Carbon Nanotube Filled Composite Material Analysis Utilizing Nano and Conventional Testing Techniques

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Abstract

The use of carbon nanotube particle filled composite materials is gaining much attention across many industries, including the printing industry. While applications of such materials are being sought, development and testing of materials is underway. Characterization of the material's properties using current techniques coupled with nano testing may be of great interest in understanding the physical properties of these materials. In general, carbon nanotube particle applications for Non-Impact Printing may include charge/developer rolls and belts, and fusing system rolls and belts. The physical properties that nano particles impart to a material may significantly enhance materials over and above those currently using conventional additives to a base polymer. Of interest to non-impact printing material science are physical properties such as surface energy, electrical resistivity, thermal diffusivity, abrasion resistance, and compressive modulus. These material properties, and others, can be modified by the addition of nano particles additives to a base polymer. The resultant properties of the addition of multi-walled carbon nanotubes to a base polymer is presented using conventional and nano testing methodologies.

In this study, conventional methods of physical properties testing (hardness / compression set / static-stress relaxation, electrical resistivity), are conducted along with DMA, nanoDMA™, nanoindentation and nanoECR™ (electrical contact resistance) methods. Correlations of nano testing with conventional static physical properties testing have been presented in previous studies by the authors. Correlation of DMA and nanoDMA™ test methodologies of nano composite materials is novel, as well as the application of nanoECR™ testing of carbon nanotube filled materials.

Introduction

Laser printers, and other electrophotographic image forming devices, use various rollers and belts that depend upon material properties to manage paper transport, toner transfer, and toner fixation. Electrostatic and thermal properties are managed in the toner transfer, transport, and fixing of the image by the physical properties of the materials used in the printer components. Of importance are the electrical and surface release properties of the composite materials, to hold and release toner particles as desired, as well as to dissipate undesirable electrostatic charges. As the paper passes between a fuser and pressure roller, thermal and electrical properties are as well considered for optimal toner management and image quality.

The recent commercialization of carbon nanotubes has prompted this investigation into using carbon nanotubes as an additive to a polymer to confer desired physical properties such as electrical conductivity. It has been noted in the research literature[1,2,3] that small amounts of carbon nanotubes increase the electrical conductivity significantly. For the purpose of this study, loadings, less than 10% of carbon nanotubes were added to rubber polymers of FKM, EPDM and silicone. Specifically for this study, very low loadings of multi-walled carbon nanotubes, less than 2% by weight, were added to a liquid silicone rubber and the physical properties measured with conventional and nano testing methodologies.

Typically properties measured include:

1. Mechanical strength
    a. Tensile Strength [T.S. (psi)]
    b. Elongation at Break [EB (%)]
    c. Hardness
    d. Modulus
2. Surface Energy for toner release
3. Thermal Conductivity/Diffusivity
4. Electrical Conductivity
5. Abrasion Resistance
6. Resistance to oils or ozone
7. Dynamic Mechanical Analysis
    a. Storage Modulus
    b. Loss Modulus
    c. Tan Delta

Conventional testing measurement techniques, and Nanomechanical and Nanoelectrical testing techniques, affords the ability to evaluate material properties over a wide spectrum. Measurement techniques employed may be:

1. Rheology
2. Dynamic Mechanical Analysis (DMA)
3. Thermal Gravimetric Analysis (TGA)
4. Differential Scanning Calorimetry (DSC)
5. NanoDMA
6. NanoECR (Electrical Contact Resistance)

This study employed a number of conventional and nano measurement techniques to evaluate carbon nanotube silicone rubber composites. Correlations between macro, micro and nano testing techniques were observed.

Experiment

Multi-walled carbon nanotubes were added to a liquid silicone rubber in the ratio of 0.1% through 2% by weight. The premise of the study was that that the carbon nanotube particles might impart some interesting properties, such as electrical conductivity at low loadings. The control elastomer was a 35 Shore A Platinum catalyzed, addition cured liquid silicone rubber. Multi-walled carbon nanotube loadings, provided by Hyperion Catalysts, Boston, MA, were set at 0.5%, 1% and 2% by weight (w/w). Multi-walled carbon nanotubes were added into each part A & B, of the two part LIM material, by Hyperion Catalysts. Part A and Part B materials were then mixed using a FlackTech® centrifugal speed mixer DAC-150-FVZ/K and shear mixing. The Rheology/Curing characteristics of each batch were measured using a moving die Rheometer (MDR2000/Alpha Technologies) at 150°C. Test slabs and buttons were molded for test and evaluation. All materials were post-cured for 4 hours at 200°C. Measurement of physical properties were made using both macro and nano techniques. Atomic Force Microscopy (AFM) and optical microscopy were also used to further understand the nature of the CNT rubber composite matrix.

Conventional methods of physical property measurements were carried out on a Shimadzu Rubber Tensile tester (model AGS-H; Autograph) for the determination of Tensile Strength (TS), Elongation at Break (EB%). Compression set was also measured according to ASTM D395-97. Dynamic Mechanical Analysis was carried out by Akron Research & Development Labs using a Visco Analyzer 2000 DMA150 in compression mode. Thermal properties were measure using a TA Instruments 2950 TGA and a TA Instruments 2010 Differential Scanning Calorimetry. Thermal conductivity was measured by a guarded heat flow method. Electrical resistivity was measured using a Trek Model 152 Resistance Meter, with 152P-CR probe.

Nanomechanical measurements were performed on a Hysitron TI 900 TriboIndenter ^{TM} by Hysitron, Inc., Minneapolis, MN and included the following:

1. Nanoindentation for hardness and reduced modulus measurement of the sample elastomer surfaces.
2. NanoDMA for the measurement of Storage Modulus (E′) and Loss Modulus (E″) as a function of frequency.
3. NanoECR for the measurement of electrical contact resistance
4. AFM and optical microscopy of the elastomer samples.

Results and Discussion

The molded samples analyzed were made of a base liquid silicone rubber and the base rubber with loadings, by weight, of 0.5%, 1% and 2% multi-walled carbon nanotubes. The results show very significant changes in the electrical conductivity with very little changes in other physical properties, indicating, that in a liquid silicone, there is no diluent behavior induced with these additions.

Physical properties of the base silicone and CNT composites are given in Table 1. Significantly, Table 1 shows that electrical resistivity, measured in Ohm.sq, changed dramatically from 10^{13} to below 10^{2}, (the resolution limit of equipment) with a 2% loading while maintaining hardness, elongation and tensile properties of the original base material. In addition, important properties such as compression set, while changed slightly, were well within an acceptable range for printer applications. Specifically, a loading of 0.5% CNT showed virtually no change in the physical properties while a dramatic change in electrical conductivity to a resistivity value of 10^{4} Ohm. sq. Thus loadings of 0.5% or less can be added to a base silicone to achieve a desired electrical resistivity value without diluting other desired physical properties.

Parameter	Base LIM	0.5% CNT	1% CNT	2% CNT
Max. Torque, lb-in	5.73	6.01	6.61	9.14
TC90, sec	17	13	20	15
Hardness Shore A	38	40	43	43
Tensile, psi	365	335	392	449
Elongation, %	256	227	230	265
Modulus, psi	168	160	197	220
Tear, ppi	30.4	28.6	41.0	52.0
Specific Gravity	1.25	1.31	1.31	1.29
Compression set, % (22hrs @ 350F)	2.0	3.2	7.0	12.5
Volume Change in silicone oil, %(22hrs @ 350F)	34.0	43.0	35.0	35.0
Electrical Resistivity Ohm/sq	10^13	5x10^4	1.3x10^3	<10^2 Out of range

Table 1. *Physical Properties of CNT composite samples*

Figure 1 plots the electrical resistivity values of the carbon nanotube composites. For the purpose of expanding the electrical properties measurement, samples of carbon nanotube loadings of 0.12% and 0.25% were also tested. It is clearly seen how the resistivity drops exponentially with loadings from 0.12% to 2%. Thus small loadings of multi-walled carbon nanotubes can infer electrical properties which may be of interest for toner transfer rollers and belts, as well as use in components requiring electrostatic properties, such as transport and fusing members.

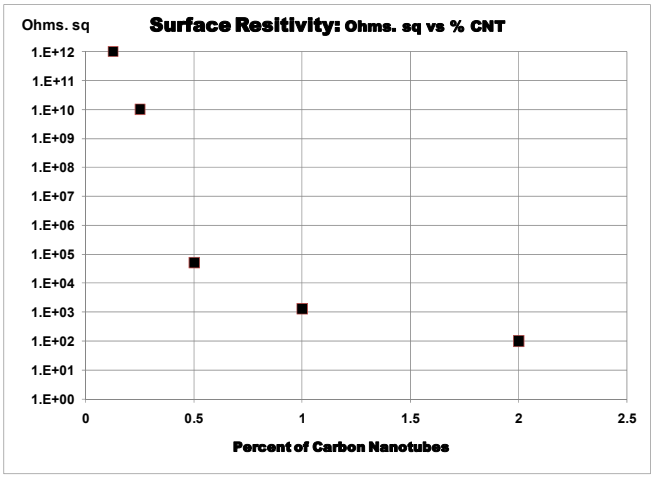

***Figure 1. Surface** Electrical Resistivity. Ohm/sq*

Nano mechanical tests were employed on samples with 0%, 0.5%, 1% and 2% CNT loadings, to characterize material properties at the micron levels. Quasi-static tests were used to reveal hardness and reduced modulus. NanoECR [4] was used to characterize the electrical properties of each sample. NanoDMA™ frequency sweep tests were performed on each sample to characterize the dynamic properties as a function of frequency.

Figure 2 is a nanoECR™ plot of the average current measured in each of the 0.5%, 1% and 2% CNT filled samples. The nano electrical conductivity, measured in micro amphers shows the exponential increase in electrical conductivity with small additions of carbon nanotubes. The nanoECR™ measurements were conducted at several points in a 10 micron region using a boron doped diamond Berkovich indenter probe. During each indent, a constant voltage of 7V was applied to the sample, with a peak depth of 4 microns. Each displacement consisted of a 5 second approach to a depth of 4 microns, a hold for 5 seconds, and a 5 second withdraw.

Figure 3 is a TroboAnalysis™ plot of force and current versus time of the nanoECR measurements of Figure 2. The results shows increasing stiffness, measured in micro Newtons, of the samples along with the electrically conductivity, measured in micron amperes. Interestingly, the current remained constant over the 5 second hold period. The control, no nanotubes, is at the base of each plot. The 0.5%, 1% and 2% nanotube composite electrical response rises logarithmically in sequence.

Thermal properties of the composites were observed using Differential Scanning Calorimetry (DSC), Thermal Gravimetric Analysis (TGA), and thermal conductivity. Thermal conductivity measurements showed no significant measurable change. TGA and DSC analysis showed only small shifts in the glass transition or decomposition. Figures 4 and 5 show the TGA and DSC results.

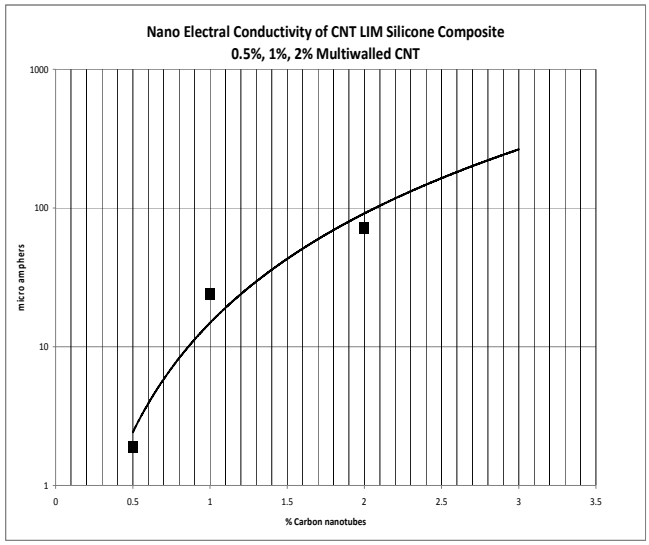

***Figure 2.** NanoECR, micro amperes*

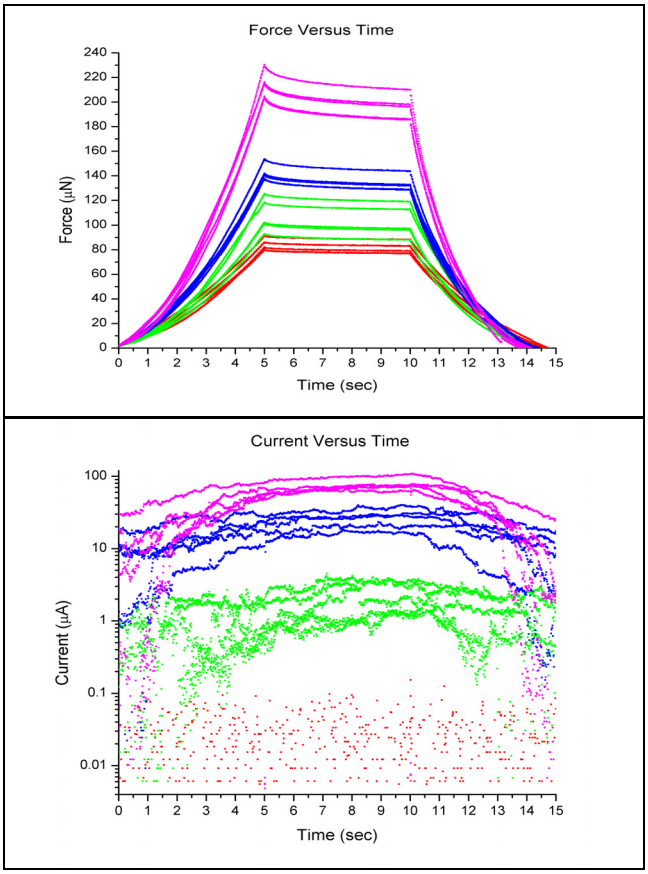

***Figure 3.** TriboAnalysis™ plots of force and current versus time from the 7 volts, 4 μm displacement-controlled indents on each sample. Note that the y-axis of the current versus time plot is logarithmic in scale. The control, no CNT, is at the base of each plot. The 0.5%, 1% and 2% CNT filled composites rise in sequence.*

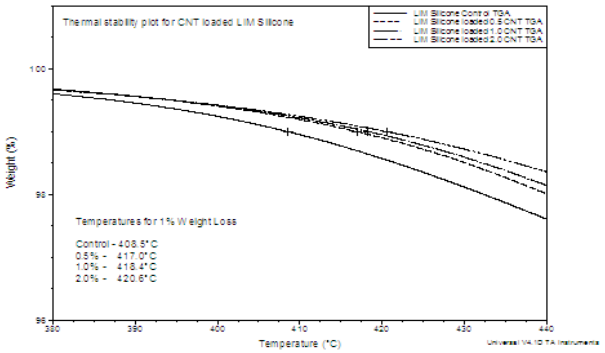

Figure 4. *TGA plot of control and CNT composites*

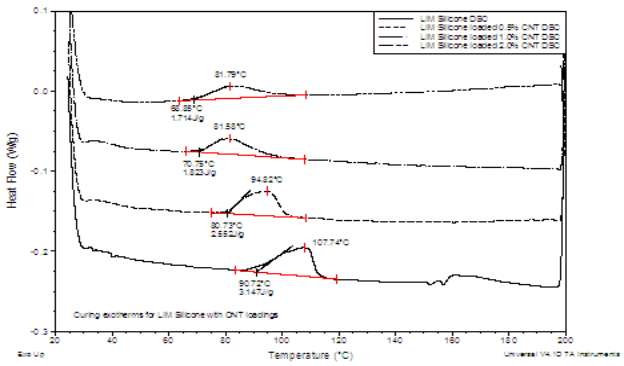

Figure 5. *DSC plot of control and CNT composites*

Of interest to the study is the characterization of the viscoelastic properties of each of the carbon nanotube composites as compared to the base material and to each other. In addition of interest to the study is the relationship or correlation between conventional DMA and nanoDMA testing methods. Dynamic Mechanical Analysis (DMA) is frequently used to measure the stress and strain over a wide range of frequency. The authors, in a previous Non Impact Printing study[5], reported nanoDMA results on the same base material of this study, but with addition of alpha alumina nanoparticles. The nanoDMA results reported here for the carbon nanotube silicone composite are combined with conventional DMA analysis over the same frequency range. The results demonstrate a direct correlation between the DMA and the nanoDMA measurement methodology for a soft material, providing a new insight into applications of nanoDMA. Conventional and nano Storage and Loss Modulus of each of the samples are combined to show how the DMA and nanoDMA tracked together with the same relationship. The frequency sweep from 20 to 200 hertz showed very uniform results with both measurement methods. Figures 5 & 6 shows the relationship between the DMA and nanoDMA measurements over those frequencies. Figure 7 is the Tan Delta plot (ratio between Storage and Loss Modulus), showing remarkable correlation between the DMA and nanoDMA measurements.

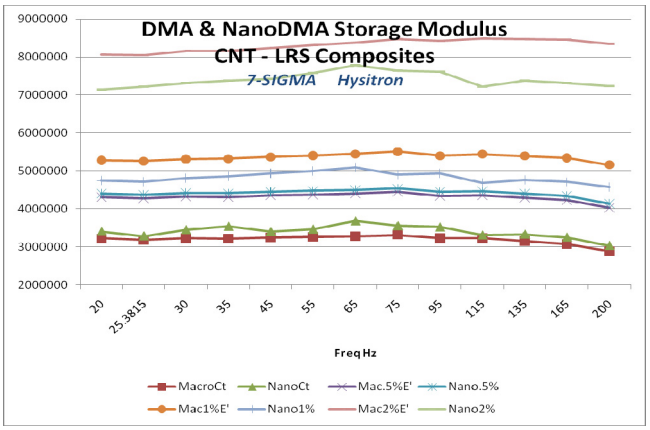

Figure 6. *DMA and NanoDMA Storage Modulus of control and CNT composites*

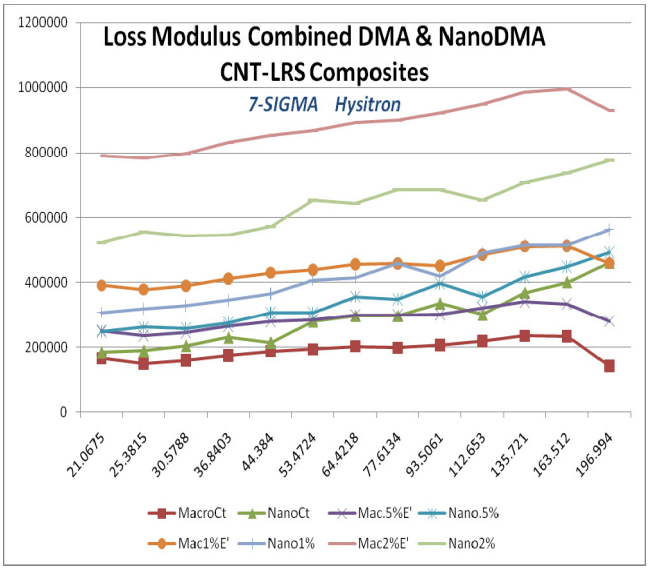

Figure 7. *DMA & NanoDMA Loss Modulus of control and CNT composites*

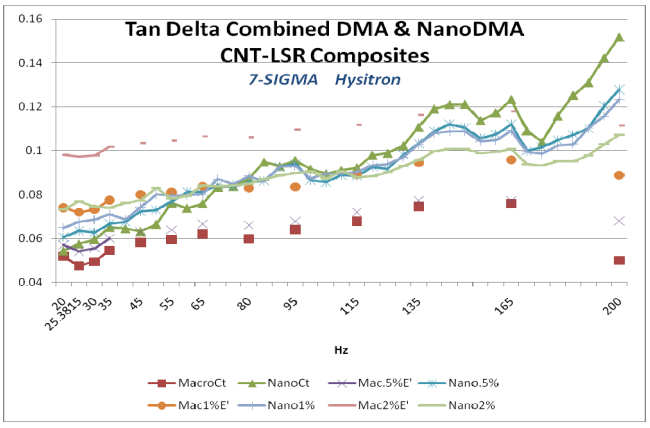

Figure 8. *DMA & NanoDMA Tan Delta of CNT composites*

Conclusions

The addition of very small amounts of multi-walled carbon nanotubes into a liquid silicone rubber has been shown to impart significant changes in the electrical conductivity without changing the physical properties of the material overall. This is supported by physical and dynamic property testing utilizing conventional and nano measurement methods. Results were obtained that demonstrate the correlation of DMA and nanoDMA testing for a soft elastomer. In addition, a novel measurement of nano electrical contact resistance was applied to a soft elastomer.

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