Nanoscale Testing of Specialized Polymers and Components used in Non Impact Printing

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Abstract

Nanoscale testing is a growing field applied across many disciplines, sciences and industries. Recently nanoscale testing of polymers used in the printing industry has been shown to supplement conventional testing of physical, dynamic and electrical properties. Nanoscale testing consists of a variety of nano testing methods that can be applied across the Non Impact Printing Industry, from material development and characterization to understanding functionality and failure modes of components. Nanoindentation, nanoscratch, nano dynamic mechanical analysis, nano modulus mapping, nano hardness, nano tensile strength and nano electrical conductivity can be measured and applied to analysis of polymer performance.

This paper will describe nanoscale testing as applied to the characterization of polymers used in fusing and charge transfer applications, as well as nano testing of toner particles and fixation to print media. In addition, nanoscale testing of surface substrates, and adhesion to substrates is discussed as may be applied to ink jet technologies, thin films, and the non impact printing of electronics, biological and pharmaceutical materials.

Non Impact Printing Material Characterization and Testing

Nanomechanical and nanoelectrical testing has been applied to non impact printing material properties characterization in recent years by 7-SIGMA and Hysitron™[1,2]. In these studies the authors applied nano testing techniques of nanohardness, nanoindentation, nanoDMA™, nano Modulus Mapping, nanotensile, and nanoECR™ (electrical contact resistance) to nanocomposite materials for application in fusing and transfer roller applications. In those studies, and others [3], correlation was also made between nano testing and conventional testing techniques. The testing was applied to nanocomposite silicone rubber materials of nanoalumina and of carbon nanotubes. Figure 1 shows an example of nanoDMA analysis of carbon nanotube silicone rubber. Here the nano Storage Modulus is plotted against the Storage Moduls obtained by conventional DMA analysis. Figure 2 shows the the nanoHardness of the carbon nanotube composite obtained by NanoIndentation® using a Hysitron TI-950 TriboIndenter™. Electrical conductivity measurement can be obtained with the addition of nanoECR™ to the TI-950. Figure 3 shows the nano electrical contact resistance of the CNT rubber composites with different loadings by weight. Electrical conductance was obtained by placement of the material on a charged plate and the current is monitored by the nanoindentor as the probe is indented to a depth of 7 microns, held for 7 seconds and released.

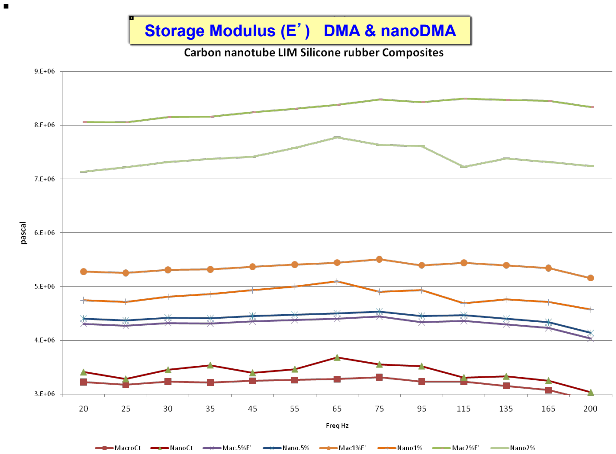

***Figure 1**. NanoDMA™ and conventional DMA of different loadings of carbon nanotubes, by wt., in a liquid silicone rubber.*

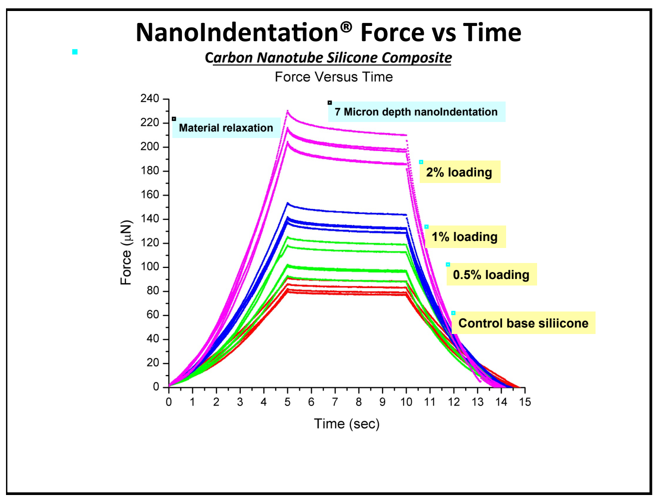

***Figure 2.** Nanohardness of different loadings of carbon nanotubes, by wt., in a liquid silicone rubber.*

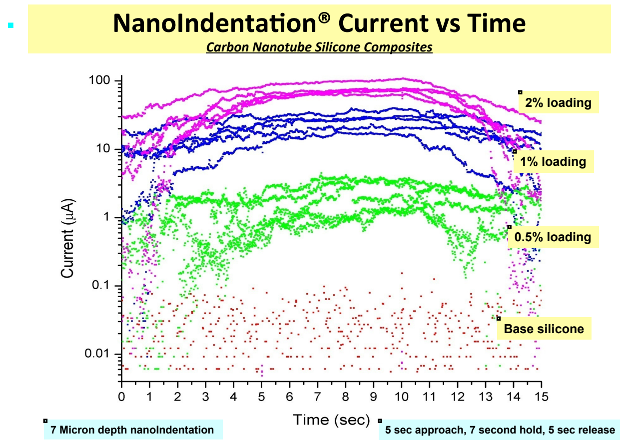

***Figure 3**. NanoECR™ (electrical conductivity in micro amps) of different loadings of carbon nanotubes, by wt., in a liquid silicone rubber.*

Toner Hardness and Adhesion Measurement

Nanomechanical testing of toner physical properties and toner adhesion to paper were studied. Toner particle compression using nanoindentation was achieved using a Hysitron TI-950 TriboIndenter™ nanomechanical test instrument. Indentation tests on a single toner particle were tested at room temperature, 40°C, 60°C, and 80°C using a diamond conical probe. On each toner particle indentation was performed to measure the force required to compress the toner particle 3µ at each temperature. Figure 4 shows the plot of the load versus displacement at each temperature. Tests were conducted at 100°C, but due to melting of the toner the test could not be completed.

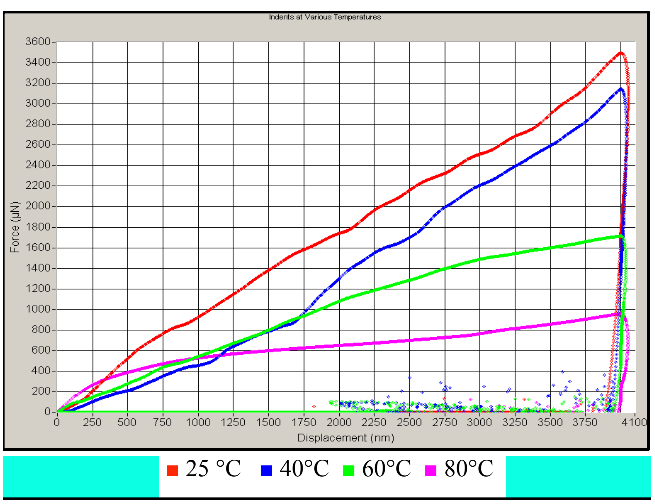

***Figure 4.** Nanoindentation of a toner particle at 25°C, 40°C, 60°C, and 80°C. Force applied, in micro Newtons, vs depth of indentation in nanometers.*

Figure 5 shows the force required for 3µ compression of 4 different toner particles at room temperature. The toner particles were from a digital color printer (DCP), a desktop color printer (DTCP) two different high speed black toner print on demand printers (POD).

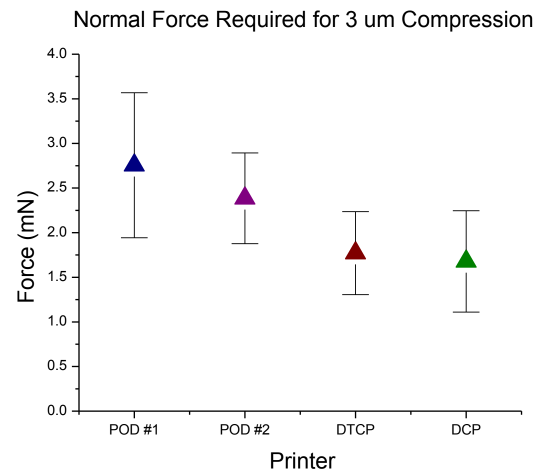

***Figure 5**. Nanoindentation of toner particles from different printers at 25°C. The average nominal force, mN, needed to compress a toner particle 3 microns.*

Nanoscratch tests were performed to determine the adhesion of various toner particles to paper substrates and the toner pile height. Scratch tests were performed using the Hysitron 3D Omniprobe to determine the lateral displacement force needed to dislodge and move a single toner particle. Figure 6 shows the toner height across a pixel. The lateral displacement across 200 microns shows the variation of toner thickness.

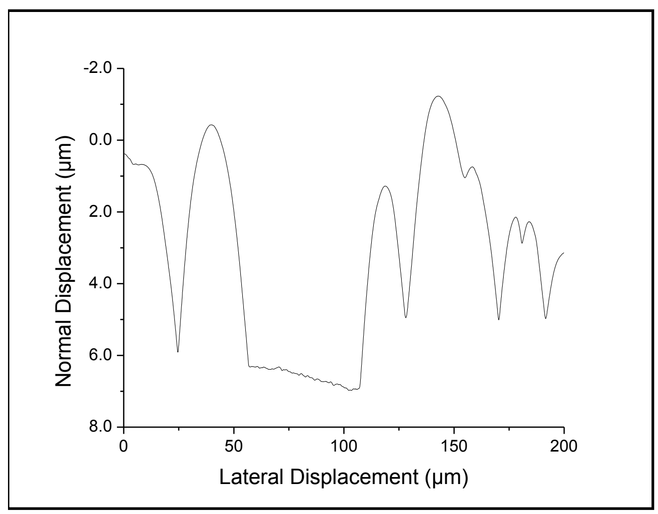

***Figure 6.** Toner depth profile across pixels.*

Figure 7 shows the lateral force required to displace a cyan colored fused toner particle on a poster produced from a digital color press. The scratch test was performed with the Hysitron 3D Omniprobe.

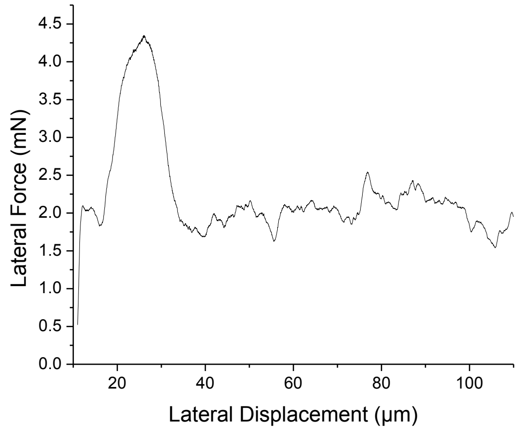

Figure 7. *Lateral force required to dislodge a cyan colored fuser toner particle.*

Adhesion Measurement of Thin Films to Substrate

The application of non impact digital printing technology for the printing of metal and electrical circuits, and applications for printing medical and biological materials onto various substrates, is a growing research area [4,5,6]. Nano testing of thin film interfacial adhesion for electronics and medical application is a well established technique. This section discusses the technique behind film adhesion, coefficient of friction, film delamination and wear resistance measurements along with key examples in relevant areas including coatings used on medical stents and nanoparticle based composite films. Advances are being made in high-end product and process engineering that require highly versatile, consistent and yet accurate characterization instrumentation that would further sharpen the established material analysis and quality control procedures. In this technique, augmentative normal force and lateral displacement is input to the system simultaneously and the resultant lateral or frictional force and normal displacement is recorded with respect to time.

A typical plot of normal displacement versus time showing the critical depth, h_{crit}, at which the failure occurs is shown in figure 8(a). At the same time, the critical load, P_{crit}, at which the film fails is recorded as a sharp fall in lateral force as shown in the plot of lateral force versus time in figure 8(b). This critical load also serves as a quantified parameter characterizing the strength of film adhesion to its substrate, while the h_{crit} also signifies the delamination depth in the normal direction and delamination point in the lateral direction. Friction coefficient (μ) from any test involving probe contact across a certain distance over a sample is simply the calculated quotient of lateral to normal force. Nanoscale wear resistance testing is performed to understand and mimic the stress induced failure of the coatings during its operation by performing multi-scratch tests across a chosen scan area, typically using a blunt Berkovich probe. In-situ Scanning Probe Microscope, SPM, imaging technique can be employed to immediately image the area scratched. Using this technique, the probe used for scratch and wear resistance testing is also used to obtain a high resolution topographical image immediately following the delamination or adhesion testing routine within the same platform and without the requirement of relocating the sample.

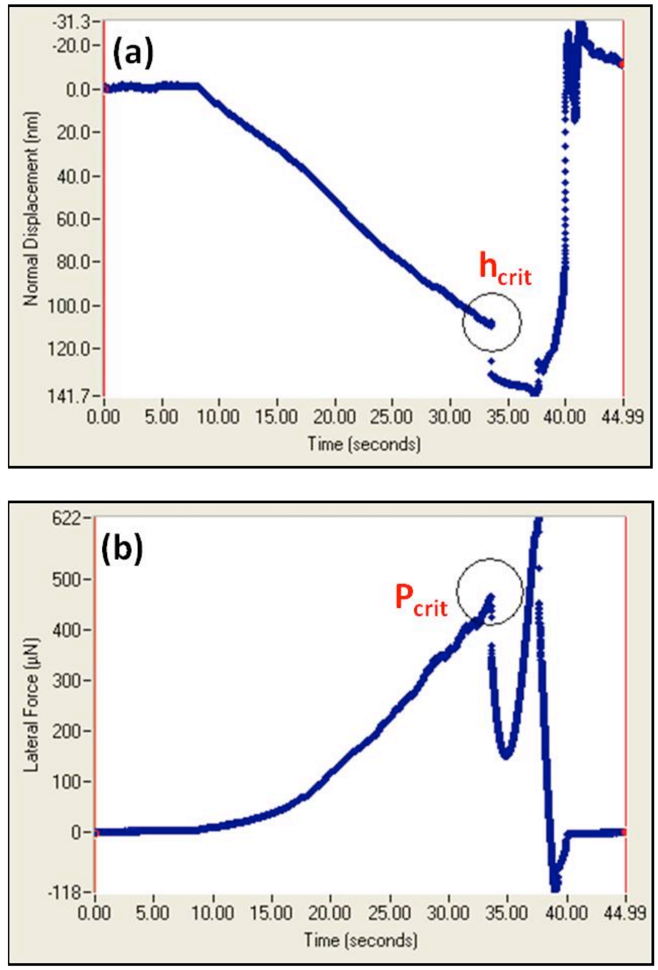

Figure 8 (a)*. Probe normal displacement profile wr.t. time and* ***(b)*** *probe lateral force profile w.r.t time of thin film interfacial adhesion.*

Extremely sensitive and highly functional coatings are also used in biomedical devices for drug delivery purposes. Thin polymeric coatings (~2 µm, Parylene C) are processed as coatings over medical stent devices to facilitate pharmacologic functioning to prevent restenosis (reblocking) and thrombosis (clotting) within the artery. Given the objective, these coatings are critical and hence form an integral part of the stent, as long as its adhesion to the stent substrate (130 µm thickness stainless steel tube) is stable and intact. Hence, measuring the interfacial adhesion of the polymeric coating is of great importance. A Hysitron TriboIndenter ™ nanomechanical testing system equipped with a 3D Omniprobe head and a 5 µm conospherical probe were used for scratch testing on these Parylene coated stent surfaces [7]. The scratch load function (software experimental routine) consisted of applying various constant normal loads ranging from 20-35 mN over a lateral displacement of 500 µm. As explained before, force and displacement were continuously recorded as a function of time in both normal and lateral directions. The chosen scratch function produced a periodic delamination pattern that can be seen in both the lateral force (LF) vs. lateral displacement (LD) data in Figure 9a, and the optical micrograph in Figure 9b. As is seen in Figure 9, there is a clear correlation between the measured force and the metrology of the delamination pattern. From the plot of lateral force versus lateral displacement, the values such as F_{min} (local minimum lateral force corresponding to the start of interfacial failure), F_i, (lateral force at any given displacement), and x_i, (corresponding lateral displacement) can further be used to calculate the energy associated with a particular delamination pattern, including coating and the substrate delamination, which in turn can be useful towards denoting the interfacial fracture toughness of the Parylene coating.

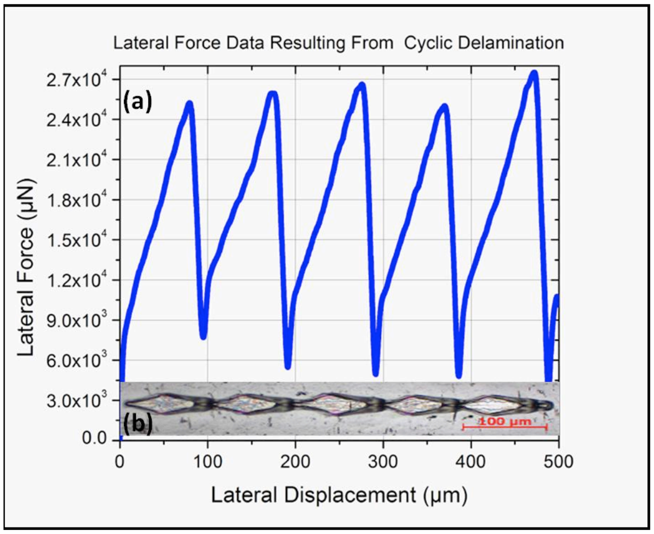

Figure 9 (a). *Probe lateral force versus lateral displacement data showing cyclic film delamination and* ***(b)****. inset showing corresponding optical micrograph of the delamination pattern*

Nanocomposite films composed of nanoparticles are being employed in printing of semiconductor and biotechnology substrates. Durability of such films is a function of adhesion of the nanoparticles with the glue or polymer matrix and to each other. In this example, nanoparticles were deposited to form nanocomposite films using Vapor Particle Deposition (VPDTM). Traditional durability testing techniques involving water erosion technique has proven to be time consuming. In this example, a Hysitron TI-950 TriboIndenter™ equipped with a diamond cube-corner probe was used to perform ScanningWear™ (nanoscale wear resistance) testing to determine wear properties upon induction of varying stress levels. In this technique, the probe was raster-scanned across a 5x5 µm area of the film in 256 scan lines while the normal force was ramped between two user-specified forces. As shown in Figure 10, failure of the film at a particular normal force was easily observed by exposure of the underlying substrate. Immediately after each wear test was completed, the worn areas were imaged using a 10x10 µm scan size and a 1µN contact force.

Conclusion

Nano testing of materials used in, or printed by, non impact printing technologies provides the ability to analyze physical and dynamic properties of materials, and provide interfacial properties of materials applied to substrates at the nano level. NanoDMA™ nanoECR™, and nanohardness techniques have been used to characterize the physical and electrical properties of carbon nanotube rubber composite and correlated with conventional testing techniques at the macro level. Nanoindentation and nanoscratch techniques tested single toner particles for physical changes over a range of temperatures and the adhesion to paper. Nano testing techniques have established protocol in the research

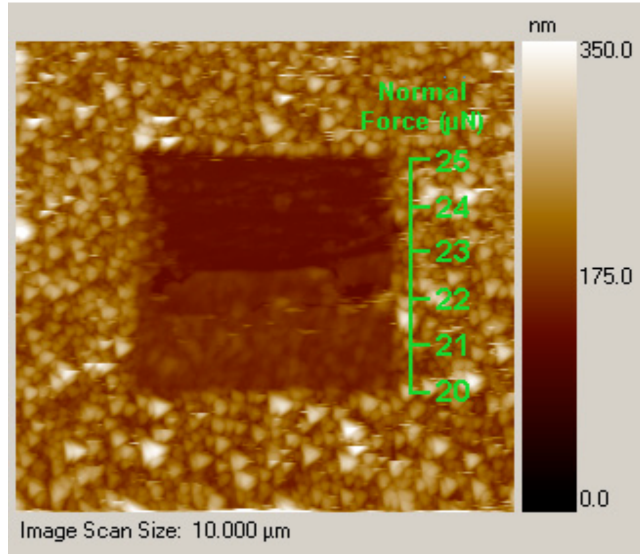

Figure 10. *10x10 µm topographical in-situ SPM image showing the 5x5 µm worn area of the nanocomposite film showing film failure at a normal force of roughly 23 µN*

testing community for interfacial adhesion of thin films to various substrates. Nanoindentation and nanoscratch in-situ with Scanning Probe Microscopy provide a valuable analysis tool for interfacial adhesion and wear properties. These techniques can easily be applied to metals and other materials applied to electrical circuitry substrates by non impact printing technology. NanoECR™ can be applied as well to determine the electrical characteristics at the sub micron level of those printed circuits. Similar techniques with these instruments can help analyze the physical properties of biological substances, such as cell scaffolding, applied by non impact printing. The adhesion of thin materials and pharmaceutical chemistry applied to medical devices, such as stents, can be accurately determined for development and quality control analysis.

References

[1] K. Murphy, W. Eichhorn, Nano Particle Application in Materials Development of Fusing Members for Non-Impact Printing. Proc. NIP22, pg. 45. (2006).

[2] W. Eichhorn, B. Avrushchenko, Carbon Nanotube Filled Composite Analysis Utilizing Nano and Conventional Testing Techniques, Proc. NIP26, (2010).

[3] Modulus Mapping of Rubbers using Micro and Nano-Indentation Techniques. Kenneth Gillen, Rubber Chemistry and Technology, Volume 74, 2001.

[4] J. Novak, Y. Li, Direct Print of Metal Nanoparticle Inks for Si Solar, Proc. NIP26, (2010).

[5] P. Laxton, Printing Nanoparticle Copper Ink to Form Functional Electronic Devices, Proc. NIP26, (2010).

[6] B. Zobrist, Laser Printing of Conductive Silver Lines, Proc. NIP26, (2010)

[7] D.Yang et al, “Method of Measuring Interfacial Adhesion Properties of Stents”, U.S. Patent 7287419, October 30, 2007.

Author Biography

Wade Eichhorn is New Technology Development manager and Product Manager for Fusing Systems . and has worked for 7-SIGMA for over 17 years. Wade is holder of 2 patents for 7-SIGMA with 3 applications in process. Recent technical development includes carbon nanotube rubber composites. weichhorn@7-sigma.com.

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