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Exploring In-Situ Nanomechanical Responses Self-Healing PDMS and Carbon Fiber

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Abstract

The intrinsic self-healing polymers are smart materials that have the capability to recuperate a crack partially or fully by intermolecular interaction such as disulfide, hydrogen bonding, hydrophobic interaction, ionic bonding, etc. This study focuses on a self-healing polymer/carbon fiber composite, synthesized using a one-pot polycondensation method. This method combines amino-terminated poly(dimethylsiloxane) (Mn = 5000) with 4,4′-methylenebis (phenyl isocyanate) and isophorone diisocyanate, applied to carbon unidirectional fiber. We envisage applications where the self-healing polymer present in the composite interfaces heals the cracks on carbon fibers. The research includes a detailed characterization of the polymer and composite, focusing on micromechanical properties such as reduced modulus, hardness, and microcrack self-healing efficiency. Nanoindentation is used to analyze the mechanical behaviors and demonstrate the healing properties of the self-healing polymer and the composite

I. INTRODUCTION

After over four decades of extensive research, advanced composites comprising high-modulus fibers in a compliant polymeric matrix have become the preferred lightweight structural materials for many aerospace and aeronautical applications. Several advantages are offered by these composites over traditional metallic materials, including high specific strength and stiffness, excellent manufacturability, and corrosion resistance. Initially developed for military

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aircraft in the 1970s, these composites now play a vital role in a wide range of modern military aerospace systems, achieving weight reductions of 10–60%, with 20–30% being common, as seen in the U.S. Air Force B2 bomber and the F-22 Raptor (24%) [1]. The commercial aviation industry has also seen a significant shift towards polymer composites. For instance, the Boeing 787 Dreamliner is composed of approximately 50% polymer composites by weight and more than 50% by volume [2, 3]. Additionally, the adoption of polymer composites in areas like lightweight composite armors and load-carrying parts in ground vehicles has been spurred by the U.S. military's need for faster, more agile ground vehicles and the civilian sector's focus on cost-saving and fuel efficiency. However, despite their growing use, challenges and barriers still exist in the widespread application of composite technology for primary transport structures such as aircraft wings and fuselages, and composite propulsion shafts in heavy-duty ground vehicles [4].

Intrinsic self-healing or autonomic-repairing polymers have the capability to automatically repair damage. These polymers, both natural and synthetic, span a range of materials including thermosets, thermoplastics, and elastomers, all possessing self-repairing potential [5]. They can heal in response to various types of damage such as impact, corrosion, or pressure. This self-healing process can be automatic or triggered by external stimuli like heat, pressure, or humidity [6].

Therefore, in this study, we propose a novel interfacial self-healing technique between the self-healing polydimethylsiloxane (PDMS) and on unidirectional carbon fiber. A proof-of-concept hybrid multiscale of weak and strong hydrogen bonding was processed via integration of the thin films of SH-PDMS and carbon fiber. Along with the chemical characterization, such as Fourier transform infrared spectroscopy (FTIR), and mechanical characterization using viscometer and nanoindentation. The micromechanical properties such as reduced modulus, hardness, and micro crack self-healing efficiency at room temperatures were investigated for both the polymer and the SH-PDMS carbon fiber composite using nanoindentation.

II. Materials and Methods:

Bis(3-aminopropyl) terminated poly(dimethylsiloxane) (PDMS monomer Mn = 5000), isophorone diisocyanate, 4,4′-methylenebis (phenyl isocyanate), methanol and chloroform were purchased from Sigma Aldrich and used as is.

A. Synthesis Procedure

Synthesis of PDMS-MPU-IU polymer: To a flame dried 250 mL Schlenk flask under nitrogen was added bis(3-aminpropyl) terminated poly(dimethylsiloxane) (15.0 grams, Mn = 5000, 1 equiv) followed by anhydrous tetrahydrofuran (THF) (30 mL). The solution was cooled to 0 °C and triethylamine (0.40 mL, 1 equiv) was added. To a 100 mL flame dried round bottom flask was added Methylenebis(phenyl isocyanate) (0.30 grams, 0.4 equiv) and Isophorone diisocyanate (0.40 grams, 1.6 equiv) followed by anhydrous THF (15 mL). The solution of diisocyanates was then added to the reaction mixture dropwise over a period of about 15 minutes. The reaction was allowed to slowly warm to room temperature and stir overnight. After 12-15 hours, the reaction is quenched with anhydrous methanol (0.5 mL, 10 equiv). The reaction was allowed to stir overnight then solvent was removed by rotary evaporation to give a solution of about 40% polymer in THF. The solution was poured into a silicone mold and cured at 100 °C for 2 hours under vacuum [8-10].

B. Nanoindentation Procedure

Nanoindentation is a powerful technique that allows to assess the mechanical properties of materials at the nanoscale. Bruker TI-980 nanoindenter system used in this work has many possible functions like high load indent, low load indent, nanoDMA, xSol high temperature-based indent, nano scratch, and nanoECR electrical based indent. In this research, testing was done using a high load indent. When applied to self-healing polymers (SH-PDMS), this approach offers valuable insights into the material's mechanical characteristics at the nanoscale and self-healing capabilities of these materials. The first step in using the nanoindenter is to load the sample and find the sample surface using an optical microscope and then create a sample boundary where the user wants to test the sample. The second step was to perform calibrations such as air indent and quick approach. In system test the contact threshold for high load should be 1500 μN and check system calibration values for high load to proceed quick approach, which is performed before the actual indentation test as it studies top surface of the test sample as indenter tip is brought into close to the sample surface.

A diamond Berkovich tip Fig. 1a was used for the nanoindentation tests. This device could apply controlled loads on the specimen and take exact measurements. The pristine SHP and self-healing PDMS with carbon fiber that were tested. The specimens were subjected to a 5mN to 30mN load using a high load tip, as of the material's softness, and 5mN force was applied in a triangular load function at 0.5mN/s loading rate. In force-displacement curve, the loading curve has a parabolic shape and has a combination of plastic and elastic deformation while in unloading, plastic deformation remains, and stored elastic energy is released. Modulus is calculated based on the slope of the unloading curve, or stiffness, and the area of contact of the probe on the material. Hardness is derived from the maximum force of the indent divided by the contact area of the probe on the material. The final step was done on the load-displacement plots and test photos to evaluate the self-healing capabilities of SH-PDMS and CF/SHP composite molecular weight 5000. The reduced modulus and hardness are calculated using the Oliver-Pharr method [7] as described by the equations 1 and 2 below.

$$\text{Reduced elastic modulus, } E_r = \frac{S\sqrt{\pi}}{2\sqrt{Ac}} \tag{1}$$

$$\text{Hardness, } H = \frac{Pmax}{Ac} \tag{2}$$

Here, S is the contact stiffness measured as the slope of unloading curve, P_{max} is the maximum applied force – measured from force-displacement curve, A_c is contact area measured from image or by knowing the area vs. contact depth for the indenter.

The study will pave the way for the use of these materials in applications where self-healing is essential such as biomedical devices, flexible electronics, and structural components by showcasing the self-healing capabilities of SH-PDMS. Also, self-healing properties of SH-PDMS materials can minimize waste and environmental effects while promoting sustainability. All things considered that self-healing polymers and their practical applications which will help create more resilient and useful materials for a variety of industries.

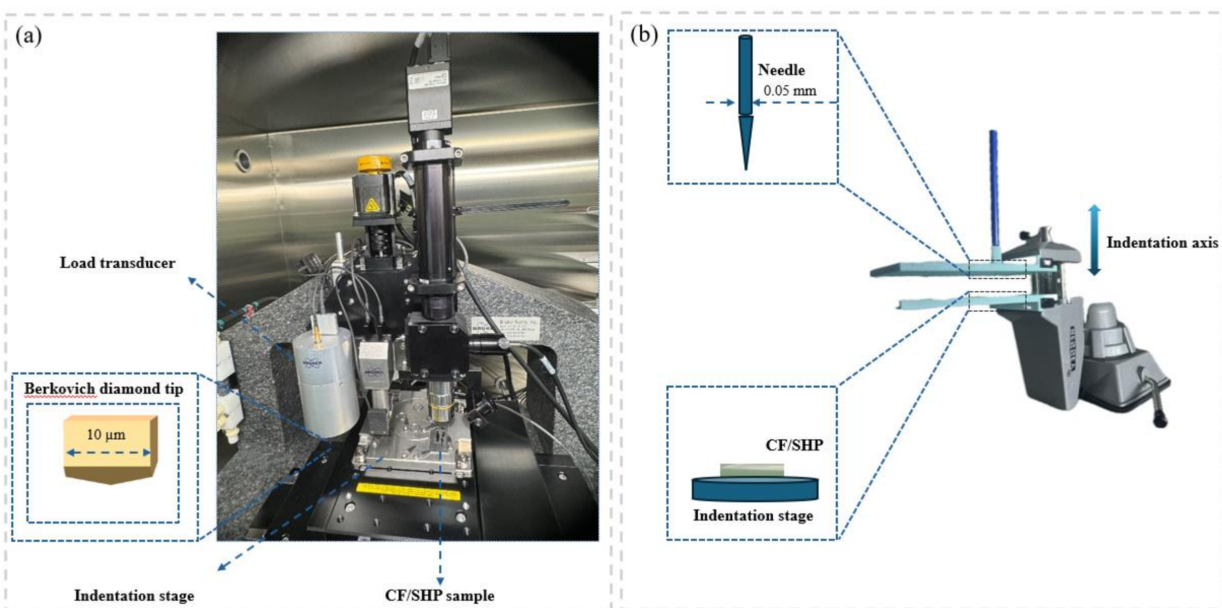

Fig. 1 CF/SHP indentation setups. (a) Bruker TI-980 nano-indentation setup with Berkovich tip. (b) Customized micro-indentation setup with sharp needle.

C. Macroscale Indentation

Macro scale indentation can be used to determine the self-healing properties of a material with larger damage area. This is useful to demonstrate the healing properties beyond the nano scale. Self-healing PDMS with carbon fiber sample is placed on an aluminum plate to provide a hard, stable surface to indent upon and to provide an easy way of moving the sample. This assembly is then placed in the customized indentation setup Fig.1 (b). Constant displacement is applied with the needle on CF/SHP molecular weight 5000 with three repetitions are performed. The optical microscope is used to find the healing rate after every 2hrs of healing at room temperature. Also, the load to indent can be controlled by moving the knob up and down. Once the process is complete, the indentation mark can be measured with an optical microscope to record the rate of healing.

D. Rheological Characterization:

In the rheological properties of polymer with molecular weights of 5000 g/mol were tested using a rheometer. The rheological tests were on SHP 5000, with a diameter of 20 mm^2. The rheological characterization involved two types of tests: viscosity measuring and storage modulus & loss modulus. The flow sweep test was conducted at shear rates ranging from 0.1 to 100 1/s, allowing for the measurement of apparent viscosity and the shear-thinning behavior. The oscillation stress was performed over a stress range of 10^{-8} to 10^{-2} MPa, enabling the determination of storage and loss moduli.

III. Results and Discussion

The room temperature curing of the SH-PDMS with starting molecular weight 5000- now termed as SH-PDMS 5000 films measures on an average of at 0.4 mm thickness. Fourier transform infrared spectroscopy (FTIR) was employed to characterize the material's composition. The peaks in the spectrum correspond to different vibrational modes of the molecules in the sample ensured the consumption of isocyanate groups around 2200 cm^{-1}, indicating complete synthesis as shown in Fig. 2(a). The scanning electron microscope image is shown in Fig. 2(b) close-up view of the material's surface morphology at a magnification of 500x.

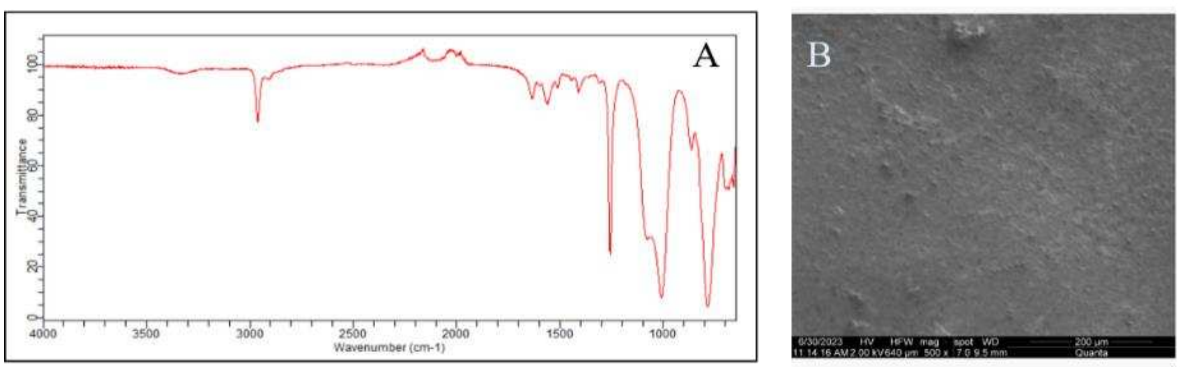

Fig. 2: (a) Fourier transform infrared spectroscopy (FTIR) of the self-healing PDMS (b) Scanning electron microscope image of the Self-healing PDMS film

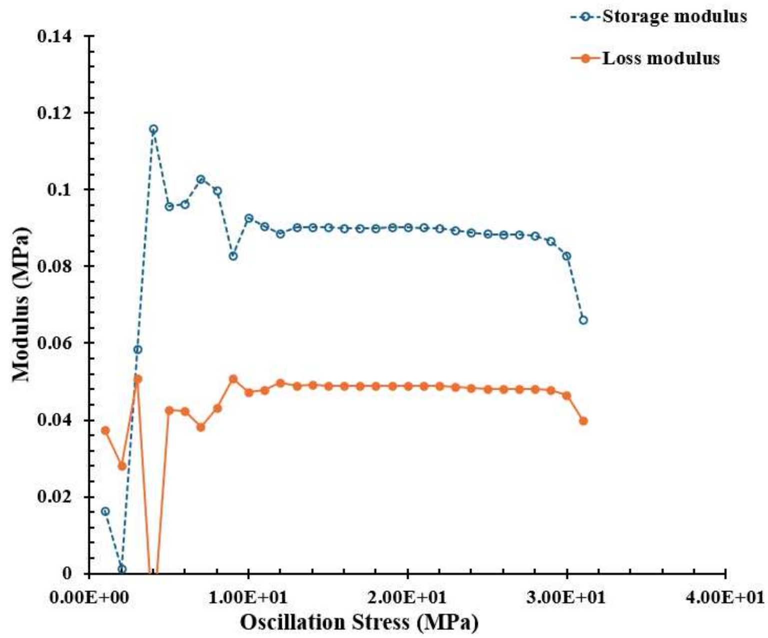

Fig. 3 Viscometer characterization for storage modulus and loss modulus of SHP-PDMS

We investigated the rheological properties of SHP with a molecular weight of 5000. The rheological characterization of pristine SH-PDMS 5000 revealed its flow behavior and viscoelastic nature of the material. As the apparent viscosity measurements from the flow sweep test shows that SH-PDMS 5000 exhibited lower viscosity value. Low viscosity indicates that SH-PDMS 5000 possesses high flowability. The oscillation stress sweep test provides viscoelastic nature of the material through the storage modulus (G') and loss modulus (G'') measurements. For SH-PDMS 5000, the gap between G' and G" was relatively small Fig. 3 and smaller the gap between these moduli suggests that the viscous component of the material's response is leading to a lower viscosity and improved flow characteristics. The low viscosity and enhanced flow properties of SH-PDMS 5000 can have significant implications for processing and applications where improved melt flow and processability are desirable.

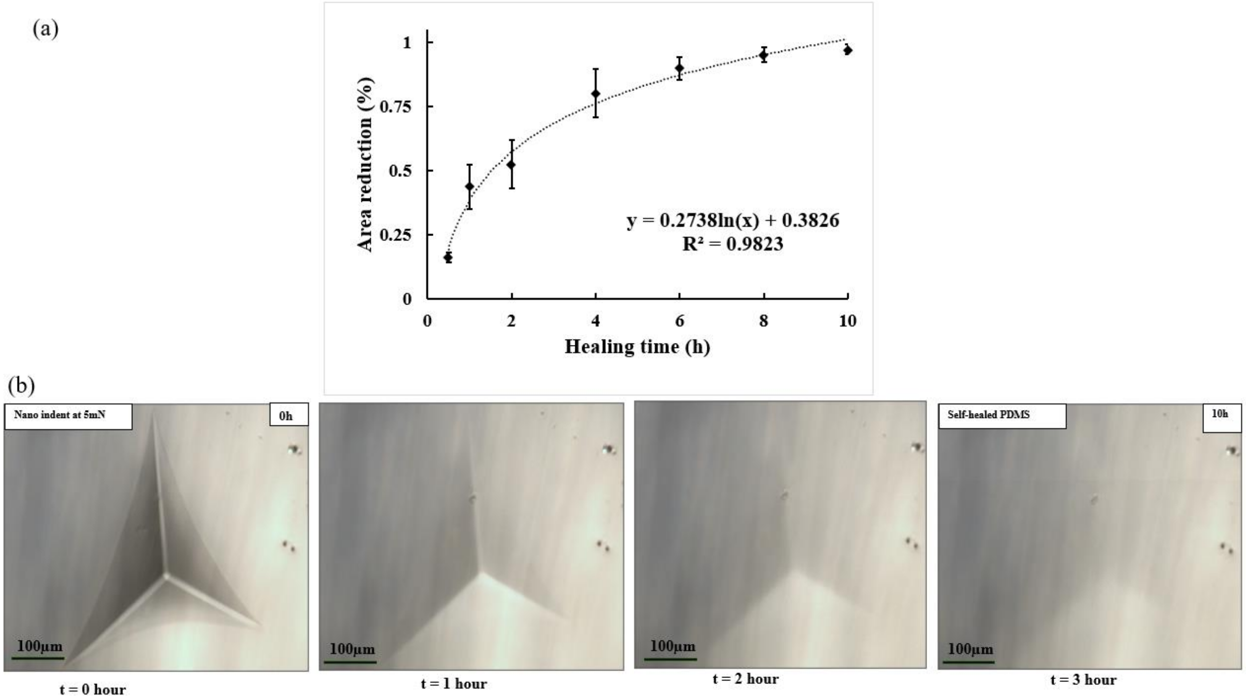

Fig. 4 CF/SHP healing curves (a) Nano-indentation healing rate (b) Nano-level healing microstructures at different times.

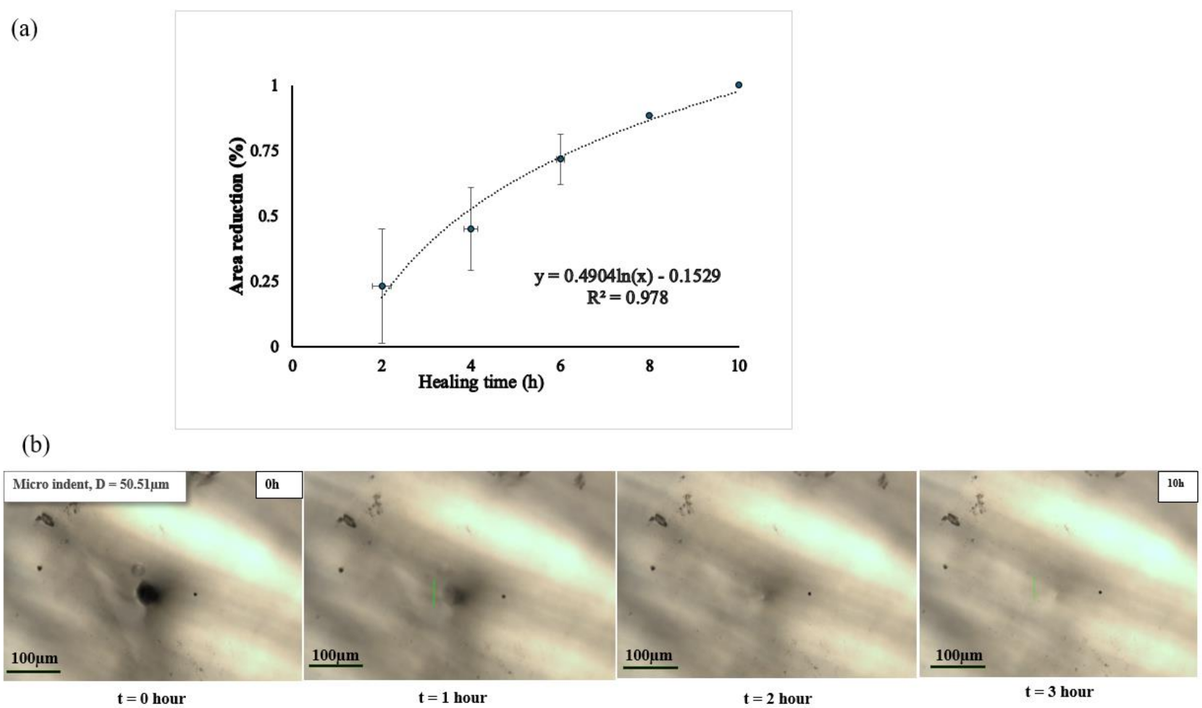

Fig. 5 CF/SHP healing curves (a) Micro-indentation healing rate (b) Micro-indentation healing microstructures at different times.

The nano-scale indentation results using load control reveal that the indentions completely healed in 10 hours. This behavior is observed in both pristine SH-PDMS and CF/PDMS molecular weight 5000, with 100% healing in both cases on 3 repetitions. As shown in Fig. 4(a) CF/SHP composite demonstrates that an indent damaging the fiber surface is repaired by the action of self-healing polymer. The healing rate is calculated by finding the area of triangle and then area reduction rate. The findings of nanoindentation will provide valuable insight into the healing kinetics of the SH-PDMS5000 material after every 2h of healing Fig.4(b) and confirm the effectiveness of the self-repair process. The error bars in the graph indicate variability on three different indents. At nanoscale it shows that there is less variability in the data on repeatability.

The micro-sale healing capability of the material is depicted in Fig. 5(a), where percentage healed from the needle hole is represented with healing time. This graph presents the self-healing performance of a material over time at room temperature for a total of 10 hours. The Indent shows an area reduction rate and length of the hole starts with 50.51µm to reduce to 14.14 µm in the healing percentage over time, indicating the material is capable of self-repairing at room temperature over 10-hour period shown Fig. 5(b). The error bars in the micro-level indent show more variability on testing three different indents. Therefore, the healing rate varies more at micro-level scale.

Mechanical testing results on SH-PDMS 5000 composite interfaces will be presented. Nanoindentation were conducted on pristine SHP and CF/SHP using a load-control indentation technique with a peak load of 5 mN, loading rate of 0.5 mN/s, and loading time of 10 seconds. The load-displacement curves exhibited a gradual increase in displacement during loading and then large jog to a much greater displacement marked to the beginning of the unloading. The unloading curves revealed a reduced modulus of 17 ± 2 MPa and hardness of 6.5 ± 1.5 MPa for pristine SHP Fig. 6(a), while the CF/SHP composite exhibited significantly higher values of 32 ± 1.5 MPa and 20 ± 5 MPa, respectively Fig. 6(b) due to the reinforcing effect of carbon fibers.

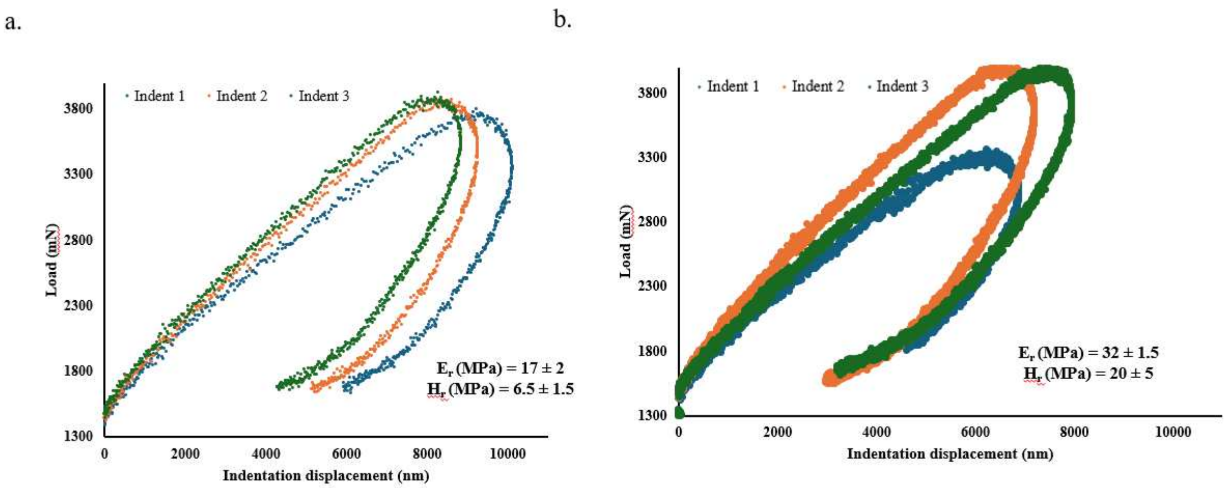

Fig. 6 Nanoindentation using load control (a) Nanoindentation on pristine SHP Mwt. 5000 (b) Nanoindentation on CF/SHP composite Mwt. 5000

IV. Conclusions

We synthesized a self-healing polydimethylsiloxane (PDMS) composite reinforced with carbon fiber and a self-healing polymer (SHP). The SHP was characterized using FTIR spectroscopy and SEM. Rheological characterization revealed that the SHP exhibits superior flowability, lower viscosity, and shear-thinning behavior. Nanoindentation studies demonstrated that the composite achieved 100% healing at the nanoscale and exhibited healing at the microscale as well. The nanoindentation testing showed that the SHP composite possesses higher mechanical properties, such as increased hardness and reduced modulus, compared to pristine SH-PDMS.

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