Localized thermal analysis of applications in non-impact printing

Authors
Khoren Sahagian[1] and Kevin Kjoller[1]
[1]*Anasys Instruments Corporation*

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Abstract

NanoTA makes use of a micro-fabricated silicon probe with an integrated heating element. This probe can be used in place of a standard Atomic Force Microscope (AFM) probe to rapidly scan a sample topography. The probe then has the novel utility of probing softening points at select locations by increasing the temperature of the probe until the surface softens due to the local temperature increasing above a transition temperature. This allows for nanoscale measurements of the transition temperature at the surface of the sample with good correlation to conventional bulk techniques.

Introduction

Bulk thermal analysis techniques such as Differential Scanning Calorimetry and Thermo-mechanical Analysis are ubiquitous methods for the determination of cure. Limitations arise in the modern world when studying thin surface coatings or with the need to spatially resolve components in complex systems. Localized thermal analysis or nanoTA™ combines high resolution structural imaging with a thermo-responsive property measurement. A strong correlation with classical bulk instrumentation[1] makes it universally applicable to problems from the nanoscale to the production line.

Crosslink density can be probed at ultra fast heating rates by monitoring the depth of penetration of the probe into the sample. A higher cross link density or degree of cure would be observed by minimal penetration [red] whereas a high rate of penetration [purple] is characteristic of under cure or low cross link formation.

A typical nanoTA measurement is made by placing a thermal probe in contact with the sample surface or a single feature of interest. Force is held to a minimum while monitoring the expansion of the sample as it pushes up against the probe.

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Heating rates can be selected in the range of conventional rates to those exceeding 100° C/s. This provides high throughput detection of thermal transitions with nanoscale sensitivity.

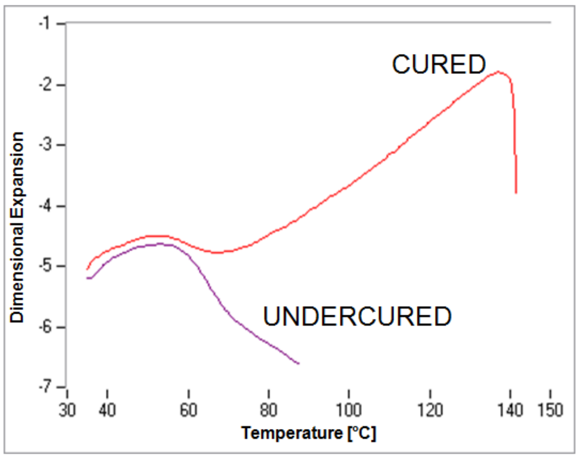

Fig 1. *nanoTA curves demonstrating an undercured [purple] & cured [red]material system; Heating Rate: 25° C/s*

Results and Discussion

Complex systems rely on the engineered placement of multiple materials. A high resolution image can provide insight into the structure that is formed but lacks in the unambiguous identification of physico-chemical composition. The results below demonstrate the intrinsic softening temperatures observed in the different regions of a single toner particle. NanoTA measurements accurately probe domains as small as 100nm. In this formulation the locations of the pigment, binder, & resin are identified (Figure 2).

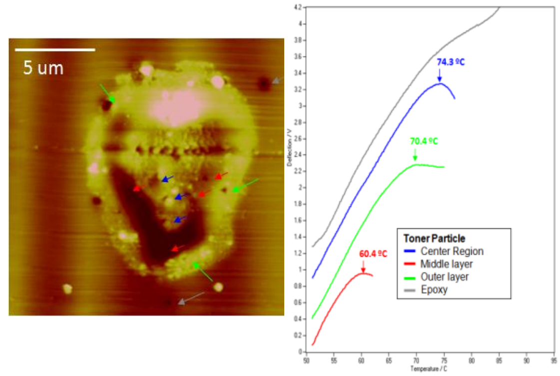

Fig 2. An Atomic Force Microscopy image of height on a single toner particle using nano-thermal probe *[left]*. Resulting nanoTA curves identifying softening temperatures of the different local components at the different regions [right].

Film Formation

Locally probing thermal transition temperatures preserves the remaining sample structure so that it may be probed at a later time or after surface treatment. For example during film formation nanoTA measurements may track the glass transition in a time resolved manner in situ and on a single sample. This is because, unlike bulk instrumentation which alters the sample's thermal history, nanoTA leaves the remainder of the sample uninfluenced by temperature.

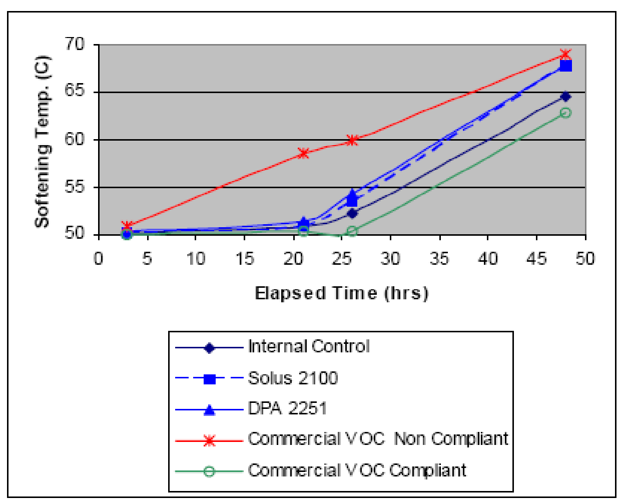

Fig 3. Time resolved study of film formation on different commercial clear coats.

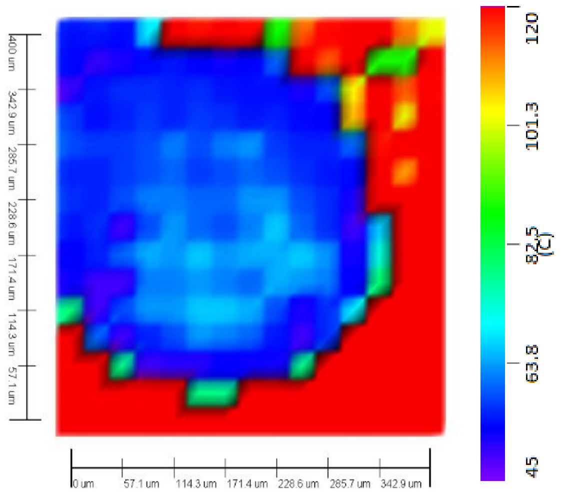

Fig 4. A 400x400 um map of transition temperatures across an ink drop on a polyethylene substrate.

Furthermore the nanoTA extends into an imaging mode whereby arrays of measurements are performed across a sample region of interest. The local transition temperatures are then used to construct a false color map. The X and Y axis represent the coordinates at which a thermal measurement was taken and the color represents the value of each thermal transition.

Defect Analysis

Unanticipated optical and mechanical defects negatively impact a coatings aesthetic or functional properties thereby necessitating a comprehensive investigation into the defect's origin. Unfortunately the task can be non-trivial when considering micro-scale aberrations which easily evade conventional spectroscopic techniques. In the example below a simple composition comprised of a multi-functional epoxy, an aromatic diamine curing agent, and a catalyst is used as a protective coating on a polymer film. After applying the solution it is oven dried to a B-stage coated film. The clear solution yields optical 'fisheye' defects.

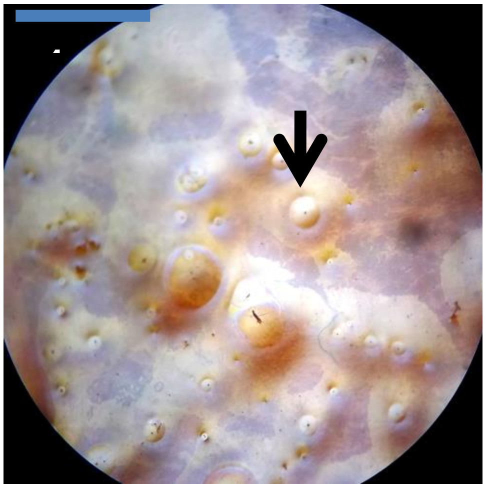

Fig 5. *A brightfield optical micrograph circular defects formed in a thin adhesive layer.*

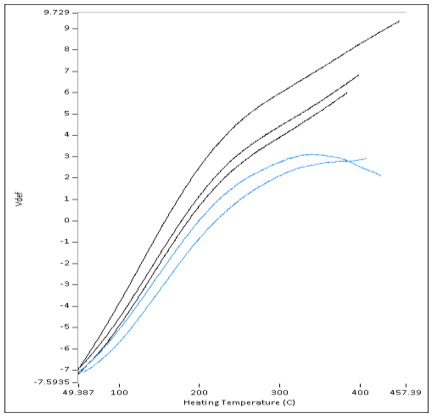

Fig 6. *nanoTA curves resulting from on the defects [blue] and around the defects [black] relating nominal transition behavior to the defective regions.*

A piece of coated film was cured unrestrained for 2 hours at 100^{o}C and the nanoTA thermal scan conducted before/after. The shapes of the blue & black curves above are characteristic of a thermosetting resin with the knee being related to the softening temperature. The transition is greater than 200^{o}C which would be anticipated for a multi-functional epoxy resin cured with an aromatic amine.

The "rubbery" characteristic of the fisheye (blue scan) is consistent with the fisheye (inclusions) being the diamine curing agent as these areas would have a stoichiometry rich in diamine, favoring the formation of a resin that is more thermoplastic in nature. When the solvent is being baked out it appears that a portion of the curing agent is precipitating manifesting as "fisheyes". Kettle advancement (adducting) of the aromatic amine curing agent with the epoxy resin was proven to prevent such separation and eliminated the fisheyes.

Conclusions

A microfabricated silicon probe with embedded heater enables high speed local thermal analysis to be conducted on complex blends, thin films, & sub micron features for allowing unambiguous property analysis.

Contact Details

Roshan@anasysinstruments.com

References

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[2] L. Germinario et al., *Nano Thermal Analysis of Polymers, Thin Films, and Coatings*, Microscopy and Microanalysis Conference, (2007).