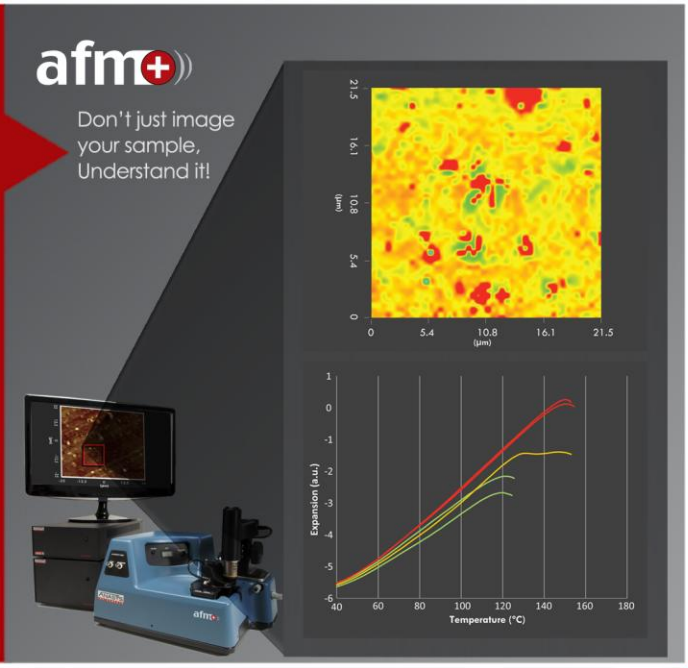
Localized Thermal Analsys: Identification of a sub-micron defect in an aromatic diamine coating



Authors

Stephen Kaplan[1], Khoren Sahagian[2]*

1. *4th State Belmont, CA*
2. *Anasys Instruments, Santa Barbara, CA*

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Application Note

Abstract

This note describes the application of nanoTA in the examination of a fisheye defect in an aromatic diamine coating. The probe tip heats the sample locally at 25ºC/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.

Background

A very 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 coating which is water clear as a solution yields a film with defect "fisheyes" in the B-Staged coating which is aesthetically unacceptable.

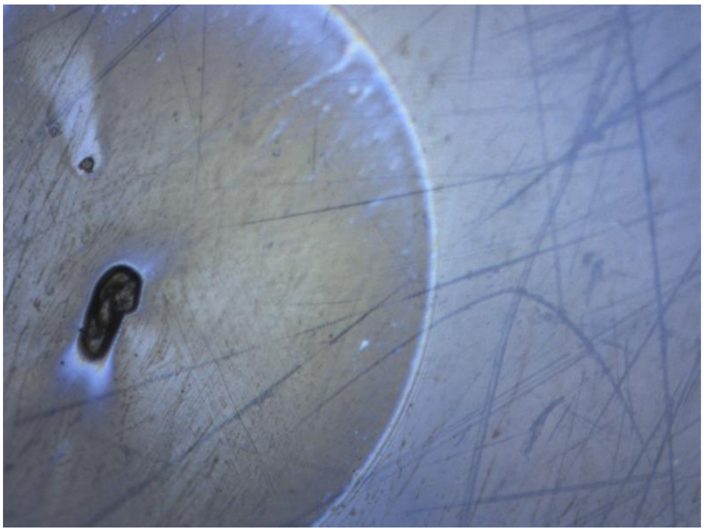

Fig 1. Optical micrograph of the fisheye defect after the coating is cured in an oven.

Discussion

An AFM cantilever with embedded heating element was used to determine the softening temperature of the "fisheye" defect. These micro-machined thermal probes have a tip height of 5um and an end radius of less than 30nm. The photomicrograph in figure 1 illustrates the defect and thermal probe cantilever which is approximately 200um long and 50 microns wide. It is the pyramidal tip on the underside that permits localized discrimination of softening temperatures on specific areas of the film being analyzed, i.e. examine differences between clear sections of the coating versus the fisheye.

ANASYS INSTRUMENTS

Multiple thermal scans from the B-staged coating in uncured state are presented in Figure 2. The blue curve represents nanoTA measurements made in the clear regions of the coating. These plots exhibit a result typical of a thermoplastic resin, i.e. thermal expansion as heated and then rapid penetration of the probe as the melting point (T_m) is approached. The red plot is of the fisheye and has a similar but the softening temperature is shifted higher. It is postulated that the fish-eye is an inclusion of the diamine curing agent (T_m = 185^{o}C) surrounded with the low melting epoxy resin.

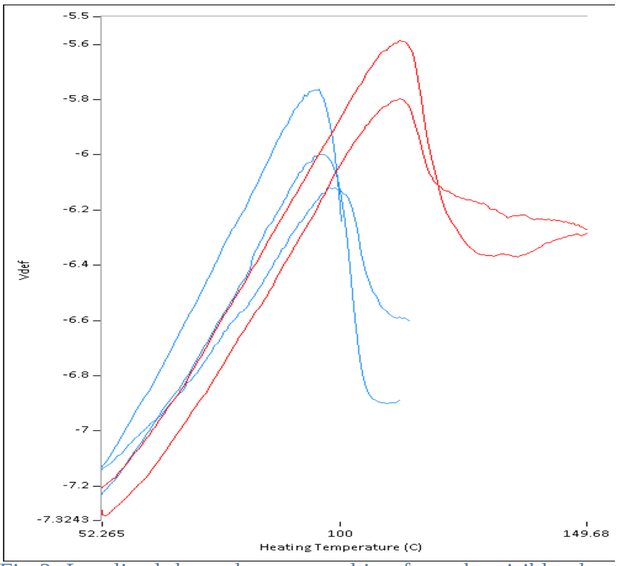

Fig 2. Localized thermal scans resulting from the visibly clear (blue) and the fisheye defect (red) regions of the uncured resin after B-stage. The higher softening transition of the defective region is attributed to a phase rich in diamine curing agent.

A piece of coated film was then cured unrestrained for 2 hours at 100^{o}C and nanoTA scans were again conducted on the coating in the cured state. Figure 3 illustrates a series of plots that compares the softening behavior from the clear and fisheye regions. The curves no longer display a rapid penetration but rather exhibit a response more characteristic of a thermoset. The knee in the curve being related to what is defined as the HDT (heat distortion temperature). The HDT is greater than 200^{o}C which would be anticipated for a multi-functional epoxy resin cured with an aromatic amine. The reduced HDT and the greater “rubbery” characteristic of the fisheye (blue scan) is consistent with the fisheyes (inclusions) being the diamine curing agent as these areas would have a stoichiometry rich in diamine favoring the formation of a resin with greater thermoplasticity.

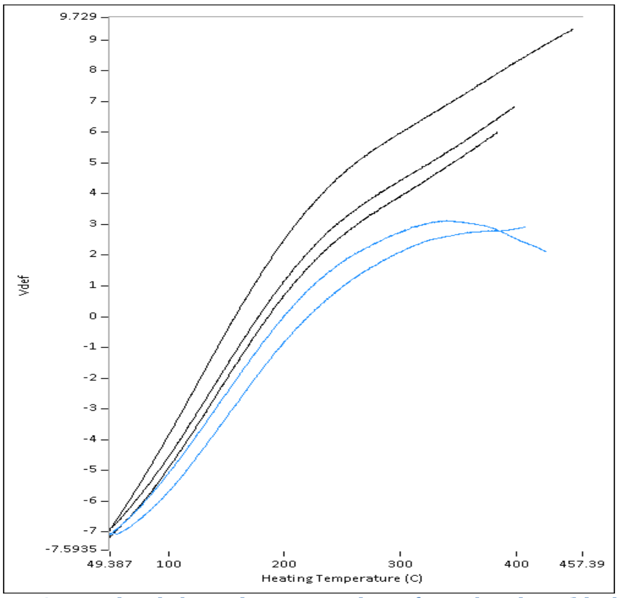

Fig 3. Localized thermal scans resulting from the clear (black) and defective (blue) regions of the film in the cured state. The diamine rich defect does not cure to the same extent.

In the preparation of the resin solution the epoxy and curing agent are only heated sufficiently to dissolve the amine curing agent in the resin. 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.

Summary

Nano-AFM provided a technique that easily allowed examination and localized discrimination of clear versus defective areas of a coated film. The Nano-AFM identified the particulate associated with the “fisheye” as a meltable solid thus the problem and a path to correct and eliminate the problem.

*Contact details
Roshan@anasysinstruments.com