Introduction
Organic polymeric materials are widely used as coatings in a variety of markets and applications, primarily to improve surface properties, appearance and performance. These applications are becoming more sophisticated, and due to the multivariate nature of coatings, their decreased dimensions often produce layers of polymers having different properties. In addition, the viscoelastic nature of most polymers leads to a marked time and temperature dependence on performance [1].
Chemically crosslinked coatings have evolved as the materials of choice and are commonly employed as automotive clearcoats to protect against environmental influences and provide scratch, mar and chip resistance, as well as corrosion and solvent resistance, while still maintaining a high gloss and appearance [2]. The addition of chemical additives to improve photostability, coupled with variable crosslinking reactions, often produce heterogeneities ranging in size from nanometers to microns that are more susceptible to degradation [3,4]. The Atomic Force Microscope (AFM) has proven to be invaluable for not only imaging polymeric systems [5], but for probing tip/sample interactions, (as in phase imaging) for mapping mechanical (elasticity, hardness, etc) and chemical properties [6,7].
The nano-TA from Anasys Instruments adds a new and valuable capability of spatially resolved thermal analysis to the AFM. It is particularly useful for thin films since it enables the measurement of transition temperatures (melting or glass) on selected spots of the sample aiding in the identification and characterization of the phases.

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. (a breakthrough in spatial resolution ~50x better than the previous state of the art, with profound implications for the fields
of Polymers and Pharmaceuticals). 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. The AFM enables a surface to be visualised at nanoscale resolution with its routine imaging modes, which allows the user to select the spatial locations at which 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**
Experiments were performed using a Veeco Dimension 3000 AFM equipped with an Anasys Instruments (AI) nano-TA module and AI nanoscale thermal probes. The heating rate used for this analysis was 2 °C/s. All images were recorded using tapping mode AFM. 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). 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. In order to confirm the tested points of interest, images are routinely recorded after performing the temperature ramp. The nano-TA probes used in this study are the type more typically used for contact mode, due to this the resonance frequency was ~20 kHz, while the typical resonant frequency would be more around 60 kHz. The probes were still capable of achieving height and phase images with sufficiently high spatial resolution to resolve polymer lamellar structures. Height images (fig. 1A) often show the presence of mounds of material associated with indentations. This deposit is most likely polymeric material that collects and solidifies around the tip after performing a local thermal analysis.

Two types of coatings were studied, (A) commercial acrylic polyol crosslinked with diisocyanate resin, catalyzed with di-butyl-tin-di-laurate (DBTDL) and cured 30 minutes at 60 C; and (B) weathered acrylic-polyurethane (AU) coatings. The weathered AU coatings consist of styrene-acrylic polymer crosslinked with polymeric 1, 6 hexamethylene diisocyanate and containing two types of TiO2 particles, Degussa P25 (average particle size ~ 20 nm; uncoated and high photoactivity) and R9 (average particle size ~ 250 nm; coated with Al2O3 (6%).

**Results and discussion**
A cross-sectional view of a typical commercial automotive coating (figure 1.) shows the complex, multi-functional nature of these coating systems. Due to the fact that the clearcoat is the first line of defense against environmental influences, understanding surface, near-surface
chemical and mechanical property development as a function of composition, cure time and environmental exposure is fundamental to improving their performance. Furthermore, the increased demand for low VOC systems in automotive refinish industry places greater demands for attaining fast cure at ambient temperature in order to reduce the investment in drying equipment and the time of repair.

Figure 1. Cross-sectional view of a typical automotive coating

The resolution of the tapping mode images produced by the nano-TA probe is comparable to regular non-thermal AFM probes. The sensitivity of the nano-TA technique was investigated using acrylic-urethane coatings. Coatings that were a few weeks old were tested by nano-TA in order to measure the coating's response to a thermal scan and determine the indentation morphology and depth.

Figure 2. Indentation produced by the thermal probe after measurement of softening point of an acrylic clearcoat film.

A topview (Fig 2.) of the acrylic coating after nano-TA testing shows the formation of a residual indent ~350 nm deep. The measured indentation depth provides an estimation of the sampling depth using nano-TA and can serve as a basis for comparison of softening points (Tg) from the same coatings with bulk film measurements by MDSC.

The dependence of the glass transition temperature on heating and cooling rates is well known and shown to be a kinetic effect that is due to a temperature dependence of structural relaxation rates. This temperature dependence also influences the shape of the heat capacity (Cp) near
the Tg. [9]. In particular, experimental measurements showed Tg to depend linearly with the logarithm of the heating rate. In order to test the ability of nano-TA to measure a heating rate dependence of softening temperature using thermal probes, experiments were conducted on acrylic clearcoat films (figure 3A). The three scan rates tested, (6, 10 and 120 C/min) by nano-TA clearly show an increase in softening temperature with increased heated rates and a linear logarithmic rate dependence (RSquare = 0.999), similar to that shown by the bulk DSC measurement (figure 3B).

![Figure 3. Dependence of (acrylic) film softening point on tip heating rate (A). In particular, softening point onset temperature shows a linear dependence on the logarithm of the tip heating rate (B).](image)

We next explored use of nano-TA for measuring cure rates from softening temperature. A coating’s softening point is a good measure of crosslink density [10]. The formation of three-dimensional networks due to chemical reactions is widely accepted as a means of improving a coating’s properties. It has been shown on a variety of clearcoat systems (1K and 2K solvent-borne clearcoat, and 1K and 2K waterborne clearcoat) cured at different times, at different temperatures, all displayed an increase in Tg, with increasing crosslink density [11]. In addition, mechanical properties of coatings also depend on the extent of crosslinks as expressed by the inverse relationship between molecular weight between crosslinks (Mx) and tensile storage modulus (E’) [1].

In order to test the utility of nano-TA for measuring cure rates, softening points of commercial acrylic coatings cured for 30 minutes at 60 C, were tested from 2 hrs to 72 hrs, after the 30 min. cure at 60 C. Figure 4 shows a gradual increase in measured softening temperature with time. A plot of cure time versus softening temperature shows a linear relationship over the cure times measured.
The next step was to use nano-TA to follow the increase in softening temperature (and crosslink density) as a function of time, 24 and 48 hrs, for select acrylic coatings after their 30 minute bake at 60 C (table 1). Pooling of the measured standard deviations of softening points, made in triplicate, from eight coating systems provided a good measure of the nano-TA test reproducibility. The calculated standard deviation for these coating is 0.26 C (Table 1A).

![Graph showing softening temperature over time](image)

**Figure 4.** Effect of curing time at ambient temperature of acrylic clearcoat on softening temperature (A). The softening temperature displays a linear relationship over the cure times measured (B).

![Table showing softening temperatures](image)

**Table 1.** Increase in softening temperatures as a function of time, 24 and 48 hrs, for select acrylic coatings (A). Bar plot (B)

**Photo-degraded Acrylic-polyurethane (AU) coatings:** These coatings were exposed, 20 weeks and 41 weeks to UV-A and UV-B. They consist of styrene-acrylic polymer crosslinked
with 1, 6 hexamethylene diisocyanate and contain two types of TiO2 particles, Degussa P25 (average particle size ~ 20 nm; uncoated and highly photoactive) and R9 (average particle size ~ 250 nm; coated with Al2O3 (6%). Figure 5 summarizes and compares softening temperatures measured by LTA (figure 5A), in comparison with Tg from MDSC, (figure 5B).

These data clearly show the surface sensitivity of nano-TA, as compared to the bulk Tg measurement using MDSC. A considerable body of knowledge has accumulated on the surface sensitivity of photodegradation processes [12]. It is therefore not surprising that nano-TA provides a sensitive measure of photooxidative effects of UV exposure for clear and TiO2-filled coatings and displays an increase in softening temperature (i.e. crosslink density) with increased UV exposure times. In comparison, the MDSC characterization of the bulk thin film is not capable of differentiating surface effects from bulk and cannot detect the surface chemical and structural degradation suffered by coatings as shown by the scanning electron micrographs from 41 week exposed coatings (figure 5C.).
Conclusions
Nano-thermal analysis in combination with AFM proves to be a very valuable tool for the study of polymeric coatings and surfaces in general, since it allows not only imaging but also direct identification and characterization of the different domains at the sample surface on a 100nm scale. The data clearly demonstrates that nano-TA is more sensitive to surface effects than MDSC which is a measure of the sample averaged or bulk property and hence cannot detect the surface chemical and structural degradation suffered by coatings.

Acknowledgements
The author expresses his gratitude to Drs. Aaron Forster and Stephanie Watson (NIST) for valuable discussions and supply of weathered, acrylic-polyurethane coatings. He also thanks Dr. Deepanjan Bhattacharya and Mr. Chip Williams for supply of acrylic clearcoats.

REFERENCES
12. D. R. Fagerburg, ”Weathering of Polyester and Copolyester Sheeting” Atlast School of Natural and Accelerated Weathering, Miami, FL; April 28, 1999.