

An Application of Micro-Thermal Analysis to Polymer Blends

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ABSTRACT: Micro-thermal analysis (micro-TA) is a new subsurface thermal analysis technology. The average of the DC signal is a function of the thermal conductivity, and the response to the AC modulation signal is a function of the thermal diffusivity of the subsurface. Using this technique, three images based on topography, thermal conductivity, and thermal diffusivity are obtained simultaneously. Specific areas and domains in these images can then be characterized by simply positioning the probe and performing a localized thermal analysis experiment. The technique has been used to study the phase separation process in a 50:50 (by weight) polystyrene (PS)–poly(vinyl methyl ether) (PVME) blend and natural rubber–nitrile rubber blends. For these polymer blends, considerable contrast between phases is obtained, based on thermal conductivity, whereas optical and electron microscopy would show them as being very similar. For example, it is difficult to image the morphology of natural and nitrile rubber blends by means of transmission electron microscopy, because of their similar chemical structures. Micro-TA gives an excellent image of the morphology of these natural–nitrile rubber blends. This opens a new way for rubber industries to study morphologies of rubber–rubber blends in general. In the 50:50 PS–PVME blend, annealed at 125°C, spinodal decomposition occurred. With increasing time, the domain size and the glass transition temperature of PS-rich domains increased, indicating that the concentration of PVME in the PS-rich phases decreases. The results imply that micro-TA can be used to image the composition in the near-surface or surface regions in multicomponent materials, if the resolution is high enough. © 2001 John Wiley & Sons, Inc. *J Appl Polym Sci* 81: 2136–2141, 2001

Key words: polymer blends; thermal analysis; micro-thermal analysis

INTRODUCTION

Thermal methods of analysis, such as differential scanning calorimetry and dynamic mechanical thermal analysis, are widely used for the characterization of polymer materials.¹ Many types of commercial polymer materials are multicompo-

nent and phase separated. The results from conventional thermal analysis measurements describe the sum of all of the constituents in the sample. For adhesion studies, information on surface and subsurface structures is required.² Enhancement of the concentration of one component at the surface in certain polymer blends has been found.^{3,4} In this case, the thermal behavior of surface and subsurface regions cannot be obtained by means of conventional thermal analysis, which responds to the composition of the entire sample.

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Thermal probe schematic

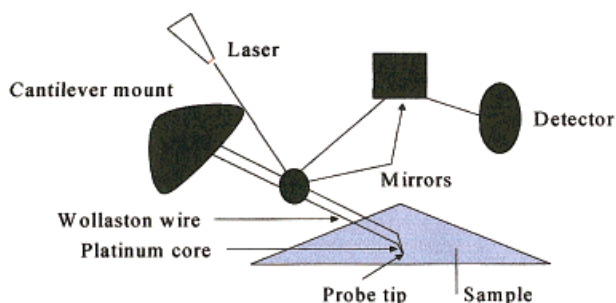


Figure 1 Schematic of micro-TA instrument. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

Transmission electron microscopy is also widely used for the characterization of morphology of polymer materials. However, it is difficult to characterize the morphology of rubber–rubber blends, because of the similar chemical structure of the constituent polymers. Staining generally produces little image contrast.

Micro-thermal analysis (micro-TA) combines the imaging capabilities of atomic force microscopy with the characterization capability of thermal analysis.^{5–9} As the probe scans the surface (Fig. 1), it is deflected by changes in surface topography. A laser beam is reflected by a mirror on the probe to a photodetector. Changes in probe

position will generate a change in voltage at the photodetector. These voltage changes are used to generate digitally a picture of the topography of the sample. Additionally, micro-TA images the thermal conductivity and thermal diffusivity of the subsurface regions. This is accomplished through the use of a patented probe design that incorporates a tiny resistance thermometer made from a Wollaston wire, enabling the probe to act, simultaneously, as a heater and a thermal sensor. While scanning the surface to make the topographical measurements described above, the temperature of the probe is modulated by a few degrees at frequencies in the kilohertz range. The average of the DC signal is a function of the thermal conductivity, and the response to the AC modulation signal is a function of the thermal diffusivity of the subsurface. Using this technique, three images based on topography, thermal conductivity, and thermal diffusivity are obtained simultaneously.^{7–9} The images are then used to select specific areas that can be characterized simply by positioning the probe and performing a localized thermal analysis experiment.

In this short communication, an application of micro-TA to the phase separation process in a 50:50 (by weight) polystyrene (PS)–poly(vinyl methyl ether) (PVME) blend and to natural rubber (NR)–nitrile rubber (NBR) blends are re-

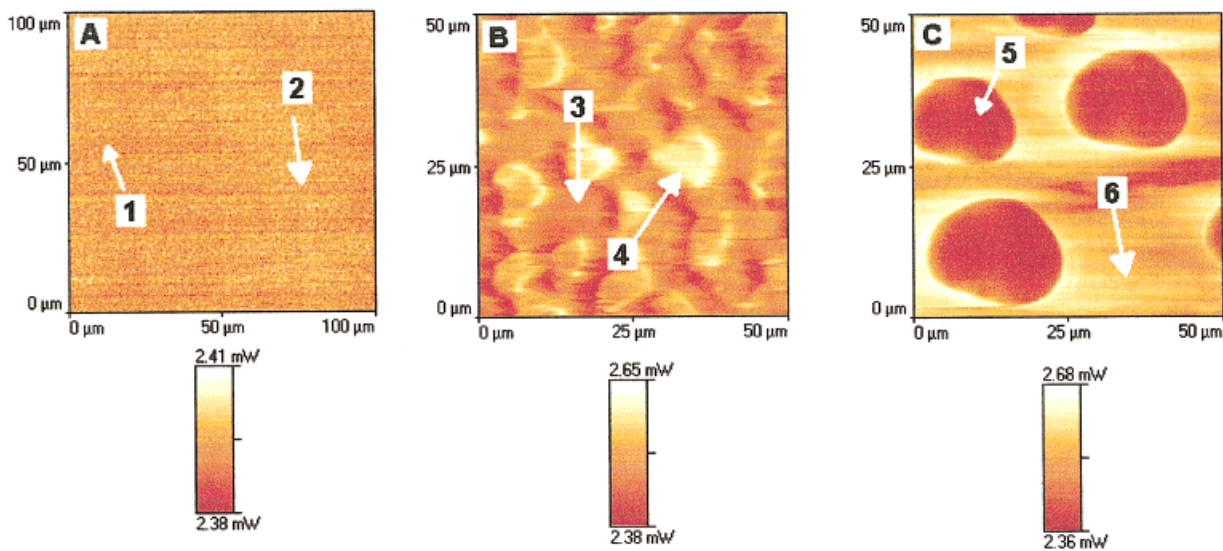


Figure 2 Thermal conductivity contrast images of the 50:50 (by weight) PS–PVME blend at different phase separation times. The phase separation temperature was 125°C. (A) As-prepared film, (B) after 20 min, and (C) after 65 min. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

ported. The aim was to demonstrate the capability of micro-TA to characterize the morphology of rubber-rubber blends and to measure concentration in phases in subsurface regions.

EXPERIMENTAL

Sample Preparation

PS-PVME blend 50:50 (by weight): PS ($M_w = 2.44 \times 10^5$, $M_w/M_n = 4.9$) and PVME ($M_w = 0.91 \times 10^5$, $M_w/M_n = 5.3$) were obtained from Aldrich (Gillingham, UK). The 50:50 (by weight) PS-PVME blend was prepared by dissolving both polymers in chloroform. The concentration was 5%. The solution was cast on a cover glass and the solvent was allowed to evaporate slowly. The film was then kept under vacuum at 40°C for 1 week. The thickness of the film is about 150 μm .

NR-NBR blends: NR ($M_w = 8.60 \times 10^5$, $M_w/M_n = 50.6$) was kindly provided by EniChem Elastomers Ltd. (Southampton, UK). NBR (30 wt % of acrylonitrile) ($M_w = 1.66 \times 10^5$, $M_w/M_n = 4.3$) was obtained from Aldrich. Mechanical blending of the NR with NBR was performed by using a Haake Rheochord. A total charge of 50g was used. The rotor speed was 80 rpm and the temperature was 138°C. The NR was added first and masticated for 30 s. The NBR was then added and blended for a further 9 min before removal of the hot blend from the mixing chamber. Then, the NR-NBR blend was mixed with 0.1 wt % of dicumyl peroxide using the Haake Rheometer at

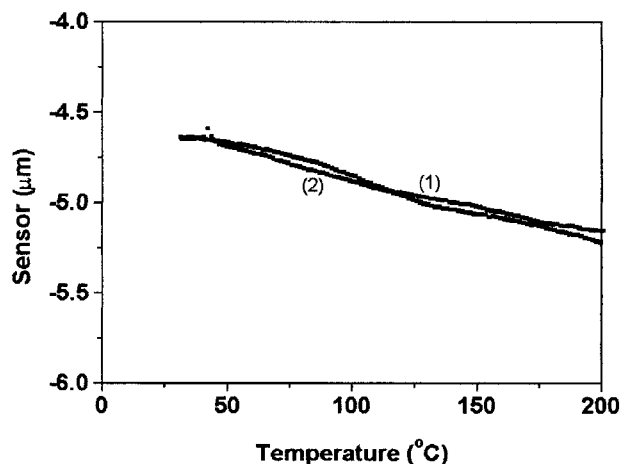


Figure 3 Sensor height position response versus temperature. These curves correspond to the locations indicated in Figure 2A.

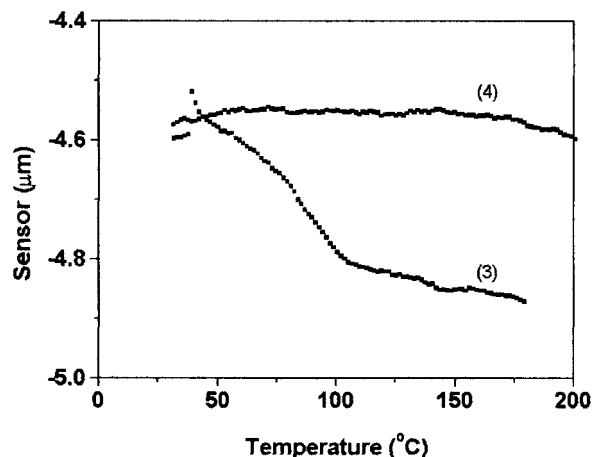


Figure 4 Sensor height position response versus temperature. These curves correspond to the locations indicated in Figure 2B.

80°C for 15 min, and pressed into sheet and vulcanized in a hot press at 160°C for 20 min. The thickness of the sample for micro-TA analysis is about 1 mm.

All of the above molecular weights and distributions were determined by gel-permeation chromatography, calibrated using PS standards.

Instrumentation

The instrument used in this work was a TA Instruments micro-TA 2990 Micro-Thermal Analyser based on the TopoMetrix Explorer TMX2100 scanning probe microscope. For the observation of morphology, the probe was held at room temperature. For the localized thermal analysis, a heating rate of 20°C/min, a frequency of 10 kHz, and amplitude of $\pm 3.0^\circ\text{C}$ were used. Temperature was calibrated by using standard PS.

RESULTS AND DISCUSSION

Figure 2 shows thermal conductivity contrast images of the 50:50 (by weight) PS-PVME blend at different phase separation times. The phase separation temperature was 125°C. The dispersed phase [Fig. 2(C)] has lower thermal conductivity than the matrix. As prepared, the sample did not show any thermal conductivity contrast because the polymer pair formed a miscible blend¹⁰ under these conditions. With increasing time at 125°C, phase separation occurred. The morphology shown in Figure 2(B) is a typical spinodal decom-

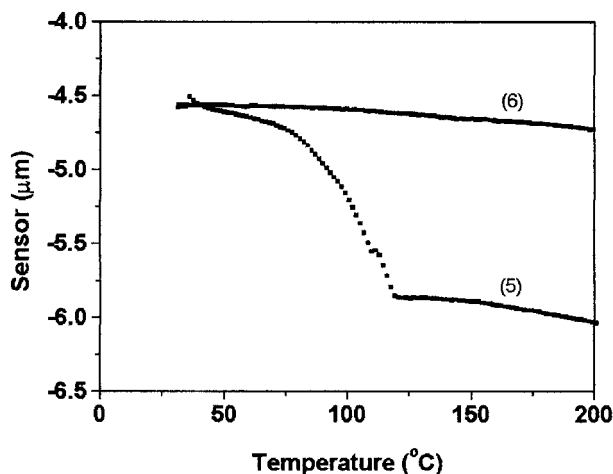


Figure 5 Sensor height position response versus temperature. These curves correspond to the locations indicated in Figure 2C.

position one. With increasing phase separation time, PS formed the dispersed phase.

For localized thermal analysis, the probe is placed at a selected point on the sample surface and the temperature of the probe ramped as in conventional thermal analysis. The *z*-axis deflection of the probe is monitored as a function of the probe temperature.⁹ This technique represents the microscopic equivalent of thermomechanical analysis.¹¹ Four signals can be measured: the sensor height position, the differential DC power required to change the probe temperature, and the differential AC power and phase. Figures 3–5 show sensor height position response versus tem-

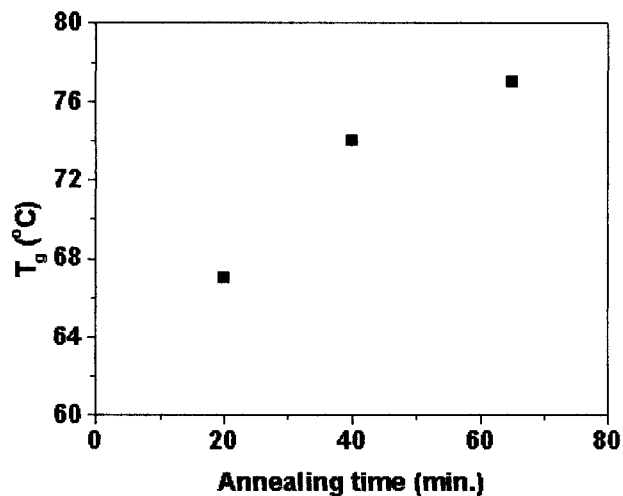


Figure 6 Glass transition temperature versus phase separation time for the PS-rich phase.

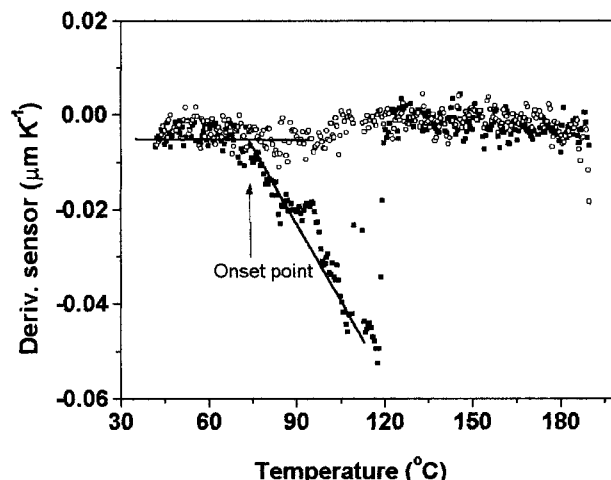


Figure 7 Determination of the glass transition temperature.

perature. These curves correspond to the locations indicated in Figure 2. The glass transition temperatures are indicative of the PS and PVME in the film. Curves 1 and 2 shown in Figure 3 are typical of PS–PVME miscible blends. Curves 3 and 4 in Figure 4, and curves 5 and 6 in Figure 5, are typical of PS–PVME phase separation. The curve 3 shown in Figure 4 and curve 5 shown in Figure 5 describe the glass transition behavior of the PS-rich phase. Curve 4 in Figure 4 and curve 6 in Figure 5 are related to the PVME-rich phase. Figure 6 shows the change of the glass transition temperature of the PS-rich phase (selected points) with phase separation time. The glass transition temperature is the onset point of differential of the sensor with temperature (illustrated by Fig. 7). With increasing time, the glass transition tem-

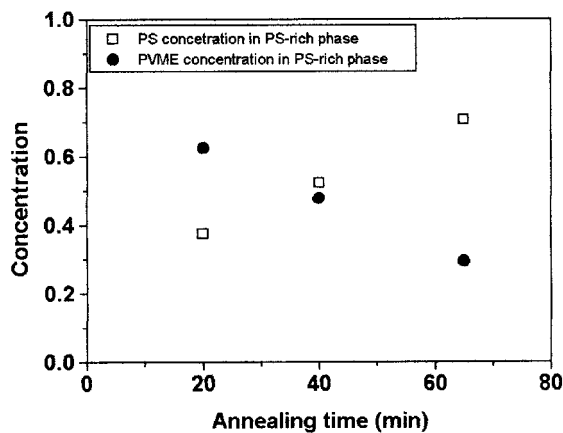


Figure 8 Concentration in the PS-rich phase in sub-surface region versus phase separation time.

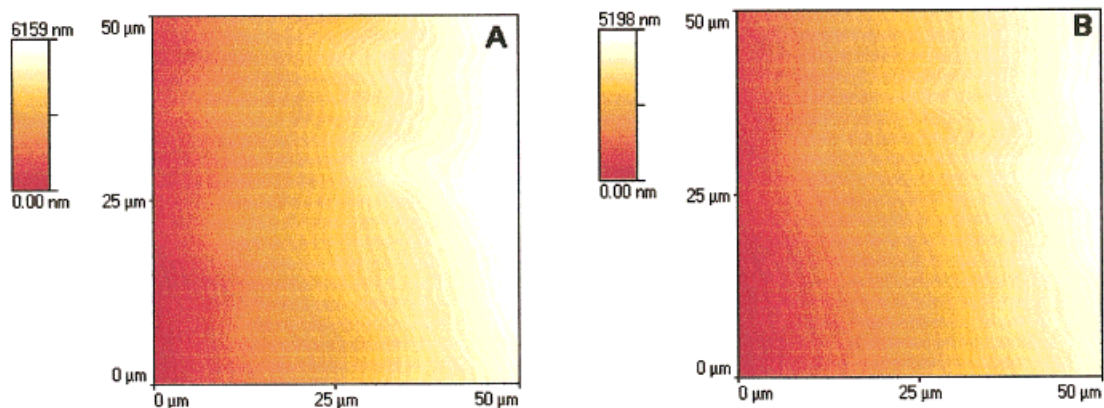


Figure 9 Topographic images of the NR–NBR blends. (A) 30 wt % of NBR and (B) 40 wt % of NBR. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

perature increases as expected in a phase separation process.

As surface enhancement in polymer blends has been fairly widely reported,^{3,4} micro-TA measurements should provide very useful information on the change of concentration in the subsurface regions of polymer blends. For miscible polymer blends, the following simple equations¹² for the glass transition temperature hold:

$$T_g = \omega_1 T_{g1} + \omega_2 T_{g2} \quad (1)$$

$$\omega_1 + \omega_2 = 1 \quad (2)$$

T_g is the glass transition temperature of the blend. T_{g1} and T_{g2} are the glass transition temperatures for polymer 1 and polymer 2, respec-

tively. ω_1 and ω_2 are polymer 1 and polymer 2 concentrations, respectively. According to these equations, we can determine the change of concentration in the subsurface regions as follows:

$$\omega_1 = (T_g - T_{g2}) / (T_{g1} - T_{g2}) \quad (3)$$

$$\omega_2 = (T_{g1} - T_g) / (T_{g1} - T_{g2}) \quad (4)$$

Figure 8 shows the change of concentration of the PS-rich phase in the subsurface region.

Figure 9 shows the topographic images of the 70:30 and 60:40 (by weight) NR–NBR blends. No phase contrast is revealed, i.e., the results do not provide any useful information on the morphology in these blends. Figure 10 shows thermal conductivity contrast images of the same regions of these

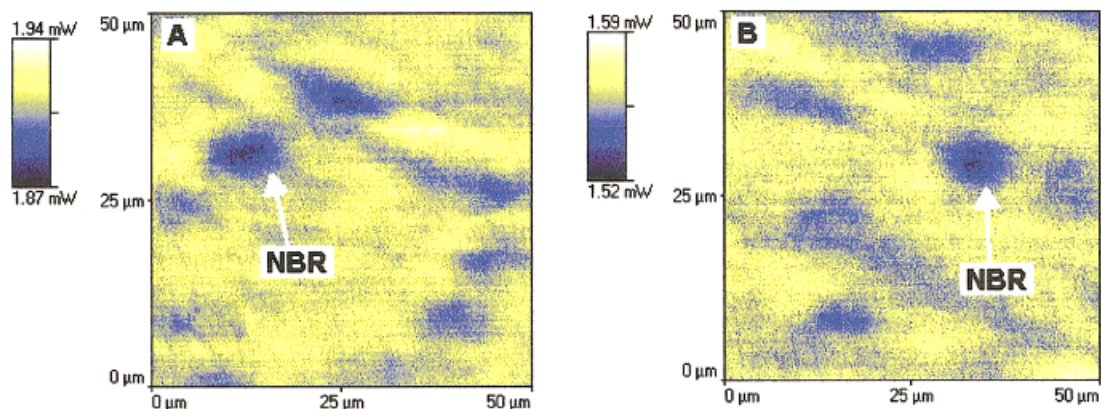


Figure 10 Thermal conductivity contrast images of NR–NBR blends. (A) 30 wt % of NBR and (B) 40 wt % of NBR. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

NR–NBR blends. The dispersed phase is the NBR component, which shows lower thermal conductivity. It is clear that micro-TA gives good images of the morphology for these natural–nitrile rubber blends. The domain size range of the NBR phase is from 10 to 15 microns.

In our experience, it is difficult to observe the morphology of NR–NBR blends by transmission electron microscopy because staining provides little image contrast. Micro-TA provides excellent image for the morphology of these blends. Micro-TA should be a very useful tool to the rubber industry for the study of the morphology of all rubber–rubber blends.

CONCLUSIONS

Micro-TA is a new subsurface thermal analysis technology, which can be used to study the thermal behavior of subsurface regions in polymer blends. Using this technique, three images, topography, thermal conductivity, and thermal diffusivity, can be obtained simultaneously. Micro-TA should prove to be a useful tool for the rubber industry in the study of the morphology of rubber–rubber blends.

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