Polymer Nano-Composite Micromachining by X-ray Lithography for MEMS Application

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Abstract

Polymer nano-composites (PNCs) have, in the past decade, emerged as a new class of materials due to much improved mechanical, thermal, electrical and optical properties as compared to their macro- and micro-composites. Recently, PNC technology has been moved quickly from the mechanical enhancement of the neat resin to multi-functional applications such as conductive PNCs, microstructures, sensors and actuators. However, there is the challenge in the integration of multi-functional PNC components into micro-electro-mechanical systems (MEMS). This issue is crucial for low cost, high precision and high performance PNC-MEMS, along with the traditional issues that are solely on the mechanical enhancement of the neat resin or the direct replacement of current filler technology. In this study, a polymer nano-composite material was patterned by X-ray lithography, and characterized for its mechanical, thermal, and structural properties. The reinforcement component of the composite was carbon black and the polymeric matrix was SU-8. The addition of carbon black was studied at 2 and 4 weight percentages, and was shown to enhance the elastic modulus of the SU-8 matrix. The addition of carbon black at these low weight fractions increased the glass transition temperature of SU-8 approximately 40 °C, and the degradation temperature of the PNC decreased approximately 13 °C. The surface roughness increased with increased carbon black percentage, and the PNC structural reduction was less than 10 % of pure SU-8. The fundamental issues regarding X-ray lithography of multifunctional PNCs (synthesis, patterning, characterization, and properties) for advanced MEMS are discussed. The emphasis is on the conjunction of a conductive PNC and high aspect ratio structured MEMS (HARMs MEMS) by X-ray lithography. The material selections for X-ray/MEMS, and property evaluation of MEMS-related issues are also mentioned.
Introduction

In recent years, polymer-based nano-particle composites, also known as PNCs, have attracted considerable attention sparked by the onset of nanotechnology, and increasing availability of nano-particles\textsuperscript{1-5}. As the search for more novel, advantageous material persists, PNCs have been targeted for use in applications pertaining to aerospace\textsuperscript{6}, bottling and packaging\textsuperscript{7}, and automobiles\textsuperscript{8}. Recently, more advanced utilization of PNC material into microelectromechanical (MEMS) has been emerging for applications such as fuel cells\textsuperscript{9}, actuators\textsuperscript{10}, and chemical sensors\textsuperscript{11}. Structural components used in MEMS are typically made from ceramics or polysilicon\textsuperscript{12}. These materials however are fixed in their properties, and hence, limit the potential functionality of micro-devices. PNCs offer engineers the ability to tailor material properties, which is largely due to polymer versatility, to fit or expand the application of MEMS technology. Additionally, PNCs are cost effective material and lighter in weight when considering commonly used bulk material.\textsuperscript{13} However, implementation of PNC material into MEMS has proven to be challenging due to fabrication difficulties such as high aspect ratio issues, and structural complexity.\textsuperscript{14}

Several reports document methods to machine PNC material. Compression molding\textsuperscript{15}, extrusion\textsuperscript{16}, and injection molding\textsuperscript{17} methods name a few. These methods have been used for large scale systems, however, and it is necessary to study their ability to machine PNC material into the dimensional and precision required of MEMS. Few have investigated the micro-machining of PNCs. Jiguet \textit{et al}\textsuperscript{14} reported on the micro-machining of a photosensitive polymer embedded with silver nano-particles. Utilizing Ultra-violet (UV) lithography they were able to achieve conductive microstructures. The structures were limited to thicknesses of 35 m or less. Utilization of X-ray lithography permits high-aspect-ratio PNC structures with high precision, and structural complexity to be fabricated but the PNC material chosen must be able to adhere to such demands.

An abundance of nano-particles are accessible which offer many choices when considering PNC fabrication by X-ray lithography. The reinforcement constituent in an X-ray machined composite should have a low probability of X-ray scattering. Furthermore, most nano-particles are costly, and therefore selection should also be considered from a cost effective viewpoint. The polymer chosen should be sensitive to X-rays, and preferably have a minimal viscosity, but sufficiently thick to produce high-aspect-ratio MEMS structures (HARMST). Most commonly used HARMST materials are SU-8 and PMMA. Material characteristics and X-ray lithography of both have been studied\textsuperscript{18-20}.

In this work, synthesis and evaluation of PNC microstructures fabricated using X-ray lithography is performed. The reinforcement used is carbon black (CB), and the polymeric matrix is SU-8. The PNC formulations in this study are 2 and 4 carbon black weight percent (wt%). Percollation threshold in a carbon black-based composite was reportedly reached between 2 and 4 carbon black wt\%.\textsuperscript{21} The PNC samples are characterized for their mechanical and thermal properties: stress-strain characteristics, elastic modulus, and glass and degradation temperature phase transitions. Emphasis is placed on the effect of dose and carbon black wt\% on the properties. For application related issues, the surface morphology and structural reduction of the PNC is evaluated and a comparison is made to pure SU-8.
Experimental

Material Selection

Considerations for PNC material selection for X-ray fabrication are reinforcement particle size and dispersion, X-ray sensitivity, and polymeric viscosity. The PNC consists of carbon black (Alfa Aesar, Ward Hill, MA) as the reinforcement and SU-8 5 (Microchem, Newton, MA) as the polymeric matrix. Carbon black is an allotrope of carbon made from the thermal decomposition of acetylene. This form of carbon has low electrical resistivity, has an average particle size of 46 nm, and has a surface area of 80 m$^2$/g. Its large surface area suggests that to impart its mechanical, thermal, and electrical properties in a polymeric matrix requires a low weight percentage. The thermoset polymeric matrix material, SU-8 5, is a negative photoresist and one of several SU-8 formulations. This formulation has 52 % solid in Gamma Butyrolactone (GBL) solvent. This SU-8 resin has a low viscosity of 290 cSt which gives good handling/processing conditions. For example, the SU-8 50 (12250 cSt), or 100 (51500 cSt) formulations are highly viscous in comparison, and are difficult to mix with 4 wt% of carbon black. The initial low viscosity reduced these processing difficulties. The fully cured SU-8 is capable of forming high aspect ratio microstructures for micro-mechanical parts or bio/chemical resistive structures.$^{22-24}$

Sample Preparation and Fabrication

Sample preparation and fabrication consisted of several steps. These are synthesis of PNC, preparation of a support substrate, PNC baking and exposure processing, and finally post-baking, developing, and removing from the substrate. The synthesis of PNC consisted of hand-mixing 2 and 4 wt% of carbon black with SU-8 5. The PNCs were prepared to study the properties of a minimum filler weight percent required to induce conductivity of a PNC. Franco et al.$^{21}$ investigated the electrical properties of a carbon black polymer nano-composite. They showed that a low weight percentage of 2 – 4 carbon black wt% was sufficient for a polymer to reach percolation threshold and become electrically conductive. These carbon black weight percentages were made and applied onto a substrate. The substrate was a 4"-diameter- n-type {100} silicon (Si). 3-µm-thick titanium (Ti) film was deposited onto the substrate. This film was then oxidized to a thickness of 1 µm to enhance the adhesion of the PNC layer to the substrate. The solution of Ti oxidation was 5.5 wt% of hydrogen peroxide and 2.6 wt% of sodium hydroxide added to a solution of de-ionized water. The oxidation temperature was at 68 °C for 2 minutes. Soft-baking to evaporate the GBL solvent was the second step in the PNC fabrication process. The soft-baking recipe began with a relaxation time of 1 hour at room temperature, then ramped up to 65 °C, at which temperature it dwelled for 5 minutes, then ramped to 95 °C and dwelled for 8 hours, and finally, ramped down to room temperature within 8 hours. Afterwards the samples were fly-cut to obtain a desired uniform thickness. The thickness of the PNC was cut to 100 ± 3 µm for structural evaluation, and 300 ± 3 µm for the mechanical and thermal testing. X-ray exposure of the PNC material was carried out with the X-ray micromachining II (XRLM2) beam line at
The synchrotron beam line was operated at the electron energy of 1.3 GeV, a magnetic field of 1.48 T, and a bending radius of 2.928 m with a transmitted bandpass spectrum of 2.6 keV – 7 keV. The samples were exposed in a 100 torr Helium environment at room temperature to X-rays using a multiple exposure routine with bottom doses of 10, 17, 20, 26, 30, 34, 40, and 43 mJ/cm² through an X-ray mask. Figure 1 shows an image of the X-ray mask, fabricated for the PNC thermal/mechanical tests and a schematic of the exposure setup. The samples were then post-baked on a hotplate with a ramping time of 15 minutes to 95 °C, at which temperature it dwelled for 30 minutes, then cooled to room temperature within 4 hours. Development of the samples was done by alternating between SU-8 Developer (Microchem, Newton, MA) and isopropanol. The samples for mechanical and thermal testing were fabricated into beams 15 mm-long by 4 mm-wide by 0.3 mm-thick. Measurement of these samples required their removal from the substrate. This was done by Si etching using a 30 % potassium hydroxide solution in water.

Two X-ray masks were fabricated in this study: one for fabricating thin films for mechanical property characterization as described above and another consisting of varying line widths for evaluating the structural resolution and surface morphology of the PNC. The masks were made of a 200 µm-thick graphite membrane with 15 µm-thick gold absorber patterns.

**Characterization**

The mechanical, thermal, and structural morphology on the carbon black/SU-8 PNC was performed for the utilization of the PNC material in MEMS devices. These properties include stress-strain characteristics, elastic modulus, glass and degradation phase transitions, surface roughness and structural reduction.

Stress-strain characteristics were evaluated using dynamic mechanical analysis (DMA) with an RSAIII (TA Instruments). Both normal SU-8 and PNC were flexural tested by 3-point bending mode, in agreement with the American Society for Testing and
Materials (ASTM) D 4065-01 standard. An applied load of 500 g was kept constant while varying the strain rate using the dynamic strain sweep test (DSST) mode.

Glass transition and degradation temperatures of the PNC were obtained using differential scanning calorimetry (DSC) with a DSC 6200 (Seiko Instruments). In accordance with ASTM D 3418-03 standard, synthetic sapphire (\(\alpha\)-Al\(_2\)O\(_3\)) was used to calibrate the instrument. Each sample measured weighed 10 mg. The run began with an isothermal hold at 27.7 °C for 5 minutes, followed by a temperature increase to 485 °C with a heating rate of 20 °C/min. The samples were then cooled to room temperature under ambient conditions.

Average surface roughness (Ra) and structural reduction of the PNC was evaluated using an optical surface profiler (Wyko NT3300, Veeco Instruments Inc.) in vertical scanning interferometer (VSI) mode. To gain pertinent information regarding the surface and structural resolution of the PNC, only the top surfaces of the samples were scanned and analyzed.

**Results and Discussion**

**Effect of Carbon Black and Dose on Elastic Modulus**

For stress-strain characteristics of pure SU-8 and the PNC, the samples for these measurements were fabricated into 15 mm by 4 mm by 0.3 mm films, and measured using DMA. The samples prepared with 2 and 4 wt% of carbon black were exposed at bottom doses of 17, 26, 34, and 43 mJ/cm\(^3\). The range of values (3.3 – 6.0 GPa) for the PNCs shows that a low wt% of carbon black added into the SU-8 matrix results in a 3 to 88% increase in stiffness. The trend for both PNC formulations at 26 and 43 mJ/cm\(^3\) is shown in Figure 2. In our preliminary study, the PNC fabricated with 15 wt% of carbon black at a bottom dose of 17 mJ/cm\(^3\) yielded an average elastic modulus of 15 GPa, nearly five times that of pure SU-8\(^27\). The average elastic modulus (E) versus X-ray bottom dose for 2 wt% and 4 wt% of carbon black is shown in Figure 3. On average, the elastic modulus is greater at 2 wt% of carbon black than at 4 wt%. The elastic modulus does not show a clear dependency on variation of dose.

It is known that at certain weight fractions, fillers can behave as stress raisers and also, the probability of achieving uniformly dispersed particles with low weight fractions in the polymer is lower than at higher weight fractions. Agarwal and Broutman\(^28\) state that there is a critical volume fraction, V\(_{\text{crit}}\), which must be exceeded for strengthening. The increase of the elastic modulus at a dose of 43 mJ/cm\(^3\) for both compositions may be characteristic of higher degree of cross linking of the SU-8 matrix. Explanation of this fluctuation in the data may be related to homogeneity of the composite. Development of a method to synthesize the PNC is necessary.
Figure 2. Stress-strain curves by 3-point bending for pure SU-8 and PNC.

Figure 3. Variation of elastic modulus (E) with respect to bottom dose.
Effect of Carbon Black and Dose on Thermal Behavior

Figure 4 shows the thermal curves for pure SU-8 and the PNC. Exothermic reactions from 50 – 100 °C signify the polymer undergoing increased cross-linkage. The completion of the cross-linking is at the glass transition phase of the thermal curve represented as a small endothermic reaction. The degradation temperature ($T_d$) of a polymer is represented by a high endothermic peak. For SU-8, the glass transition temperature ($T_g$) is shown to be approximately 125 °C. This is a lower value than reported from the literature value of 200 °C$^{29}$. The $T_d$ of pure SU-8 was observed to be around 390 – 420 °C. This value is higher than the reported findings of about 380 °C$^{30}$. The addition of carbon black into SU-8 resulted in an initial increase of about 5 °C in both phase transitions of SU-8. As carbon black wt% increased, the $T_g$ of the PNC on average increased by 40 °C and the phase became less prominent. An average decrease in $T_d$ of 13 °C was shown with an increase in carbon black wt%. The plot below shows this tendency for both PNC formulations at 26 mJ/cm$^3$, highlighting the phase transitions. For both carbon black wt% investigated, at a bottom dose of 17 mJ/cm$^3$, no change was observed in either $T_g$ or $T_d$.

Effect of Carbon Black and Dose on Structural Reduction and Surface Roughness

Structural reduction, shown in Figure 5 was also evaluated. Percent deviation from pure SU-8 with respect to the pure SU-8 structural width is plotted. An increase in structural size from SU-8 to PNC was less than 10 %, as the wt% of carbon black increased. The
average surface roughness as a function of carbon black wt% with varying bottom doses of 10, 20, 30, and 40 mJ/cm$^3$ was measured by scanning and analyzing the surface with an optical profiler. Surface roughness measurements revealed an average roughness increase of 75.79 nm for pure SU-8, 277.58 nm for 2 wt% and 395.37 for 4 wt% of carbon black. It may also be suggested that the sidewall conditions deteriorated as the dose increased.

![Graph](image)

**Figure 5. Structural reduction of the PNC compared to pure SU-8.**

**X-ray Micromachining of PNC**

Figure 6 shows X-ray machined PNC microstructures from a low magnification, Figure 6(a) and 6(b), to a higher magnification image at an angle 6(c), using a stereomicroscope. Figure 6(b) shows a top-down view of fabricated PNC columns with a width of 43 µm at a pitch of 130 µm. Figure 6(c) shows the height of the PNC columns at 100 µm. Samples exposed at doses greater than 20 mJ/cm$^3$ were not fully developed, and resulted in rough sidewalls which became apparent in the structural morphology tests. X-ray lithography of the PNC resulted in straight side-walls at a dose of 10 mJ/cm$^3$. Preliminary studies considered the feasibility of micro-fabrication of a micro-particle-filled polymer composite$^{24}$. The necessity of nano-particles and X-rays became apparent after this initial study was conducted. It was observed that UV-lithography of this micro-composite was hardly possible because of UV light scattering and reduced matrix sensitivity to UV light.
Conclusions

Polymer nano-composites were fabricated by X-ray lithography and the elastic modulus, phase transitions, surface roughness and structural resolution were evaluated. From the flexural 3-point bending tests, for 2 – 4 CB wt%, the elastic modulus is in a range between 3.3 and 6 GPa exposed at a bottom dose between 17 and 43 mJ/cm$^3$. The range of values, do not fall below the measured pure SU-8 sample of 3.2 GPa. This shows that the addition of carbon black into the SU-8 matrix enhances rather than deteriorates the mechanical stiffness of the polymeric matrix. The thermal behavior of the PNCs exhibited a glass transition temperature increase from around 125 °C (SU-8) to about 165 °C. The peak degradation temperature decreased 13 °C from pure SU-8 with an increase in wt% of carbon black. The surface roughness increased with increased CB wt% from an average roughness of 277.58 nm for 2 carbon black wt% to an average of 395.37 nm for 4 carbon black wt%. Bottom dose showed no optical variation on surface roughness or the structural resolution. The structural resolution of the PNC was less than 10 % of pure SU-8. Parameters for achieving a conductive carbon black/SU-8 PNC with increased glass and degradation temperatures from that of pure SU-8, and minimal surface roughness and reduction, warrant a carbon black wt% of 4, with a bottom dose between 10 and 17 mJ/cm$^3$. The elastic modulus of this PNC would increase about 20 % from pure SU-8.

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