nano-TA™: Nano Thermal Analysis

Application Note #5
Heated tip-AFM of nanocomposite Polymer Membranes
Authors: Jason Killgore and Professor René Overney Ph.D
Department of Chemical Engineering, University of Washington

Introduction

Nanocomposite Polymer Membranes: Unlike traditional composite materials whose properties are influenced largely by the constituent components, nanocomposites exhibit such large specific surface areas that interfacial properties can significantly affect bulk behaviour. Poly trimethyl silyl propyne (PTMSP) has garnered attention since its discovery due to its very high permeability, high Tg and exhibited reverse selectivity[1, 2]. However, it was the discovery that the permeability and reverse selectivity could be significantly enhanced by the addition of silica nanoparticles that has generated most recent interest in the material[3-7]. This enhancement was particularly significant because it contradicted the Maxwell equation which predicts a reduction in permeability with the addition of an impermeable phase. Further studies on filler size and surface chemistry suggested that the addition of silica resulted in an increased fractional free volume in the polymer[8]. While the importance of the nanoscale PTMSP-Silica interface has been acknowledged, most of the data currently published is based on macroscopic and microscopic measurements and little is known about the local nanoscale properties of the material. Complex organic systems such as these are particularly well suited for bottom-up, molecular design approaches. In solid state form, these systems are known to exhibit bulk deviating material and transport properties due to finite size limitations and interfacial constraints. Practical examples are found in photonics, light emitting diode materials, nanoelectromechanical systems (NEMS), and organic and inorganic hybrid systems, such as nanocomposites.

A common way to gain fundamental insight into material and transport properties is to perform both a structural and a relaxation analysis. However a big challenge lies in obtaining convenient access to the molecular mobility of material arrangements that are interfacially-constrained. Generally, the molecular mobility is not directly accessible for constrained systems with

spectroscopic methods. The availability of the nanoscale thermal probes enables us to directly access the interface and characterize the polymer via the Heated Tip-AFM mode (a term that we define below).

The aim of this work was to use HT-AFM for the following:

1. To use nano-thermomechanical analysis to locally probe the heterogeneous nanocomposite membrane films.
2. To characterize the interfacial interaction between the dispersed nanoparticles and the polymer matrix by determining the shear forces

Heated Tip AFM (HT-AFM) refers to any AFM operation where a heated tip is used instead of a normal tip. Nearly any AFM mode (tapping/contact/Force-Volume etc.) can accommodate a heated tip to yield new information tied to the thermal properties of the sample. Compared to substrate heating methods, HT-AFM offers some distinct advantages. Foremost is the ability to heat to higher temperatures. With substrate heating, significant warming of the materials in contact with the sample occurs which can include the piezoelectric crystal used for scanning. This can cause problems with the calibration of the scan as well as the possibility of damage to the scanner at high temperatures. Another advantage with the heated tip is that it has much less thermally induced drift. With substrate heating, spatial displacements of many microns are observed over relatively small temperature ranges. With the heated tip, displacements of less than a micron are observed over hundreds of degrees. Other advantages include the ability to operate at very high heating rates due to the low thermal mass, and the ability to perform multiple measurements on specimens that are highly sensitive to thermal history.

nano-TA is a local thermal analysis technique which combines the high spatial resolution imaging capabilities of atomic force microscopy with the ability to obtain understanding of the thermal behaviour of materials with a spatial resolution of sub-100nm. The conventional AFM tip is replaced by a special nano-TA probe that has an embedded miniature heater and is controlled by the specially designed nano-TA hardware and software. HT-AFM enables a surface to be visualised at nanoscale resolution with the AFM's routine imaging modes which enables the user to select the spatial locations at which they would like to investigate the thermal properties of the surface. The user then obtains this information by applying heat locally via the probe tip and measuring the thermomechanical response.

Experimental Setup

The results were obtained using an Explorer AFM with custom drive electronics. The nano-TA data presented are of the probe cantilever deflection (whilst in contact with the sample surface) plotted against probe tip temperature. This measurement is analogous to the well established technique of thermo-mechanical analysis (TMA) and is known as nano-TA. Events such as melting or glass transitions that result in the softening of the material beneath the tip, produce a downward deflection of the cantilever. Further information on the technique can be obtained at www.anasysinstruments.com.

Sample Preparation

Poly(trimethylsilylpropyne), PTMSP, with >95% purity was obtained from Gelest, Inc. 200nm diameter silica particles were prepared by mixing 200 ml anhydrous ethanol, 6 ml tetraethyl orthosilicate and 12 ml of 30 wt% ammonia in water in a glass beaker. The solution was stirred for 12 hours, then dried and redispersed in toluene. Trace amounts of the silica-toluene dispersion were mixed with pure toluene to produce a dilute silica-toluene dispersion. PTMSP was added to the silica-toluene dispersion to make a 3 wt% solution. The solution was spin cast onto a glass substrate, producing film thickness of ~1µm.

Results and discussion

nano-TA on the PTMSP membrane revealed a Tg of 190 °C using a 60 °C/min heating rate. Figure 1 shows a surface plot of the thermomechanical analysis hole pattern from the scan. The tip radius is approximately 50 nm and local heating area prior to tip penetration is less than 100 nm. Due to the relatively fast heating rate, tip penetration occurs quickly after Tg. The lack of thermal drift in the technique is evident by the symmetry of the hole. Figure 1 shows the results of nano-TA on this sample to be a 130nm deep hole with a 35nm rim. The rim to rim diameter is ~500nm.

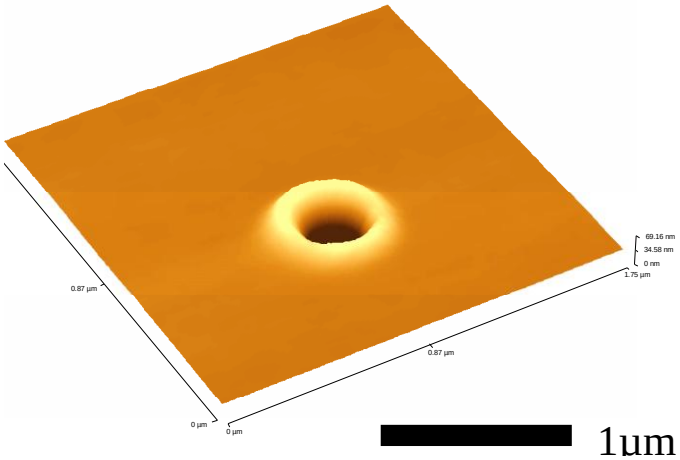

Fig. 1. nano-TA on PTMSP

When operating the heated tip in scanning mode, the tip is constantly moving, and the sample never reaches thermal equilibrium with the tip. As a result, it is possible to scan with the tip above the Tg of the material without initiating a thermal transition at the surface. The actual

temperature at the surface depends on contact resistance, tip temperature, and scan speed. Figure 2 below shows a series of heated tip scans on a PTMSP composite taken at tip temperatures above, but with equilibrium scan temperatures below the Tg of the matrix. The HT-AFM is operated over a region with exposed silica particles, while increasing temperature in 10°C increments with each new scan. When a critical temperature is reached (290°C for the series under investigation), the forces acting on the particle, coupled with potential thermally induced instabilities, are sufficient to debond the particle from the matrix. The lack of matrix deformation around the particle suggests that the debonding occurred below Tg and most likely in an elastic manner.

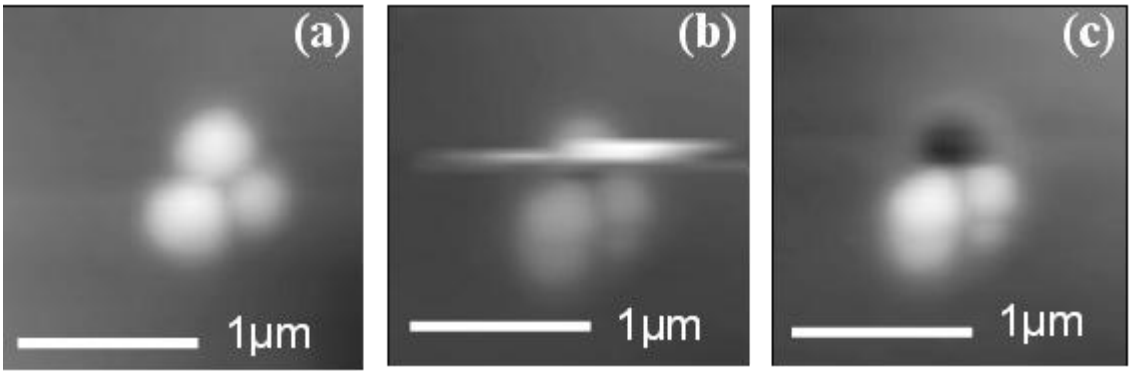

Fig. 2. Series of scanning heated tip images taken at tip temperatures at 220 °C (a), 290 °C (b) and 300°C (c). The streaking in image b shows the debonding event and subsequent dragging of the particle.

The lateral forces associated with debonding were determined by investigation of the lateral force microscopy signal. Figure 3 shows a characteristic lateral force scan. The large peak is associated with the torsional deflection of the cantilever as the tip contacts the particle. Eventually, the tip slides past the contact point and a slight decrease in friction relative to the matrix is observed. The dependence of the lateral force on temperature, for another thermally debonded particle, was determined by finding the local L-R signal maximum at the polymer-particle interface from the series temperature scans. As shown in Figure 4, increasing temperature leads to an increasing peak lateral force on the particle. Impact force is relatively constant below Tg, but increases significantly as the tip temperature is increased above Tg. The maximum observed force at 10°C below the debonding temperature was 220nN. The temperature dependence is likely associated with the increased time the tip spends at the particle interface as a result of the deforming lever. This increased time would allow for a locally higher equilibrium temperature at the interface, and could be a sufficient initiator for debonding.

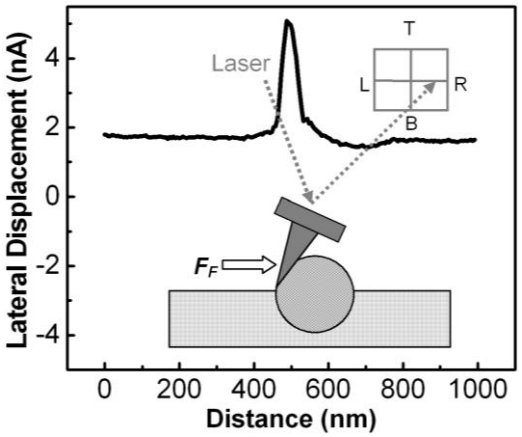

Figure 3: Characteristic forward friction scan across stable silica particle when scanned with heated tip.

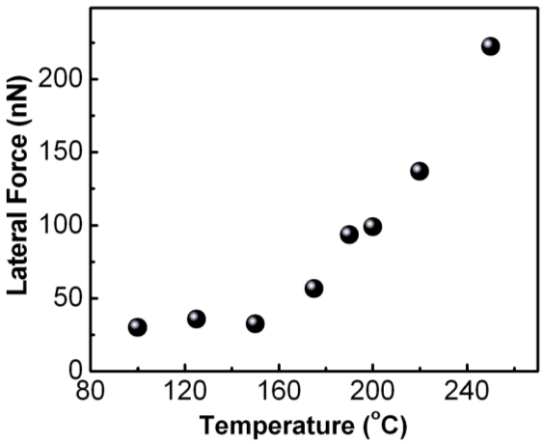

Figure 4: Maximum lateral force subjected to particle as a function of temperature.

Conclusions

HT-AFM was used to identify the matrix Tg of the composite film, while also acting as a manipulating tool for investigating the lateral forces exerted during particle-matrix debonding. By studying the particle matrix adhesion, it may be possible to design the interface for optimum reverse selective membrane properties.

References:

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