Abstract
This note describes the application of nanoTA in the examination of a SAN/PC polyblend. The probe tip heats the sample locally at 25°C/sec while simultaneously monitoring the softening as the sample undergoes a glass transition Tg. Transition Temperature Microscopy is used to map mixing behavior and variations in phase composition originating at the nanoscale. Pure SAN and PC domains had lateral dimensions on the micron scale.

Introduction
Polymers are tailored to suit the most demanding applications on Earth, in space, and even in the human body. The engineering of material properties is accomplished primarily through the mixing of chemistries and the manipulation of structure. Sometimes in two identical compositions different morphology may arise. Factors influencing morphology may include processing conditions, molecular weight (MW) distribution, impurity, and lot to lot variation. In most applications, a reliable understanding and control over a given morphology accelerates research and can enhance output. High resolution morphology and structural organization define the overall bulk properties [1]. Transition Temperature Microscopy (TTM) is used to measure compositional variations in an amorphous polymer blend composed of polycarbonate (PC) and styrene-acrylonitrile (SAN). The $T_g$ of SAN and PC was measured by DSC to be $115\pm6°C$ & $149\pm6°C$ respectively (figure 1).

Thermal analysis methods will detect a single glass transition temperature in a binary blend if the two components are miscible. If the components are not miscible then there will be an individual Tg for each. In some non-miscible polymer blends the lower Tg is shifted higher in temperature than found in its pure state while the component with the higher Tg is lowered from its pure component Tg. In this
case there is some mixing between the major phases [2].

![DSC heating curves](image1)

**Fig 1.** DSC heating curves at 15° C/min of styrene-acrylonitrile copolymer (SAN), polycarbonate (PC), and their apparent blend.

**afm+™ Imaging**

The structural morphology of a blend is a product of compositional variations formed in the micro-nano scales. Atomic Force Microscopy produces high resolution images of the sample topography by monitoring the physical displacement of a cantilever interacting with a sample surface. Phase separation is observable in immiscible or partially miscible blends. High resolution imaging provides useful information pertaining to the domain size and morphological character.

![Height image](image2)

**Fig 2.** A 25 x 25um afm+ height image of a styrene-acrylonitrile copolymer (SAN), polycarbonate (PC) blend showing phase separation with domains ranging in size between 0.5-5um

**nanoTA Property Measurement**

The Thermalever™ probe adds direct property measurement to the imaging capabilities of the afm+ system. The cantilever probe is locally heated in contact with a feature on the sample. Displacement, resulting from local thermal expansion, captures thermal events such as glass or melt transitions via a particular regions softening temperature. Initially the probe deflects upward followed by a drastic change in slope as the thermal probe is no longer supported by the softened surface. In effect, the transition temperature enables characterization of the structural composition of surface features with <100nm lateral resolution. Softening temperature measurements are good indicators of molecular weight, crystallinity, blend composition, stress, and other structural-chemical properties.

![Thermalever curve](image3)

**Fig 3.** nanoTA curves identifying the softening transition for <500nm domains as visualized in the afm+ topography.

**Transition Temperature Mapping (TTM™)**

nanoTA extends into an imaging mode whereby an automated array of measurements maps the variations in softening temperature across a user defined region. In polymer blends this enables rich structure property correlation and visualization of surface composition. The example below shows a polymer blend with the two major phases distributed in varying
composition across the surface. Pure SAN domains are depicted in green & pure PC domains are depicted in red; their respective transition temperatures are 115°C & 149°C. The continuous phase is composed of a heterogeneous blend of the two components. The transition temperatures of the mixed phase vary anywhere in between that of the two pure phases.

Ultra-fast heating rates up to 600,000°C/min allow high throughput data acquisition and ‘as received’ characterization of samples. This is important in the study of copolymer blends whereby conventional bulk heating rates sometimes allow demixing of the components due to thermal perturbations.

Furthermore the <100nm resolution of local heating adds a spatial dimension to thermal analysis making the technique more suitable to the investigation of local properties like interfaces, surface effects, unwanted precipitates or contaminants.

**Conclusions**

NanoTA unambiguously identifies SAN and PC domains in a polymer blend. Although the two major amorphous phases are not miscible, Tg shifts indicate partial miscibility exists in this polyblend. The color coded TTM transition map visualizes heterogeneous mixing of SAN and PC into a continuous domain. A pure phase of constituent polymers still exists in micro and nano scale domains.

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**References**

