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Material Characterization of Carbon-Nanotube-Reinforced Polymer Composite

Soonwan Chung, Sandeep Makhar, Harold Ackler, and Seungbae Park*

Department of Mechanical Engineering, State University of New York at Binghamton
Binghamton, NY 13902, U.S.A.

The material properties of Carbon-Nanotube (CNT) reinforced polymer composite are characterized by tensile testing to find the potential application of multi-walled carbon nano-tube (MWNT) to micro-devices and electronic packaging. SU-8 is used as a polymer material and mixed with MWNT of 0.2 wt%. Dogbone samples of 0.1 mm thickness are prepared by micro-fabrication process, which is composed of spin coat, soft bake, expose and post exposure bake. Young's modulus and Poisson's ratio are measured by changing applied strain rate at elevated temperatures. In this study, an in-house tensile testing setup called Nano Characterization System (NCS) was utilized for accurate force measurement of micro-scale specimen. Also, Digital Image Correlation (DIC), in-situ strain measurement technique, was used to measure accurate strain. The material properties of CNT-reinforced SU-8 are compared with those of SU-8 material. In addition, the viscoelastic material properties of SU-8 are measured by stress relaxation test and dynamic mechanical analysis.

Keywords: multi-walled carbon nano-tube, SU-8, strain rate effect, temperature effect, dynamic mechanical analysis

1. INTRODUCTION

For the successful utilization of SU-8 in MEMS, it should be warranted to understand the material behavior such as mechanical and thermal properties in MEMS scale. Therefore, the mechanical characterization has been conducted through many works. Biaxial modulus of elasticity and the CTE of SU-8 were determined by measuring warpage of a 20 μm thick resist layer on Si substrates subjected to thermal loading from 20 to 95 ^{o}C[1]. The shear strength of the cantilevered SU-8 micro-posts fabricated on silicon substrates was measured using the static cantilever beam bending[2]. The depth-sensing micro-indentation test was proposed to obtain Young's modulus and hardness of thin films[3]. The effects of processing conditions such as thermal baking time, thermal baking temperature and UV exposure dose to the thermal and mechanical properties were evaluated, also[4]. In the previous works, Young's modulus of SU-8 have been investigated[1, 5, 6], where it can be seen that the elastic modulus after being exposed to UV radiation or against proton exposure dose is about 3.9 - 5.5GPa. For the use of SU-8 as a material of micro-fluid channel where hot liquid flows, the authors performed tensile tests at elevated temperatures to see the change of Young's modulus and Poisson's ratio of SU-8 according to temperature[7]. Recently, the use of carbon nanotube within a polymer matrix has been proposed for outstanding mechanical, electrical and thermal properties[8-10]. The elastic modulus of MWNT-reinforced epoxy composite thin film was determined using a shaft-loaded blister test, and a 20% increase in elastic modulus was seen compared to net resin thin films when 0.1 wt% MWNTs were added[9]. It was shown that functional carbon nanotubes could be chemically bonded to SU-8 resin by opening the epoxide group in acidic conditions, and the influence of factors such as acidity, reaction temperature and the nanotube concentration were investigated[10].

In this study, the multifunctional polymer composite reinforced with carbon nanotube (CNT) is characterized at various temperatures and applied displacement rates from tensile test. The tensile test setup developed in our laboratory was used to measure accurate load data. Digital Image Correlation (DIC) technique, a form of photogrammetry, is a non-contact optical deformation measurement technique in which the surface features of the object are traced in digital images. It has some features such as the simplicity in measurement procedure and relaxed surface condition requirements. Young's modulus and Poisson's ratio of CNT-reinforced SU-8 is compared with that of SU-8 polymer. Since viscoelasticity provides a usable engineering approximation for many applications in polymer and composites

*Corresponding author: sbpark@binghamton.edu

engineering[11], the viscoelastic material characterization of CNT-reinforced polymer composite is important for the modeling and simulation works. In this study, the viscoelastic material testing is performed at various temperature environments. The variation of applied strain rate, stress relaxation test[12-15] and dynamic mechanical characterization test[16] are considered for viscoelastic testing.

2. SAMPLE PREPARATION

2.1. Fabrication of SU-8 samples

In this study, tensile tests were performed on SU-8 and CNT-reinforced SU-8 composite dog-bone shaped samples with identical dimensions, which are 20 mm gauge length, 4mm width and 0.1 mm thickness. Since SU-8 is a negative photoresist, wherein the area of the resist exposed to UV light solidifies during development and the area unexposed to UV dissolves in the developer, dog-bone shaped bright openings were created in the dark field. Figure 1 shows the fabrication process flow of SU-8. SU-8 belongs to the epoxy group of polymers that are characterized by excellent adhesion. Moreover, cross-linked SU-8 is known to be extremely difficult to remove. Hence this process uses OmniCoat, an adhesion promoter / release layer specifically produced to reduce adhesion between SU-8 and silicon, produced by Microchem Corp. OmniCoat was coated on wafer by spinning and dynamic dispense. Thickness of OmniCoat was about 17 nm. The wafer was baked for 1 minute at 200 °C on a hotplate and then allowed to cool to room temperature before beginning the SU-8 processing.

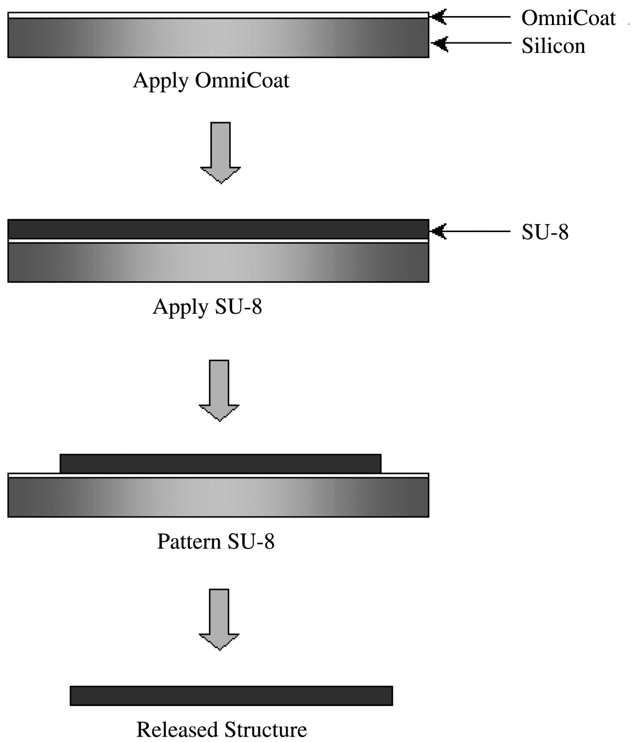


Fig. 1. Tensile test samples fabrication flow.

The SU-8 processing consists of spin coat, soft bake, expose, post exposure bake (PEB), development and an optional hard bake. SU-8 was coated by static dispense followed by spread cycle for 10 seconds at 500 rpm and spin cycle for 35 - 40 seconds at 1350 - 2900 rpm. Time and speed during spin cycle varied depending on desired SU-8 film thickness. After spinning, the substrate was soft baked at 65 °C for 30 minutes and then at 95 °C for 90 minutes to evaporate the solvent and densify the film. After baking, the substrate was allowed to cool to room temperature and then exposed. The mask, printed on a transparency, was placed on the wafer and then a glass plate was put over it. UVP B-100 AP, 365 nm wavelength exposure tool, was used for UV exposure. The wafer was exposed in dose steps with 60 seconds interval between consecutive exposures. This allowed better absorption of energy and light induced reactions to take place and avoided the hardening of the top surface that could affect the film quality, due to high exposure dose and long exposure time. After a hold time of about an hour, PEB was carried out. PEB was done for 2 minutes at 65 °C and 20 minutes at 95 °C to cross-link exposed regions.

2.2. Fabrication of CNT-reinforced SU-8 samples

Functionalized CNT, obtained from Zyvex Corp., and SU-8 were mixed by weight percentage using a laboratory blender to get the CNT reinforced polymer composite. The blending was performed in steps at various speeds between 3,500 rpm and 22,000 rpm. This was done to get a good dispersion of the MWNTs in the SU-8 matrix and avoid heating of the composite and solvent evaporation. Long blend time, more than 15 - 20 seconds, caused fumes from the material blended and heating of the blender and the material. Low rpm or low time does not yield good dispersion of the

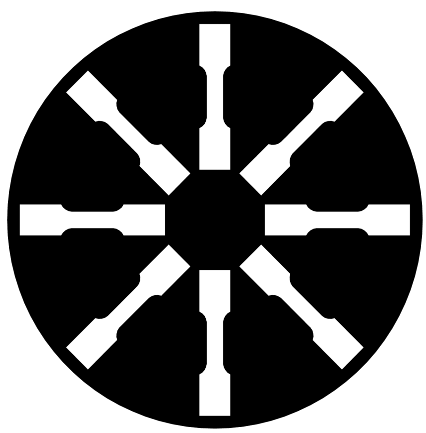


Fig. 2. Layout of polymer composite on the mask.

MWNTs in the matrix. The composite prepared had gasses trapped in them. These gases were removed by applying vacuum using a degasser. The process had to be repeated a few times to remove air bubbles.

Composite sample fabrication is similar to the SU-8 sample fabrication with some changes made to better suit the material. The mask was initially same for both the composite and SU-8. However, this yields samples with random CNT orientation and can cause inconsistency in the results during testing. Therefore, to avoid discrepancy in the results and orient the fibers in the axial direction, the mask was modified as shown in Fig. 2. The test samples were radially oriented to get the CNT orientations along the axial direction during spin cycle. OmniCoat was coated on wafer by spinning and dynamic dispense. The wafer was baked for 1 minute at 200 °C on a hotplate and then allowed to cool to room temperature. SU-8 with MWNTs was coated by static dispense followed by spread cycle for 10 sec at 500 rpm and spin cycle for 35-40 sec at 1000 rpm. The wafer was soft baked at 65 °C for 30 minutes and then at 95 °C for 90 minutes. This allowed absorption of energy and light induced reactions to take place. PEB was done for 2 minutes at 65 °C and 20 minutes at 95 °C to cross-link exposed regions. The composite was then developed in SU-8 developer for about 5 minutes with agitation.

3. EXPERIMENTAL SETUP

Basically, all the pulling tests were performed through tensile tester, Nano Characterization System. This system is comprised of precision linear stages which function as the loading mechanism, a six-axis force transducer, a custom environmental chamber, a DIC System (Digital Image Correlation), and a custom LabVIEW user interface and data acquisition system. The system is capable of XYZ movement through a combination of two precision linear stages and one micro stage, all with strokes of 25 mm. The strain was measured by DIC (Digital Image Correlation) technique. In case of the slippage of grip at high temperature condition, the strain from optical measurement technique is supported. In addition to more reliable result, Poisson's ratio can be calculated through DIC technique since not only longitudinal strain but also transverse strain can be measured. When the products made from polymeric materials are designed, the prediction of performance over long periods of time is important. The amount of deformation after short or long term loading has to be known in advance. Stress relaxation tests are carried out for long term viscoelastic characterization, and DMA (dynamic mechanical analysis) is performed for short term viscoelastic characterization. For DMA, BOSE ELF3200 micro tester was utilized.

4. EXPERIMENTAL RESULTS

4.1. SU-8

4.1.1. Young's modulus and Poisson's ratio

The variation of Young's modulus and Poisson's ratio according to applied strain rate is investigated using SU-8 material. The strain rates used are between 5 and 25 ($\times 10^{-5}$ / sec). As shown in Fig. 3, Young's modulus increases as the increase of loading rate at all temperatures. It can be seen that Young's modulus decreases according to the increase of temperature, also. For Poisson's ratio, it is hard to find a tendency related to loading rate effect. That is, the effect of loading rate on Poisson's ratio can be negligible compared to that on Young's modulus. The increase of Poisson's ratio can be confirmed as the increase of loading rate.

4.1.2. Stress relaxation

To investigate the characteristics of SU-8 for stress

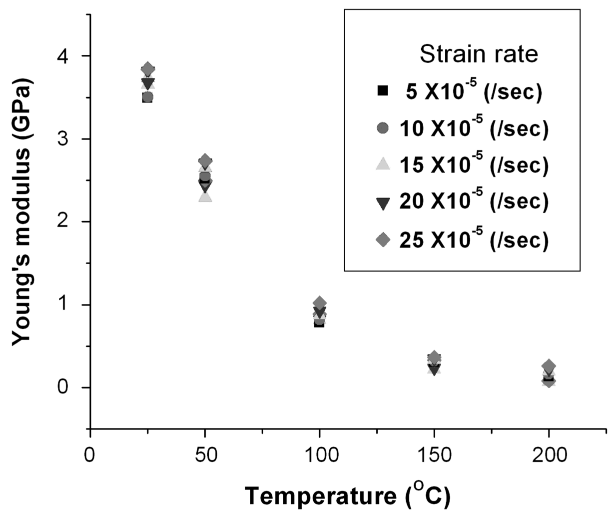


Fig. 3. Young's modulus of SU-8 vs. Temperature.

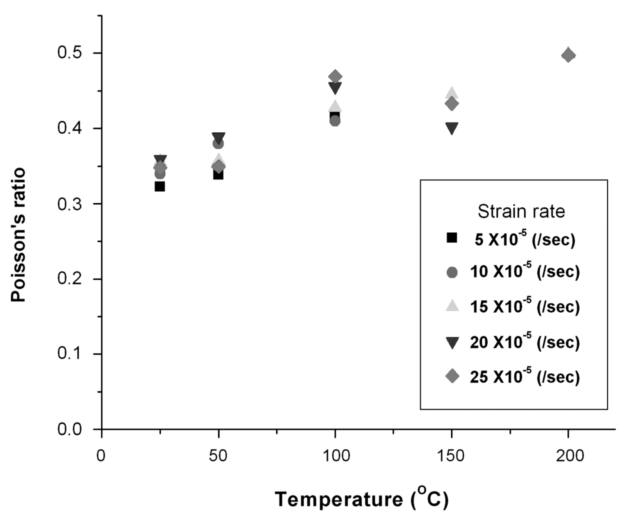
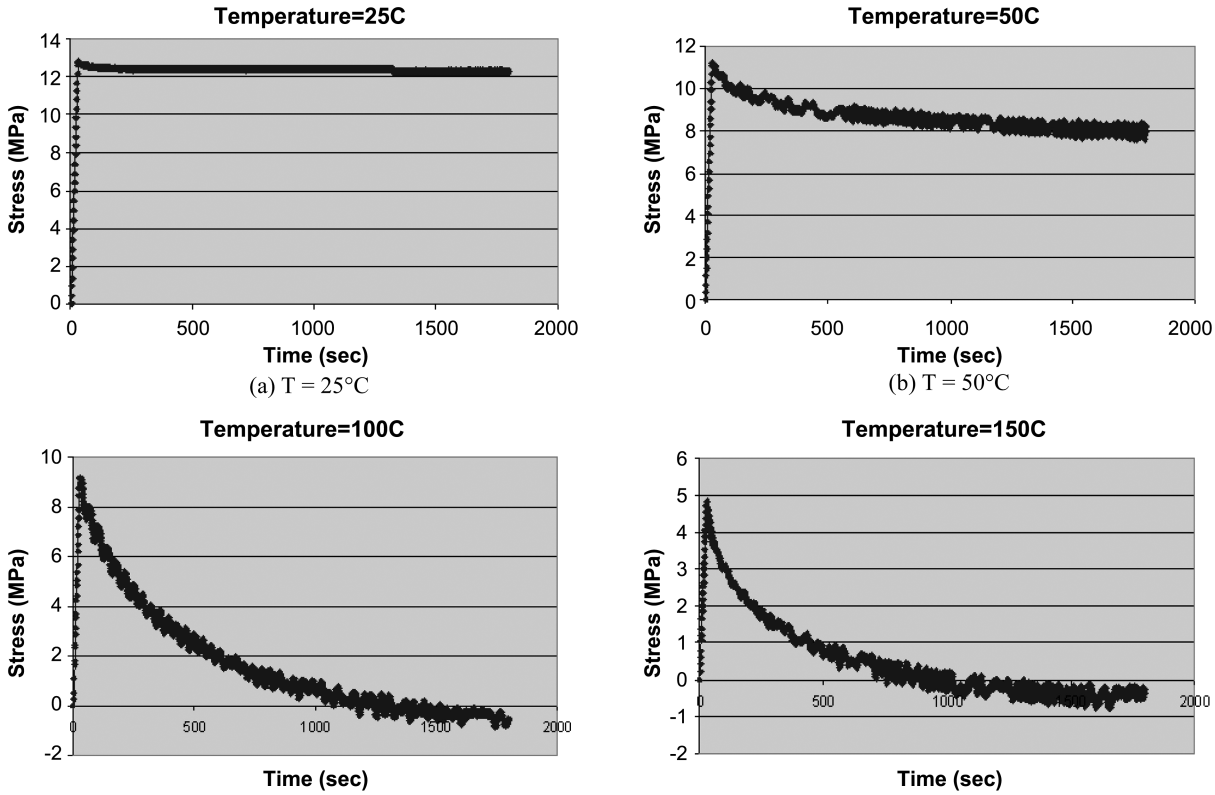


Fig. 4. Poisson's ratio of SU-8 vs. Temperature.



(a) T = 25°C (b) T = 50°C (c) T = 100°C (d) T=150°C

Fig. 5. Time history of required stress during stress relaxation.

Table 1. Stress relaxation test

Temperature (°C)	Resulting stress (MPa)	Drop of stress after 10min (MPa)	Ratio of load drop (%)
25	12.8	12.4	3.1
50	11.2	9.26	17.3
100	9.2	3.8	58.7
150	4.8	1.48	69.2
200	3.2	1.35	57.8

relaxation test, the samples were stretched by 0.08mm at the strain rate 15×10^{-5} / sec. The temperatures used are 25, 50, 100, 150 and 200 °C, and the corresponding time histories of resulting stresses are shown in Fig. 5. As the temperature increases, the stress to reach displacement 0.08 mm decreases due to the reduced Young's modulus. Furthermore, large drop of stress is clearly seen at high temperature. The resulting stress and the drop of stress after 10 minutes are summarized in Table 1. From the results, it can be confirmed that the temperature effect on stress relaxation of SU-8 is so great. Based on time history, the stress relaxation modulus can be calculated. The discrete Maxwell model, which is Prony series[12], can implement the stress reduction in accordance with time. In the near future, a unified stress relaxation model will be suggested to include the effects of applied strain level and temperature[17].

4.1.3. Dynamic Mechanical Analysis

To measure viscoelastic material properties of pure SU-8 material, DMA (dynamic mechanical analysis) was carried out with variation in amplitude and frequency as shown in Fig. 6. For one amplitude condition, various frequencies from 0.1 to 10 Hz were applied. It was also performed at elevated temperatures up to 200 °C. Figure 7 shows the storage modulus, loss modulus and loss factor (tan δ) as a function of temperature. It is known at glass transition temperature that the drop in storage modulus and the peak in loss modulus or loss factor occur. From DMA results, glass transition temperature of SU-8 used in this study seems to be in the range of 120 - 150 °C. As frequency increases, glass transition temperature also increases.

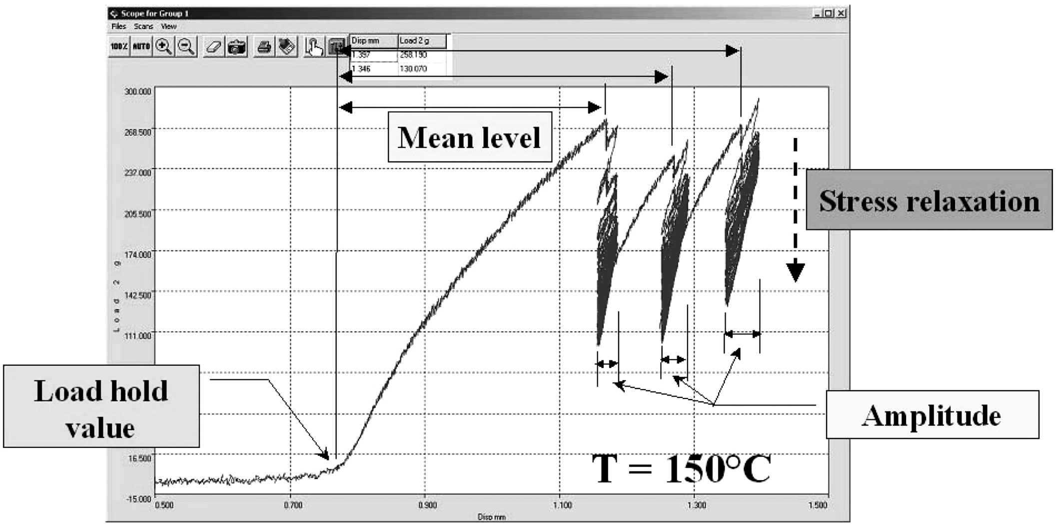
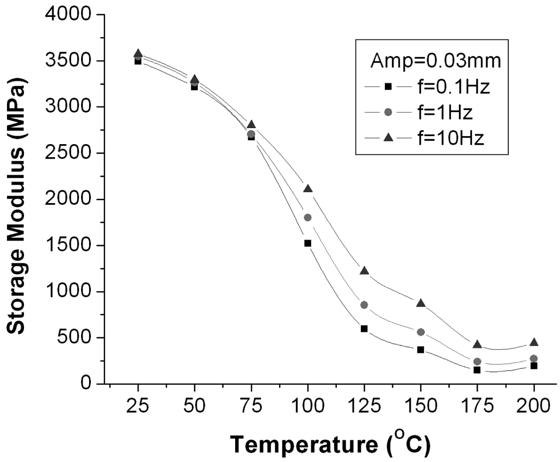
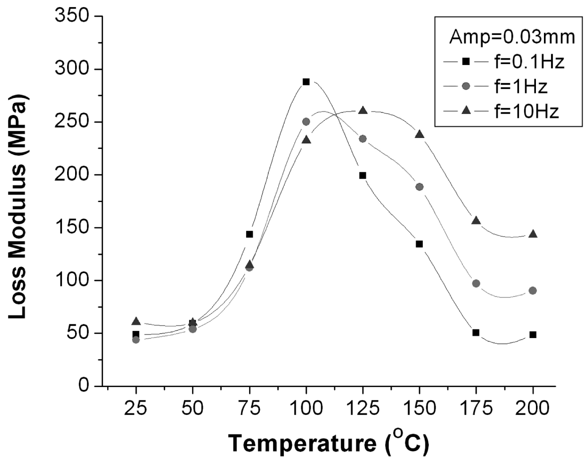


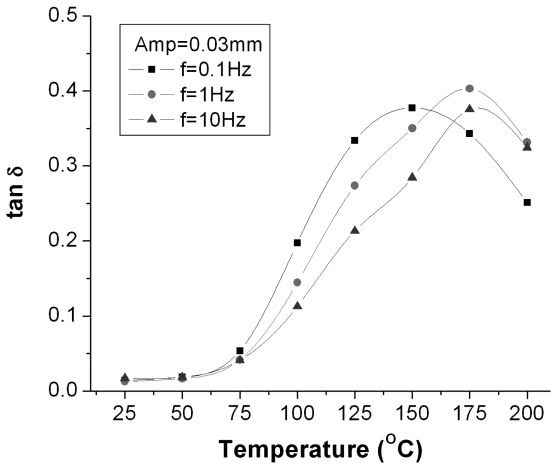
Fig. 6. Typical testing profile for DMA.



(a) Storage modulus



(b) Loss modulus



(c) Loss factor

Fig. 7. DMA results with respect to temperature.

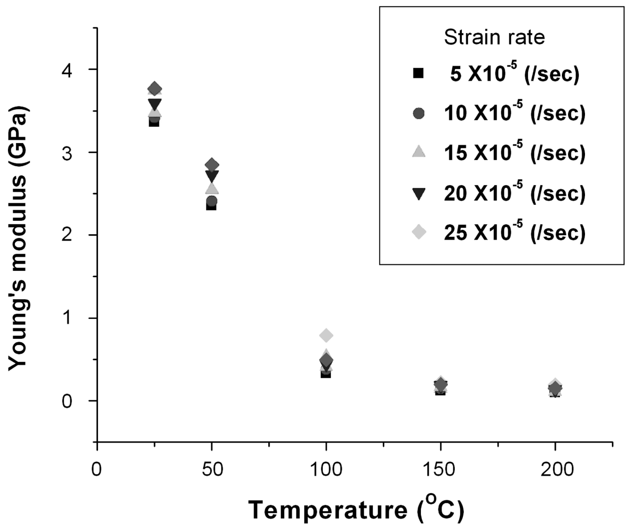


Fig. 8. Young's modulus of CNT-reinforced SU-8 vs. Temperature.

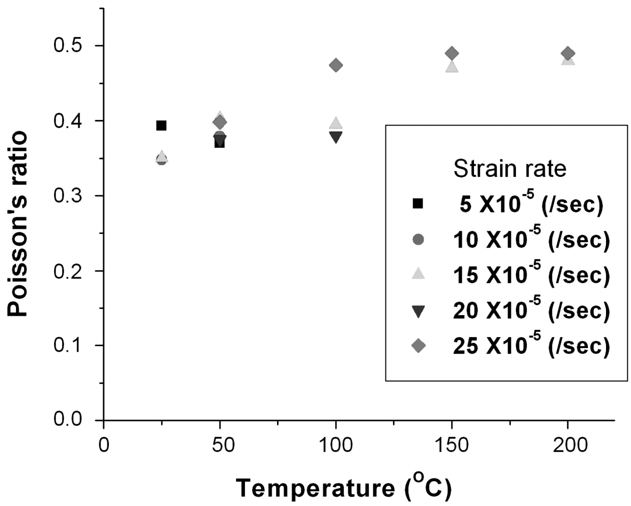


Fig. 9. Poisson's ratio of CNT-reinforced SU-8 vs. Temperature.

4.2. CNT-reinforced SU-8 composite

As the same way of SU-8 testing, Young's modulus and Poisson's ratio of CNT-reinforced SU-8 were extracted by pulling test. The sample contains CNT of 0.2 wt%. Figure 8 and 9 show Young's modulus and Poisson's ratio, respectively. Young's modulus of CNT reinforced SU-8 composite is a little larger than the one of pristine SU-8. However, the authors couldn't see large increase in Young's modulus of CNT polymer composite as expected. Concerning these results, several issues can be discussed. One is the lumped CNT in the sample. For the fabrication of composite polymer material, MWNT were mixed with SU-8 solution to get a good dispersion of MWNT. However, some MWNT were conglomerated over the sample, so the effect of CNT didn't show well. The other thing is the misalignment of MWNT along the axial direction. The authors have tried to get MWNT orientation along the axial direction by making test samples to be radially oriented, but good alignment was not easy due to conglomeration of CNT. More study on cutting MWNT will be performed to solve the problem. Poisson's ratio of composite polymer material is about 0.35-0.5 at elevated temperatures.

5. CONCLUSIONS

The material properties of SU-8 and CNT-reinforced SU-8 composite were investigated by fabricating based on patterning. Micro tensile tester systems were utilized to apply tensile and cyclic forces and DIC measurement technique was utilized to measure accurate longitudinal and transverse strain. Young's modulus increases as the applied strain rate increases in both materials. Poisson's ratio increases as temperature increases. It is shown in stress relaxation test of SU-8 that stress is reduced so fast at high temperature. Viscoelastic material properties were obtained as a function of frequency by DMA. The feasibility of CNT-reinforced SU-8 composite is studied comparing with SU-8 material properties. There are many issues regarding the fabrication of CNT because it is very difficult to get well-mixed CNT polymer composite. Further research on the fabrication will be worked.

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