Nano Particle Application in Material Development of Fusing Members for Non-Impact Printing: A preliminary study

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Abstract

The use of nano particles and associated nano measurement techniques may be of great importance for the advancement of Non-Impact Printing (NIP) Technologies. The physical properties that nano particles impart to a material may significantly enhance materials over that of current macro and micro particle size additives to a base polymer. In order to study the effects of nanoparticle additives in comparison with macro and micro particle additives, current methods of physical properties testing are conducted along with new nano particle test methods, i.e. Atomic Force Microscopy (AFM), nanoindentation and Nano Dynamic Mechanical Analysis (nanoDMA). The correlations of test methodologies and effects of particle size on properties of particle filled elastomers are discussed.

Introduction

For many years refractory materials, such as tabular α-Alumina, have been used to confer specific thermal properties to soft elastomers used for fusing applications. Particle size of these fillers are in the micron range or larger. High loadings of these fillers often dramatically reduce the mechanical properties of the resultant material. The thermal transport properties of these soft conformable elastomers are key for the NIP fusing process. This is especially true at higher printing speeds where energy transfer at the fusing station is required for fast thermal recovery. The growth of the color printer market in the past five years has further highlighted this issue, due to the increased pile heights of toner seen at the fusing station.

With the advent of commercially available nano fillers, it was decided to explore the effect of nanosize α-Alumina on the mechanical and thermal properties of a liquid silicone rubber (L.S.R.). In order to design and develop improved materials for N.I.P. fusing applications, a balance of mechanical and thermal properties are needed. Typically the properties include:

1. Mechanical strength
    a. Tensile Strength [T.S. (psi)]
    b. Elongation at Break [E_B (%)]
2. Surface Energy for toner release
3. Thermal Conductivity/Diffusivity
4. Abrasion Resistance

Nanomechanical testing, and the resultant nanomechanical properties measured, affords the ability to generate data in indentation mode, under nanoscale deformations, to study fundamental properties of materials at nanoscale. This testing method is a widely accepted technique for characterization of mechanical properties of thin films, coatings, and nanoparticles[1,2,3]. This preliminary study is the first attempt to investigate the applicability of nanoindentation to characterize non-impact printing materials. The other objective of this study is to establish correlation between nanomechanical testing and conventional elastomer testing methods, such as ASTM D2240, ASTM D395-97 and ASTM D412.

Experiment

Two sizes of α-Alumina were chosen for this work, nano filler (sub micron) and regular filler (macro). It was thought that the finer nanoparticle size, spherical morphology and increased surface area, might impart some interesting properties. The control elastomer was a 33˚ JIS A Platinum catalyzed, addition cured liquid silicone rubber. Filler loadings were set at 15% and 25% by weight (w/w). The materials were mixed using a FlackTech® centrifugal speed mixer DAC-150-FVZ/K. The Rheology/Curing characteristics of each batch were measured using a moving die Rheometer (MDR2000/Alpha Technologies) at 120˚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 rubber 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 (E_B%). Compression set was also measured according to ASTM D395-97.

Nanomechanical measurements were performed on a Hysitron TriboIndenter® 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. AFM and optical microscopy of the elastomer samples.

Quasi-static nanoindentation tests, using a Berkovich geometry diamond indenter on the control and nanofilled materials were conducted. Eighty (80) indents were performed on the surface of each material with a peak force of 800 μN. The relatively large number of indents was chosen to increase the statistical significance of the results, and to help minimize the effects of surface roughness and individual particles on the results.

Measurements were made on a control, 15% & 25%, by weight, nanoparticle -Alumina and 15% & 25%, by weight, macro -Alumina. The data gathered from both nano and macro measurements were subsequently examined for “correlation” between the test methods.

Results and Discussion

In conventional organic elastomers such a natural rubber (NR), carbon blacks are used as the primary reinforcing filler[4,5]. Typical features of reinforcement, is an increase in modulus and hardness of the elastomer matrix, and the retention of other important properties such as E_B (%) and compression set. Reinforcement of silicone elastomers is normally achieved using fumed silica as the reinforcing filler[5,6].

Diluent behavior is shown when the physical properties of the elastomer matrix stay the same or decrease as a function of filler loading. Normally these non-reinforcing fillers are added to reduce the manufacturing cost of a product or to confer specific handling and processing properties to an elastomer.

The study data indicates several interesting trends in physical properties. Results of the macro testing carried out at 7-SIGMA, Inc., are detailed in Table 1. The nanometer -Alumina filler is behaving as reinforcing filler, whereas the regular macro -Alumina is behaving as a diluent filler.

Table 1 Conventional data from the control, nanoparticle filled, and the macroparticle filled elastomers

Property	Control	15% nano	25% nano	15% macro	25% macro
Maximum Torque (lb/in)	5.0	7.6	8.5	5.8	6.4
Hardness (Shore A)	33	46	52	40	40
Tensile Strength (psi)	364	416	467	209	161
E_B (%)	158	160	144	91	74
Δ Thermal Conductivity		10%	12%	8.5%	10%
Specific Gravity	1.31	1.42	1.50	1.41	1.49
Compression Set, % 22hrs@180˚C	4.0	8.5	11.8	15.0	21.5

It also is observed that both the 15% w/w and the 25% w/w nanofiller addition increases Shore A hardness progressively while the E_B (%) remains steady. The specific gravity increases in line with the percent of filler added, while the compression set increase still yields values suitable for use as fuser roller materials; i.e. ≈ 10%. This is typical reinforcing behavior in an elastomer matrix.

The macro -Alumina filled elastomer shows a significant decrease in Tensile Strength (TS) and E_B (%). The Shore A hardness of it is increased, but not to the values of the nano -Alumina filled elastomer. The specific gravity (SG) for the macro -Alumina filled elastomer is in line with the values expected. The measured compression set of 15% and 21.5% is significantly worse than the nano filled elastomers and not suitable for fuser roller materials.

The thermal conductivity, as measured by a Guarded Heat Flow method[8], showed a slightly greater percentage increase for the nano filled elastomer than that of the macro filled elastomer.

Results of the quasi-static nanoindentation using a Hysitron TriboIndenter® on the samples (control, 15% and 25% w/w nano -Alumina, and 15% and 25% macro -Alumina) are summarized below:

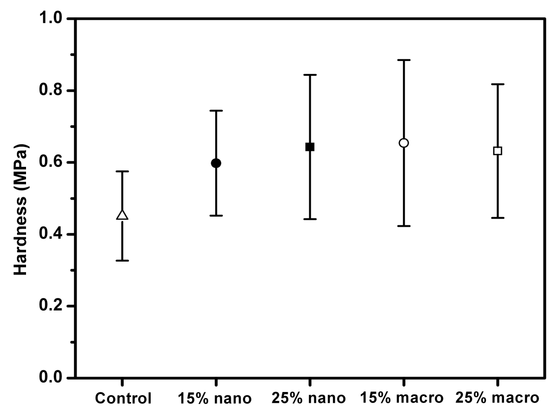

Figure 1. *nanoindentation hardness data plots with standard deviation bars.*

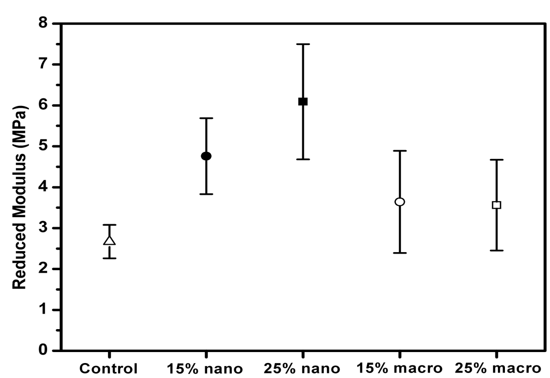

Figure 2. *nanoindentation reduced modulus data plots with standard deviation bars.*

Figures 1,2 are the nanohardness and reduced modulus of all the samples. Figures 3,4 are the nanoDMA measurements of Storage Modulus (E) and Loss Modulus (E) as a function of frequency. It is interesting and encouraging to notice that the reduced modulus results obtained through nanoindentation (see Fig. 2) shows the same trend as the results of macroscale Shore A hardness tests (see Table 1) on how the filler materials influence the properties. The correlation agrees well with the practical point of view that the results of a Shore A hardness test depend primarily on the Young's modulus of the sample[9]. On the other hand, the nanohardness test does not indicate the same effect of filler on materials as the Shore A hardness or the reduced modulus does because the nanoindentation test involves a sharper indenter and nanohardness reflects material resistance to both elastic and plastic deformation. The addition of the particles, regardless of size, increases the nanohardness of the resultant materials. Figures 3 and 4 are the nanoDMA measurements of the reduced storage modulus (E_r') and reduced loss modulus (E_r''), as functions of frequency. These two figures depict the viscoelastic characteristics of the control and particle filled materials under sinusoidal dynamic loading. The storage modulus and loss modulus information shown in these two figures is considered useful and complementary to the nanohardness and modulus data obtained from the quasi-static nanoindentation tests. It can be seen from these figures that the nano-size fillers increased the storage and loss moduli of the control sample while the macro-size fillers have almost no significant effect on these dynamic properties of the silicone rubber material. Further, both storage and loss moduli of all rubber samples with or without particle addition tend to increase with the increase of the loading frequency.

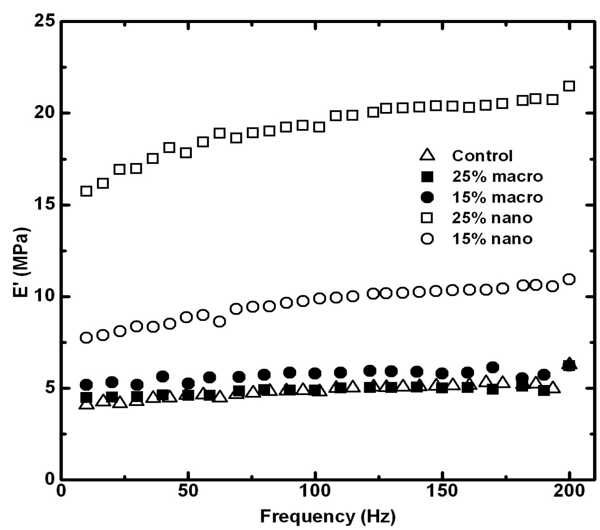

Figure 3. *NanoDMA storage modulus (E') versus frequency.*

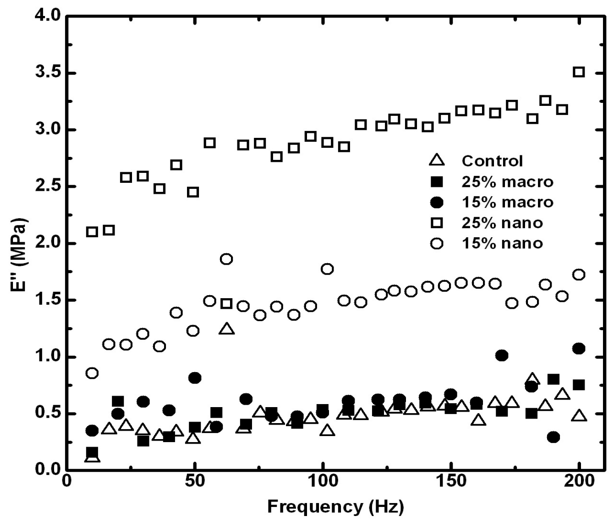

Figure 4. *NanoDMA loss modulus (E") verses frequency.*

Bright field, dark field and differential interference contrast (D.I.C.) were used to obtain optical images [Zeiss Axio Imager® A1M microscope] at 100x, 200x, 500x and 1000x magnification. Figure 5 is a typical image that shows reasonable filler dispersion.

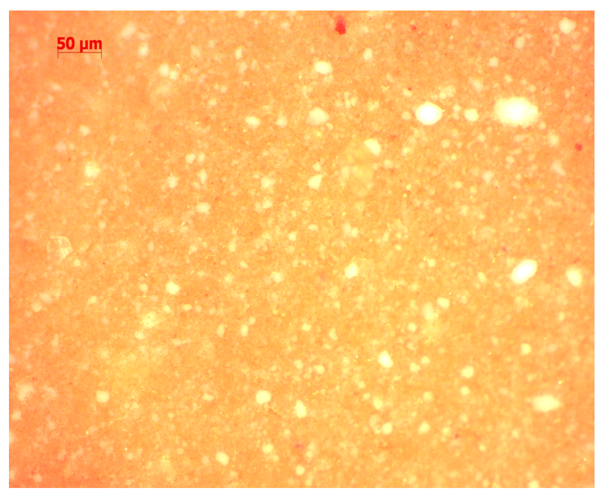

Figure 5. *DIC picture of 25% α-Alumina filled polymer @200x with aggregation of nano α-Alumina.*

AFM equipped on the Hysitron TriboIndenter® further enhanced the imaging capabilities. With a contact force of ≈ 100nN, it was possible to capture high resolution images due to a smaller tip radius and geometry. The pictures obtained clearly showed the phases present in the elastomer samples. More importantly, this image reveals that the wetting out of the nanoparticle filler and the elastomer matrix is very good. There is no abrupt interface observed between these two phases.

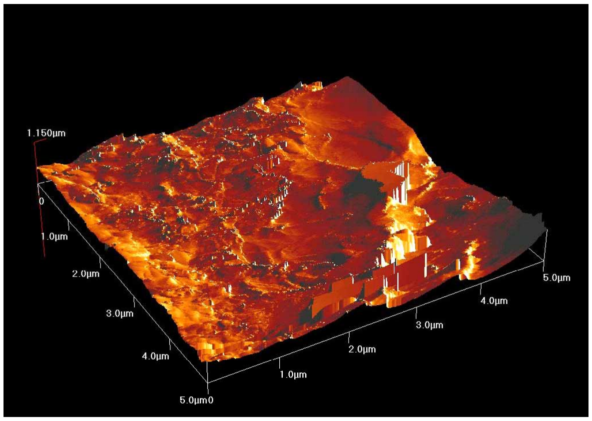

Figure 6. *3-D AFM image taken on an interface (along the diagonal of the surface) between an agglomerate of Al_2O_3 nano particles (left portion of the image) and the elastomer matrix (right portion of the image).*

Conclusions

Based upon the experimental results and resultant analysis of the study, the following conclusions can be drawn:

- ❖ Incorporation of nano □-Alumina filler in a liquid silicone rubber clearly shows reinforcing behavior, whereas the macro □-Alumina exhibits diluent behavior.
- ❖ Strong correlation between modulus obtained through nanoindentation tests and macroscale Shore A hardness was identified.
- ❖ Nanoindentation and nanoDMA dynamic test techniques were applied to supply additional and complementary information on the properties of the liquid silicone rubber materials.
- ❖ AFM offers a way to study polymer/filler wetting-out, and the phases present in nanoparticle filled liquid silicone rubber materials.

Acknowledgments

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