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TECHNICAL NOTE

Laser induced deformation in polydimethylsiloxane membranes with embedded carbon nanopowder

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Abstract
We demonstrate optically induced micron-range deformation of polydimethylsiloxane (PDMS) membranes with embedded carbon nanopowder. The mechanical deformation can be controlled by low power laser irradiation of the samples and the resulting surface modifications are analyzed via dynamic speckle measurements. Photothermal effects due to optical absorption by the nanopowder are shown to deform the polymer samples leading to localized mechanical stresses induced via thermal expansion of the PDMS.

(Some figures may appear in colour only in the online journal)

1. Introduction

Polymeric materials with customized optical and mechanical properties have received increasing attention due to their scientific and technological significance. Stimulus-responsive materials such as shape memory polymers (SMPs) are considered to be promising candidates for developing smart devices for medical and biophotonic applications [1, 2]. Typically, SMPs respond to thermal, optical or electrical stimulation, and improved shape memory effects can be obtained upon adding conductive fillers in the polymer matrix. Fillers are usually sought to enhance the thermal and/or electrical conductivities of SMPs, thus the addition of fillers like carbon nanotubes has led to improvement in the performance of these materials [3, 4]. Gold and carbon nanoparticles have further been shown to have a striking ability to generate extremely localized heat through optical absorption, and they have also been combined with polymer matrices for various applications.

Carbon and metallic nanoparticles embedded in optically transparent polymer media have been shown to produce photothermal effects via optical absorption and subsequent heat release into the polymer matrix [5]. The improved photothermal properties of polymer films containing nanoparticles have been linked to enhanced local electromagnetic fields, which can be orders of magnitude larger than the incident radiation [6]. This leads to energy dissipation through phonon–phonon interactions thereby producing high local temperature changes under low power continuous irradiation [7, 8]. In general, heat dissipation to a host medium is dependent on nanoparticle features such as shape and size, as well as on the dielectric properties of the medium [9].

Nanoparticles have recently been mixed with polydimethylsiloxane (PDMS) [6], a polymer of particular interest due to its many useful properties for microfabrication and high biocompatibility. Gold nanoshells uniformly distributed in PDMS have been shown to absorb light and generate heat that is released into the host medium [9]. Synthesis

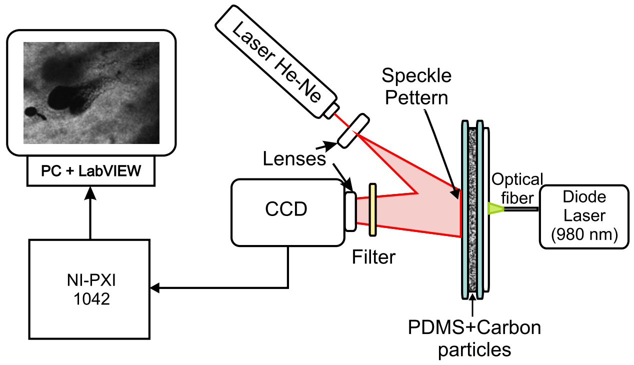

Figure 1. The experimental setup for the speckle measurements. The CCD camera was replaced by a thermographic camera for registering photothermal activity.

of metal nanoparticles (silver, gold, platinum) directly into PDMS composites has provided selective light absorption due to surface plasmon excitation in an otherwise transparent host [10]. Similarly, incorporation of gold nanoparticles in a membrane structure has allowed for the generation of heat via optical absorption in separation processes [8]. Other types of thermo-adaptive smart materials may also be obtained upon modifying the PDMS structure on demand by means of localized heat [11]. In this paper, we demonstrate light induced deformation of PDMS membranes with embedded carbon nanopowder that can be used for obtaining micron-range displacements controlled by light. Using dynamic speckle analysis and digital image correlation (DIC), we demonstrate induced deformation in the PDMS due to optical absorption by the nanopowder. We further evaluate the mechanical stresses induced within the sample, showing that photothermal effects play an important role in the photoinduced deformations of the polymer samples.

2. Experiments and sample preparation

The surface changes due to optically induced deformation of the polymer samples with embedded nanopowder were first evaluated by means of dynamic speckle analysis [12]. As shown in figure 1, speckle analysis is carried out using a He–Ne laser to illuminate the sample. The resulting speckle pattern is captured by a conventional CCD camera and fed to a computer for subsequent processing. From the opposite end, a CW fiber-coupled laser diode (JDSU, 975 nm, 70 mW maximum output power) is used for irradiating the sample. Residual IR radiation in the acquired images is avoided by an IR filter placed in front of the camera. Finally, the changes in the speckle images captured during laser diode irradiation are analyzed using the time history speckle pattern (THSP). This is based on reconstructing an image using a sequence of speckle pattern variations and correlating the changes in the THSP image [13].

Polymer samples were prepared using PDMS (Sylgard 184, Dow Corning) mixed with curing agent in a 10:1 ratio. The carbon nanopowder hosted by the PDMS was obtained from Sigma Aldrich (Part No. 633100). Membranes were prepared by spreading the PDMS mixture onto glass slides and scattering the carbon nanopowder in the mixture. Sandwiched samples with two layers of this carbon modified PDMS were readily formed upon joining two slides. The thickness of the polymer membranes contained within the slides was measured to be approximately 70 μm. Finally, curing of the PDMS was performed by heating the samples in a convective oven at 90 °C for 2 h.

The thermal variations in the PDMS samples with embedded nanopowder were monitored by replacing the CCD camera with a thermographic camera (Fluke, Ti45 FlexCam). For these measurements, the He–Ne laser was turned off and the samples were only irradiated with the laser diode. In order to avoid any filtering effects induced by the glass on the images, the PDMS membranes were removed from the glass slides. The acquired thermographic images thus provide evidence of thermal activity within the polymer membranes induced via optical absorption by the nanopowder.

3. Results

3.1. Speckle measurements

A typical speckle image obtained from a PDMS sample is shown in figure 2(a). Nanoparticle clusters in some areas of the sample are clearly distinguishable in the figure. When the laser diode was turned on, changes in the speckle pattern were clearly noticed and these were analyzed using the THSP. This was constructed using a specific zone of the image sample during irradiation with the laser diode. Thus, a sequence of images was acquired showing changes in the speckle pattern registered at the times when the laser diode was turned on and off. The THSP obtained from the column indicated by the dashed line in figure 2(a) is shown in figure 2(b); from this sequence, changes on the surface of the sample as a function of time can be estimated by correlating the changes along the horizontal direction of the figure. The resulting correlation index is also plotted in figure 2(b) and the arrows indicate the times at which the laser diode (LD) was turned on and off. As indicated by the abrupt changes in the correlation index, the surface of the sample is affected when the laser diode is turned on. The correlation index returns to close to its initial value after the laser diode is turned off, following a relaxation process showing that the PDMS membrane returns to its initial shape. This response to laser irradiation is further confirmed by the average changes in correlation index shown in figure 2(c).

The correlation index for different laser diode powers is shown in figure 2(d). Each point for every laser power on the curve was obtained after averaging four correlation indices registered while the laser was turned on. Also shown in the figure is the relaxation time measured after the laser was turned off and until the correlation index reached its initial value. Aside from the last two points, it is clear that the correlation index varies inversely with laser power; thus, increasing the irradiation power leads to larger variations in the shape of the PDMS samples. This is further confirmed by the relaxation times, which increase as a function of laser

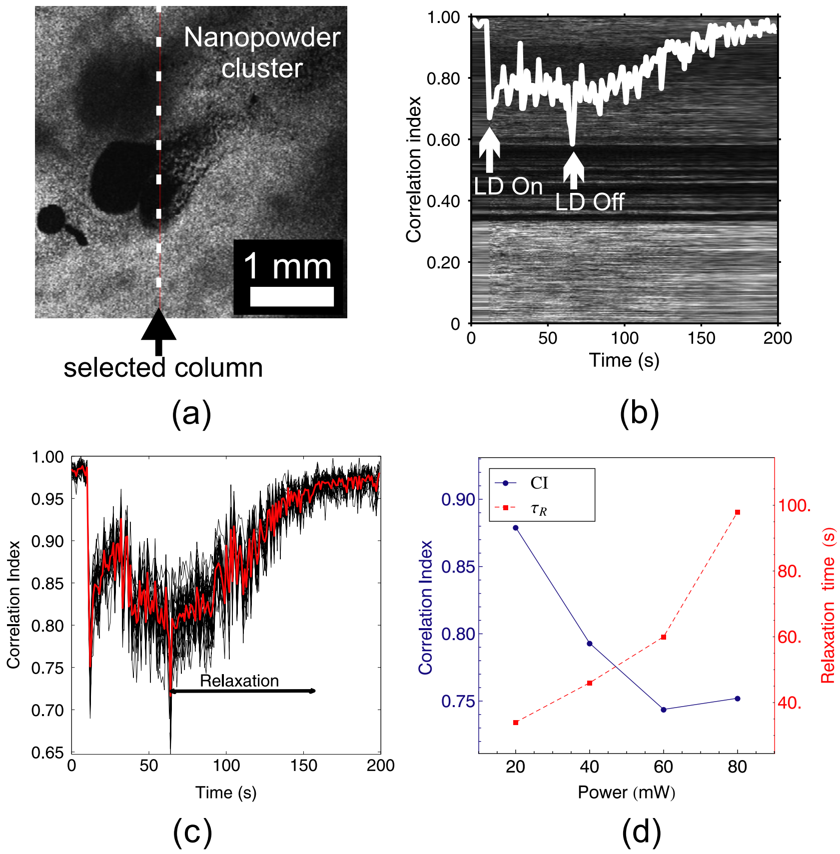

Figure 2. Surface changes induced by laser diode irradiation detected with speckle measurements. (a) The speckle pattern of the carbon clusters embedded in PDMS under He–Ne illumination; (b) time history speckle pattern (THSP) analysis and the corresponding correlation index for the column indicated in (a); (c) average curve of the speckle analysis; (d) changes in correlation index (CI) and relaxation time (τ_g) as a function of optical power.

power, thereby suggesting that larger changes in the surfaces of the samples are attained for higher optical powers.

Clearly, our experimental results show that all the surface activity registered in the carbon modified PDMS samples is triggered by IR laser exposure. As this is a surface sensitive technique, the THSP results suggest that changes in the PDMS occur during laser irradiation at least at the surface level. It is well known, however, that this polymer is transparent for the wavelengths used in our experiments; thus, the embedded nanopowder plays an important role in the observed effects. Optical absorption by carbon particles is known to provoke photothermal effects, which in turn may lead to particle migration when using a liquid host [14]. In our samples, the cured PDMS provides a rigid surrounding for the carbon nanopowder making particle displacement hard to achieve. Nonetheless, photothermal effects may lead to localized thermal expansion of the PDMS that can be readily detected with THSP analysis.

3.2. Thermographic measurements

The thermal activity in the samples was evaluated with the thermographic camera. As shown in figures 3(a) and (b), considerable thermal changes are obtained in the PDMS sample with embedded carbon nanopowder when the laser diode is turned on. Remarkably, the central region of the irradiated area reaches a temperature close to 150 °C almost immediately; this increase in temperature is larger than those reported for PDMS membranes with gold nanoparticles [6]. Notice also that this photothermal effect is extremely localized due to the small cross section of the optical fiber used at the output of the laser diode (HI 1060 single-mode fiber, 5.9 μm mode field diameter). In contrast, we did not register any thermal changes in PDMS samples without carbon nanopowder. Thus, the inclusion of carbon nanopowder in the PDMS membranes leads to an important increase in temperature, which in turn can cause refractive index changes and thermal expansion of the PDMS [15]. Changes at the surface of the sample driven by volumetric thermal expansion can therefore be registered with THSP measurements.

3.3. In-plane strain measurements

Further evidence of deformation due to the observed photothermal effects was obtained by evaluating the micromechanical response of the PDMS samples. For these measurements, a grid pattern was imprinted on the PDMS samples using a laser microfabrication device [16]. This was carried out in order to enhance the image correlation analysis. A scanning electron microscope (SEM) image of the patterned sample is shown in figure 4(a). The micromechanical response of the samples to laser diode irradiation was evaluated

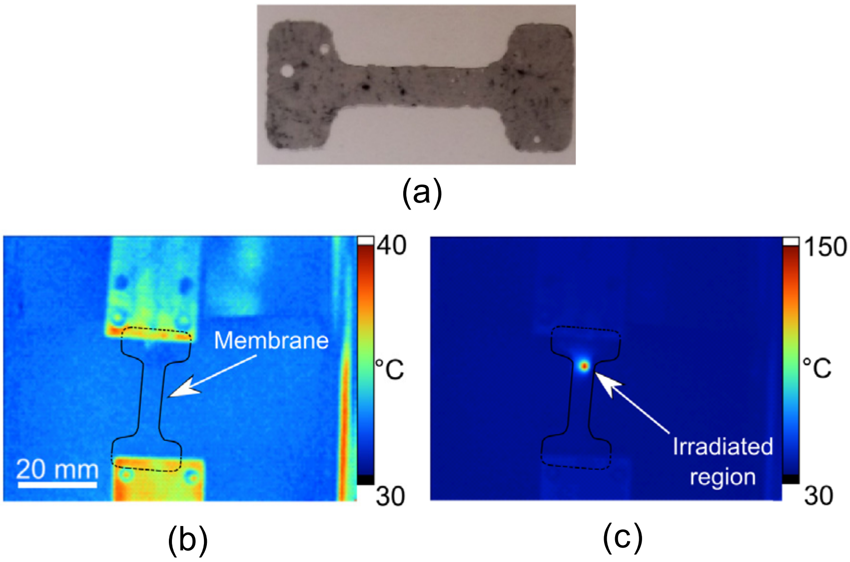

Figure 3. The photoinduced thermal activity in the PDMS samples: (a) a sample of a PDMS membrane with embedded carbon nanopowder; (b) thermal image of the sample (outlined) with the laser diode off; (b) thermal image of the sample with the laser diode on.

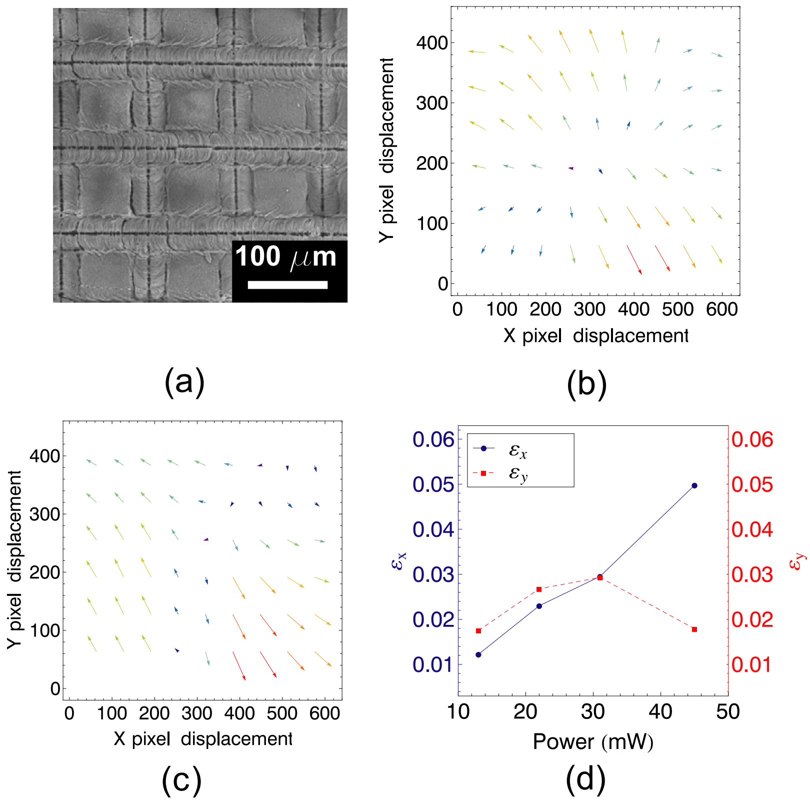

Figure 4. Digital image correlation results. (a) SEM image showing the imprinted grid on the PDMS membrane with embedded carbon nanopowder; (b) displacement vector field without rigid body motion calculated from DIC analysis (laser diode power: 10 mW); (c) displacement vector field without rigid body motion (laser diode power: 45 mW); (d) in-plane strain response as a function of laser diode power.

via digital image correlation (DIC) analysis [12]. This analysis yields the displacement vector fields calculated from a sequence of images obtained for different irradiation powers. As shown in figures 4(b) and (c), the resulting micron-range displacement vectors increase in magnitude as the laser diode power is raised to higher levels. In these calculations, the rigid body motion contributions have already been removed, thus, the displacement vectors represent only localized deformations.

The displacement vector fields obtained for different laser diode powers were further used for estimating the in-plane strains [12]. These results are presented in figure 4(d), showing that upon increasing the irradiation power the calculated strains increase accordingly. This is similar behavior to that obtained from biaxial tension tests, although the last points of the curves suggest that a shearing effect occurs at the highest optical power used in these measurements. Shearing contributions may appear due to sample asymmetries, but further tests are required to get a full understanding of the photoinduced micromechanical effects registered in our experiments. Nonetheless, our results show that a photoinduced deformation within a range between 3 and 5% is readily achieved in the samples due to photothermal effects.

The enhanced photothermal effects attainable with the proposed membranes could prove useful for the development of bilayered thermally adaptive materials [11]. It is also worth noticing that the fabrication of the membranes did not involve any elaborate procedure and thus may offer an inexpensive option for realizing optically activated devices. As an example, contactless deformable membranes could represent a great alternative to electrically actuated membranes for micropumping applications [17].

4. Conclusions

We have demonstrated micron-range deformations of PDMS membranes with embedded carbon nanopowder that can be controlled by low power laser light. As verified by the thermographic camera measurements, light absorption by the nanopowder leads to a highly localized increase in temperature, thus leading to thermal expansion in the PDMS. Further analysis of this micron-range mechanical deformation was carried out by means of in-plane strain calculations, showing that PDMS with embedded carbon nanopowder can be readily deformed by low power laser irradiation. Since the deformation directly depends on the laser intensity, these effects may be of interest for the development of light activated deformable polymer devices as well as optically controlled micropump valves.

Acknowledgments

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