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Dynamic mechanical analysis at the submicron scale

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Abstract

Dynamic mechanical analysis (DMA) is traditionally performed on bulk samples. However, studies of polymer blends would be enhanced if DMA could be applied on a local scale in order to enable a new form of microthermal analysis. Mounting a sample on a vibrating heating stage and observing the resulting amplitude and phase of the motion of an atomic force microscope cantilever allows the local elastic and visco-elastic properties to be studied. It is demonstrated in this article on samples of polyethersulfone/poly (acryonitrile-*co*-styrene) and polystyrene/poly(methyl methacrylate) (PS/PMMA) blends, and PMMA, PS and polytetrafluoroethylene homopolymers. Images at a specific temperature and spectroscopic data as a function of temperature of (nominally) a single point were collected. Primary and secondary relaxations were detected; the lateral resolution is better than 100 nm. We discuss the promising and limiting aspects of this new technique.

Keywords: Polymer blends; Dynamic mechanical analysis; Micro-thermal analysis

1. Introduction

Stresses are propagated across the interfaces between the different constituents of immiscible polymer blends. Interfaces may exist in such polymer blends, whose properties will be modified from those of the ingredients. The bulk properties of a polymer blend and their change with temperature may be determined by means of dynamic mechanical analysis (DMA) [1,2]. Bulk DMA measurements are often very useful for characterising the microstructure of polymer systems. However, while the phases present can often be identified, structural detail must be inferred. DMA provides no direct information about how phases are distributed in space. Being able to visualise the structure of phases on the basis of their thermo-mechanical properties would have wide applications in all branches of polymer science.

A logical way to make a micro version of DMA would be to modify an atomic force microscope (AFM) [3]. Already there is extensive literature on polymer morphology as seen with AFM [4,5]. Some groups use the AFM tip as a probe of the mechanical properties of polymers [6–8], but very little work has been done as a function of temperature. Our approach [9,10] has been to place a transducer underneath the sample that applies cyclic stress, and the inertia of the AFM cantilever, in contact with the sample, produces cyclic strain in the sample. Working in the inertial regime increases the linearity of and sensitivity to the sample response. The cantilever's amplitude and phase are related to the material's elastic and visco-elastic properties.

The transducer is part of a heating stage; therefore the sample may be thermally cycled. There are two data acquisition modes: imaging at a fixed temperature and spectroscopy as a function of temperature. With the former, the morphology of the blend and the homogeneity of phase transitions and relaxations can be studied as a function of position on the sample. The latter allows the temperatures of primary and secondary relaxations to be identified.

In this article, we describe the ideas behind our approach, and show results from polyethersulfone/poly(acryonitrile-*co*-styrene) (PES/SAN) and polystyrene/poly(methyl methacrylate) (PS/PMMA) polymer blends and from pure PMMA, PS and polytetrafluoroethylene (PTFE) samples. Where appropriate, the local data are compared to bulk calorimetry. A discussion of the exciting potential as well as the limitations of the technique follows.

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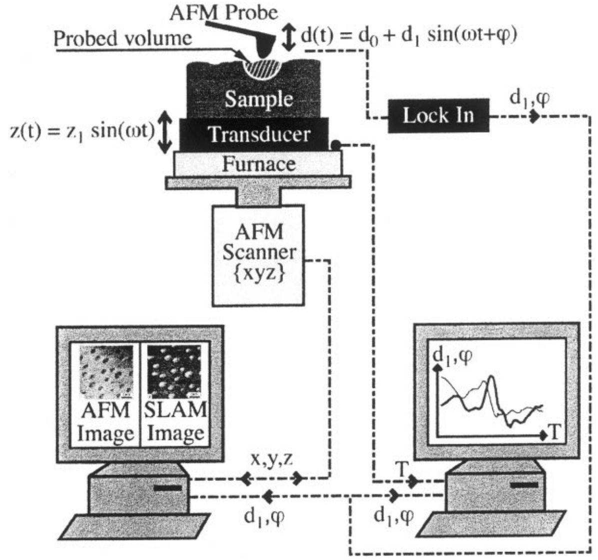

Fig. 1. Schematic of the instrumentation. The transducer applies a vertical oscillation *z(t)* to the sample, and the cantilever response *d*(*t*) is recorded. The cantilever response has an amplitude d_1 and a phase φ. For the spectroscopy mode (local DMA), the nominal position of the sample is held constant, and the temperature is ramped by the furnace. For the imaging mode of data acquisition (T-SLAM), the temperature is held fixed, and the AFM scanner is moved in a raster pattern.

2. Technique

Fig. 1 presents the instrument's operating principles. The transducer applies a vertical oscillation *z(t)* to the sample, and the cantilever response, *d(t)*, is recorded. The cantilever response has an amplitude d_1 and a phase φ. For the spectroscopy mode (local DMA), the nominal position of the sample is held constant and the temperature is ramped by the furnace. A thermocouple measures the temperature of the furnace, which may be different from the sample surface. The data are presented as d_1 and φ as a function of the temperature *T*. Because of thermal drift between the cantilever probe and the sample surface, the position of the probe relative to the surface at the beginning of the temperature ramp may be different from its position at the end of the ramp.

For the imaging mode of data acquisition (variable-temperature scanning local acceleration microscopy, T-SLAM), the temperature is held fixed, and the AFM scanner is moved in a raster pattern. The AFM's feedback circuit holds the vertical position of the cantilever constant, and the voltage required to do so forms a standard AFM topography (more properly, constant normal force [11]) image. Simultaneously with the topography measurement, the amplitude and phase of the cantilever are measured by a lock-in amplifier and the lock-in outputs of d_1 and φ are sent to the auxiliary data acquisition channels of the computer. These latter form amplitude and phase images.

For both local DMA and T-SLAM, 1 V of excitation was applied to a PXE 5 transducer (nominal frequency 500 kHz or 1 MHz) at 320–540 kHz. The cantilevers ranged in stiffness from 1.1 to 3 N/m, with eigenfrequencies from 62 to 120 kHz.

As explained in detail in other publications [9,10], the amplitude and phase are not direct measures of the sample's elasticity and visco-elasticity, but rather reveal the stiffness of the contact and the phase difference between the probe's tip and the sample. Thus the measurement is affected by the local topography, the shape and mass of the tip, the stiffness of the cantilever, and the excitation frequency. A frequency just higher than the resonant frequency of the contact is optimal for linearising the system's response to stiffness and for using the inertia of the probe for increasing the strain on the sample, and therefore the sensitivity to stiffness. Still, the amplitude of the cantilever response is directly proportional to the elastic modulus of the sample, and the phase is proportional to both the damping and the modulus. In both cases, the sample roughness must be significantly less than the tip curvature in order that these hold true.

In some fields, the ratio of the energy lost to the elastic energy stored per cycle of oscillation is frequently used to interpret the data. This is the internal friction (IF), and can be represented as [12]

$$\mathrm{IF} = \left(\frac{1}{2}\,\frac{k_\mathrm{e}}{k_\mathrm{c} - m\omega^2}\right)\frac{\sin\varphi}{d_1/z_1},$$

where k_e is the stiffness representing the elastic part of the sample, k_c is the stiffness of the cantilever, *m* is the effective mass of the cantilever, and ω is the excitation frequency. Because we have not yet quantified the oscillatory amplitudes of d_1 and z_1, the IF data reported here are the simplified ratio φ/d_1.

Depending on the background and interests of potential readers, the data acquisition modes that are the subjects of this paper have been called local DMA, local mechanical spectroscopy, scanning local acceleration microscopy (SLAM), or dynamic mechano-thermal analysis by scanning microscopy (D-MASM). It has not been our intention to add profusely to the alphabet soup of names of techniques, but rather to be as descriptive as possible to each group of people who may be interested in our approach. Hence several different names for the same instrumentation may be found in the literature.

This local DMA technique differs from our earlier methods of micro-thermomechanical analysis [13,14] in three ways. First, a normal AFM tip and a heating stage are used, rather than a thermal probe. Thus, the temperature ramp is applied to the whole sample, rather than to a particular region. Second, a mechanical modulation is applied in addition, so that measurements over a range of frequencies are possible. Third, in the imaging mode of data acquisition, image contrast depends on variations in the dynamic mechanical response.

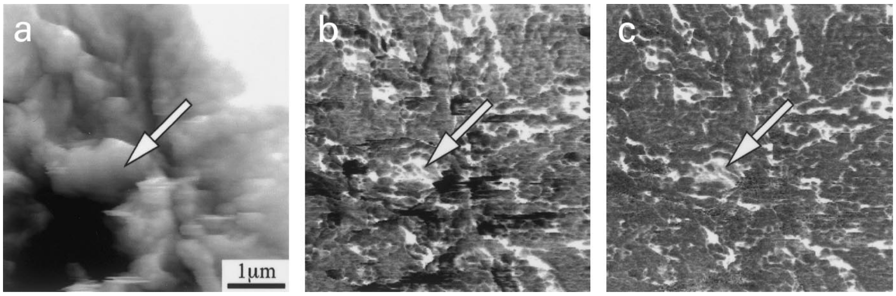

Fig. 2. (a) Topography, (b) amplitude (∼elasticity), and (c) phase (∼visco-elasticity) simultaneously acquired images of PES/SAN. The scale bar applies to all three images.

3. Samples

Two polymer blends were studied in the T-SLAM (imaging) mode. They were PES/SAN and PS/PMMA. A first set of images taken on an untreated sample revealed little contrast across the surface. Frequently one species of polymer preferentially segregates to the surface of a blend. After polishing the sample with 4 μm SiC particles to obtain a “bulk” face, good contrast in the amplitude and phases images was obtained. PES/SAN was chosen because its anticipated small domain size would be a good test of the lateral *resolution* of our system.

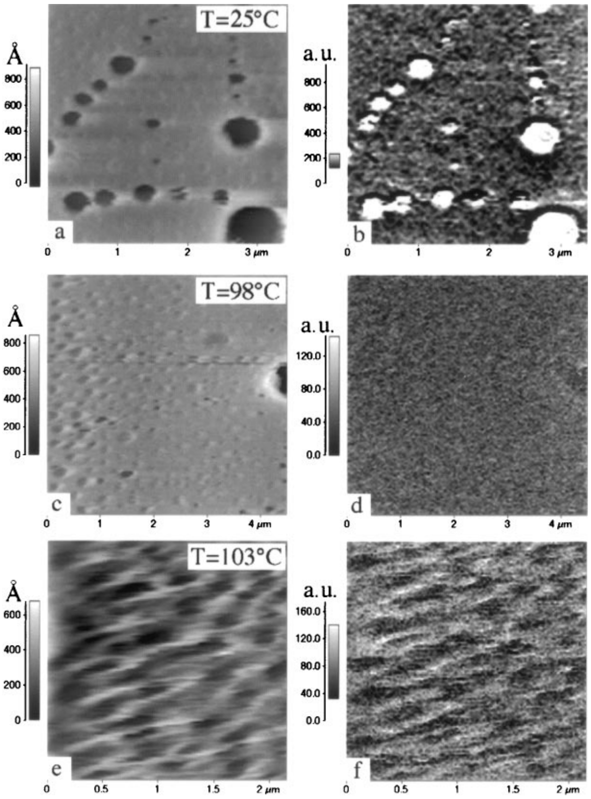

Fig. 3. The left-hand images are topography of PS/PMMA on glass; the right-hand ones are simultaneously acquired amplitude (∼elasticity) images. The top set were taken at 25°C, the middle at 98°C, and the bottom at 103°C. Because of thermal drift, the three sets of images represent similar, but not the same, locations. The scan ranges are slightly different.

The combination of PS and PMMA was selected because both are amorphous materials with very similar glass transition temperatures—near 100°C for PS and near 118°C for PMMA. Their elastic properties at room temperature are expected to be very similar, and therefore this combination of polymers is a good test of the *sensitivity* of our system. Above 100°C, the PS becomes very viscous, and the contrast between the phases should be easy to detect. This sample was prepared by spin coating.

Because of the possibility of drifting from one constituent of a sample to another during a temperature ramp, four homogeneous samples were characterised by the local DMA (spectroscopy) mode. They were: glass (to serve as a reference), PS, PMMA, and PTFE. The amorphous materials, PS and PMMA, should show glass transitions within the temperature range of the instrument (20–380°C). A secondary relaxation should be observed in PMMA, but not in PS. Amorphous regions of the semicrystalline material, PTFE, have a glass transition near 127°C. This choice of test samples was thought to be *representative* of a wide range of materials [2].

As a *check*, calorimetry was performed on the same polymer materials. With the exception of PTFE, the polymers were subjected to at least one thermal cycle before local DMA was carried out, this being to ensure reproducibility in the local DMA data, whereas calorimetry was performed on as-received samples. As for the PES/SAN sample, the homogeneous polymers were polished with SiC particles. In all cases the samples were held in place on the sample holder with fast-drying glue.

4. Results

The three images in Fig. 2 are the simultaneous topography, amplitude, and phase images of PES/SAN. The scale bar in the topography image also applies to the other two images. In (b), the amplitude image corresponding to elasticity, three different grey levels are observed, suggesting three different phases. The size of the domains is typically 100–200 nm, demonstrating that a lateral resolution of better than 100 nm was achieved. As a function of time, the lateral resolution degraded, implying that some material

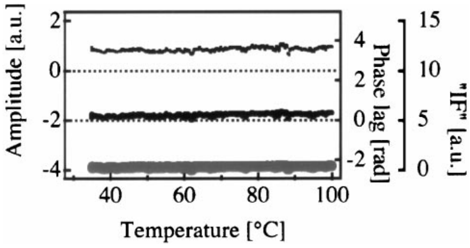

Fig. 4. Local DMA of glass. The topmost curve is amplitude, the middle one phase, and the bottom IF. Amplitude and IF are in arbitrary units.

was sticking to the tip and making its contact with the sample larger. The images shown are the third set of a series at the same location.

Topography and amplitude images of a PS/PMMA blend comprise Fig. 3, with the topography images on the left and the amplitude images on the right. The top set was taken at 25°C, the middle at 98°C, and the bottom at 103°C, over regions in close proximity to each other. The scan ranges differ. The grey scales for the topography images cover approximately the same range; the same holds for the amplitude images. The top two images show holes in the spin-coated film, where the glass substrate is probed by the tip, giving high contrast in the amplitude image. At 98°C, the contrast in the amplitude image degrades to the noise level, whereas some small features can be seen in topography. The bottom images, at 103°C, start to show contrast again because the PS became viscous. The features appear distorted. Indeed, the main limitation of the technique is that the tip damages viscous material. At 118°C, reproducible imaging was no longer possible.

The stability of the instrumentation was checked by collecting spectra of glass as a function of temperature. The amplitude (top) and phase (middle) of the cantilever, and the calculated IF (bottom) are displayed in Fig. 4. No features in the curves are apparent. Ergo, peaks in the polymer spectra can be associated with the behaviour of the sample.

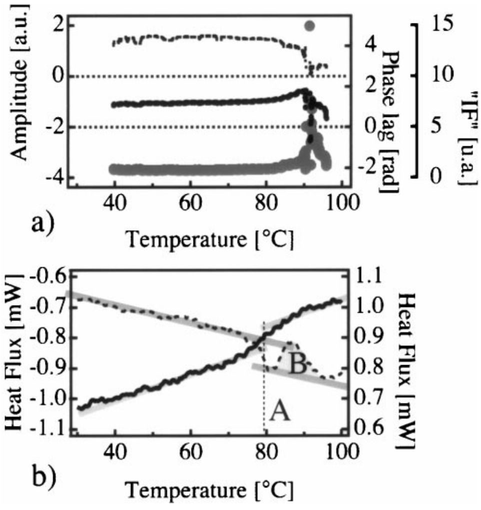

Fig. 5. (a) Local DMA of PS. The upper curve is amplitude, the middle one phase, and the lower IF. A primary relaxation occurs at 92°C. (b) Calorimetry of PS. The dotted curve is heating, the thick curve cooling. An exothermic event is marked “B”, and the transition temperature is denoted as “A”.

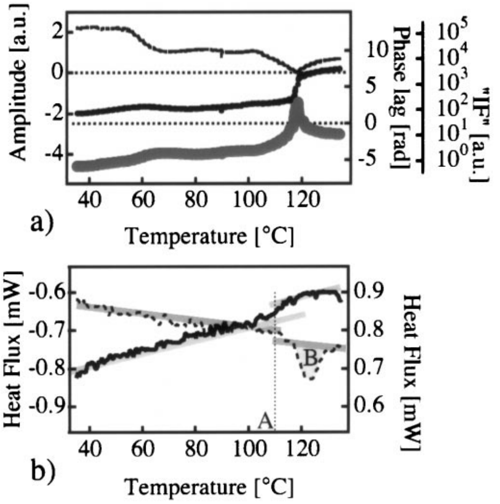

Fig. 6. (a) Local DMA of PMMA. From top to bottom, the curves are amplitude, phase, and IF. The temperature of the primary relaxation is assigned to be 118°C, that of the secondary approximately 60°C. (b) Calorimetry of PMMA. Heating is the dotted curve, the thick curve cooling. The glass transition temperature is indicated as “A”, and an endothermic event is marked “B”.

The local DMA spectra—once again the amplitude, phase, and internal friction—and the corresponding calorimetry data, are shown in Figs. 5–7 for PS, PMMA and PTFE, respectively. Primary relaxations are evident in all three materials in the mechanical spectra. The IF maxima

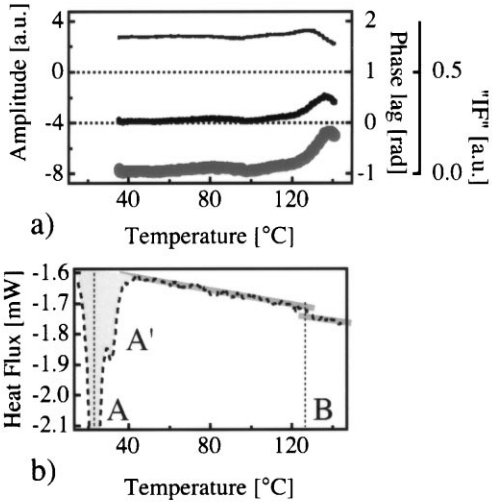

Fig. 7. (a) Local DMA spectra of PTFE. The top curve is amplitude, the middle phase, and the bottom IF. The primary relaxation occurs at 128°C, a small secondary near 80°C. (b) Calorimetry of PTFE upon heating. Two endothermic events are noted, “A” and “A′”. The glass transition temperature is marked “B”.

occur at 92, 118 and 138°C. Smaller secondary relaxations are seen in PMMA and PTFE, appearing at 60 and 80°C, respectively. The secondary relaxation is expected in PMMA and crystalline PTFE**,** but not in amorphous PTFE.

The surface of the semicrystalline PTFE was found to be homogeneous by T-SLAM. It was thus either wholly amorphous or wholly crystalline to the limits of the T-SLAM resolution. In bulk PTFE, the secondary relaxation is usually more significant. Thus, coupled with the sample preparation procedure (polishing), it is thought that the surface is amorphous within the limits of T-SLAM resolution. But the presence of the secondary relaxation indicates some influence of the crystalline phase. It could be that beneath the amorphous surface layer, there was some crystalline material that was probed, as in other studies [9]. Or, small crystalline phases were dispersed near the surface that were too small to be observed by T-SLAM.

The calorimetry data reveal endothermic and exothermic events in addition to steps associated with glass transitions. The temperatures of 78, 110, and 128°C were assigned to the T_g of PS, PMMA and PTFE, respectively. In all cases, the IF peaks, corresponding to T_α, were at higher temperatures than T_g. However, the expected temperature shift of 40–50°C between T_g and T_α due to the high excitation frequencies [1,2] was not observed. Clearly further work is required to obtain a full understanding of the effects of the different methods of probing the sample properties, surface effects and differences between the nominally similar systems that have been examined.

5. Discussion

The lateral resolution of T-SLAM is better than 100 nm, as evident from Fig. 2. The sensitivity to elastic modulus is not currently high enough to distinguish between two amorphous polymers with similar transition temperatures when they are both glassy, but easily detects the difference in stiffness between PS, PMMA and the glass substrate. Contrast returns when one of the materials becomes rubbery. The ultimate resolution that one could expect is of the order of a few nanometers, which corresponds to the best AFM resolution in typical laboratory conditions [3]. At present, the amplitude and phase images are qualitative. Quantitative amplitude and phase images would require that the oscillatory amplitudes of the sample and tip be calibrated, and the shape of the tip be well known. The same applies to the spectra.

The spectra reveal both primary and secondary relaxations, although at present the reason(s) for the discrepancies in transition temperatures is (are) not understood. Even so, the spectra are unique to the sample. Thermal drift prevented the collection of spectra at a fixed point on the sample surface, which is an exciting prospect for this technique. If the thermal drift could be reduced by a factor of ten, to 5 nm/°C, then spectra at a “fixed point” would become feasible for submicron domains.

A limitation of T-SLAM and local DMA is that it seems that the sample can stick to the tip. Treating the tip before use may be a way to ameliorate this problem. A bigger limitation is that T-SLAM and local DMA are non-destructive only for glassy polymers. The tip remains in continuous contact with the surface, and the entire sample is heated. Alternatives could include using the instrument in the less destructive intermittent-contact mode [15] or locally heating the sample with the tip [13,14], in which case only a small volume of the sample would be damaged. The disadvantage of intermittent-contact mode is that it is difficult to interpret [15]. A new mode of operation could be developed that would remove the tip from the surface for the scanning motion, then place it on the surface for the T-SLAM measurement.

6. Conclusions

Primary and secondary relaxations in polymer blends were observed as a function of temperature using a modified AFM. In the imaging mode of data acquisition, the lateral resolution is better than 100 nm, though ultimately one could expect the lateral resolution to be a few nanometers. In the spectroscopic data acquisition mode, the lateral resolution is limited by thermal drift, which is currently 50 nm/°C, and the accuracy of the temperature measurement is approximately ±5°C. The spectra showed features unique to each sample. In future instruments, the accuracy and the drift may be improved by up to a factor of ten, and the vertical displacements, thus the elastic and visco-elastic properties, quantified.

Acknowledgements

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