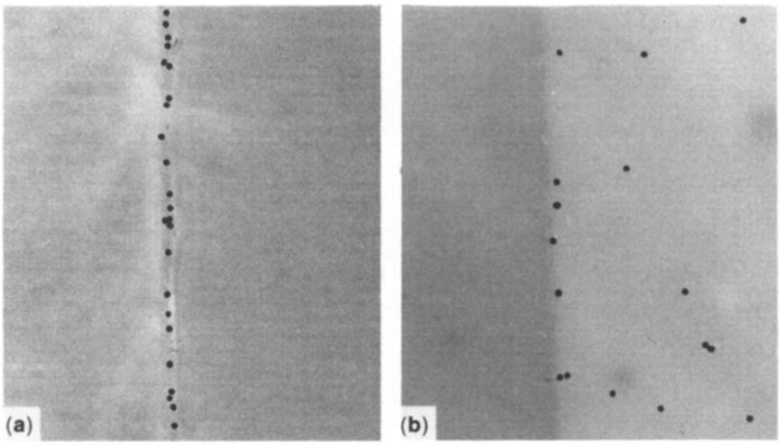

Figure 3 Cross-sectional TEM micrograph showing the distribution of colloidal gold particles near the inteface between PS (left) and PVP (right): (a) before and (b) after annealing for 71 h at 179°C

a precise means of examining the equilibrium morphology of block copolymer melts.

The second example[26] illustrates the way in which the technique can be extended to studies of polymer/polymer interfaces and to unconventional interface structures. The questions asked in this experiment were: Do colloidal gold particles diffuse away from an interface between PS and PVP? How far and in which direction do they move? The first preparation step was the spin-casting of a thin film of PVP from dimethylformamide onto the Ultem substrate. A drop of an aqueous solution of 20 nm colloidal gold particles was placed on top of the dried PVP film. A minute later the excess solution was suctioned off by means of a filter paper. In this way a homogeneous two-dimensional distribution of isolated gold particles at the surface was produced. In a separate step a PS film of comparable thickness was spun onto a clean glass slide. After drying it was floated off onto distilled water. This PS film was then picked up with the PVP/Au sample to produce samples having the gold particles sandwiched between the PS and PVP layers. These composite samples were then annealed at 179°C for various periods of time and subsequently microtomed. (Annealing the sample for one minute at 179°C improved the adhesion between PVP and PS enough to do the microtoming.)

Figure 3a shows a section of the PVP/Au/PS sample with the gold particles as dark spheres aligned nicely at the interface between PS and PVP. As can be seen in *Figure 3b*, annealing for 71 h at 179°C in vacuum resulted in diffusion of the gold particles into the PVP phase only. The preferential diffusion into the PVP indicates that there is a more favourable interaction of gold with PVP than with PS. From the distance that the gold particles diffused away from the interface a diffusion coefficient of $2.5 \times 10^{-15}\,\mathrm{cm^2\,s^{-1}}$ could be estimated using the thin film solution to the diffusion equation. The diffusion coefficient was confirmed by Rutherford backscattering spectrometry measurements on similar samples[26]. The Stoke–Einstein relation can be used to relate the viscosity η of the polymer matrix to the measured diffusion coefficient D and the radius r of the gold particles:

$$D = \frac{k_B T}{6\pi\eta r}$$

Substitution of $D = 2.5 \times 10^{-15}\,\mathrm{cm^2\,s^{-1}}$ and $r = 10\,\mathrm{nm}$ into this equation gives $\eta = 1.3 \times 10^6$ poise for the viscosity of the PVP polymer at 179°C. Efforts are currently underway to relate the 'microscopic' viscosity probed by the small gold particles to the bulk viscosity of the polymer.

Conclusion

The examples presented here illustrated the high flexibility and ease of use of our method for obtaining cross-sectional images of thin polymer films by TEM. Embedding techniques are avoided by preparing thin polymer films directly on sectionable polyetherimide substrates. Of equal importance is the fact that the manner in which the substrate interacts with the thin film specimen can be changed by evaporation of a thin metal layer onto the substrate. From the examples shown it is evident that these preparation techniques can be used to study a wide range of polymer/polymer or polymer/non-polymer interfaces by cross-sectional TEM.

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