Laser-assisted photothermal imprinting of nanocomposite

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We report on a laser-assisted photothermal imprinting method for directly patterning carbon nanofiber-reinforced polyethylene nanocomposite. A single laser pulse from a solid state Nd:YAG laser (10 ns pluse, 532 and 355 nm wavelengths) is used to melt/soften a thin skin layer of the polymer nanocomposite. Meanwhile, a fused quartz mold with micro sized surface relief structures is pressed against the surface of the composite. Successful pattern transfer is realized upon releasing the quartz mold. Although polyethylene is transparent to the laser beam, the carbon nanofibers in the high density polyethylene (HDPE) matrix absorb the laser energy and convert it into heat. Numerical heat conduction simulation shows the HDPE matrix is partially melted or softened, allowing for easier imprinting of the relief pattern of the quartz mold. © *2004 American Institute of Physics*. [DOI: 10.1063/1.1789239]

Thermal embossing/imprinting has been proven as a low cost, mass fabrication method for direct patterning of thermoplastic polymers.[1,2] Micron-sized features have been imprinted on polymers such as poly(methylmethacrylate) (PMMA) and poly(lactic acid) for biomedical applications, using silicon based molds.[3,4] By employing a SiO_2/Si mold fabricated by reactive ion etching and *e*-beam lithography, features as small as 25 nm have been imprinted on PMMA when both the mold and PMMA were heated to a temperature above the glass transition temperature of PMMA $(105\,^{\circ}C)^5$. Most recently, the time of the imprinting process has been dramatically shortened by using a pulsed laser as the heating source.[6] As compared to heating the mold or the substrate using conventional heaters, an UV laser beam passes through a transparent quartz mold to heat a thin layer of polymer and the underlying silicon substrate. The viscosity of the polymer layer is reduced by melting and the relief pattern on the mold is successfully imprinted into the polymer within a very short time. However, weak light absorption by the polymer and heat penetration to the silicon substrate has been identified as potential problems.

On the other hand, carbon nanofibers have been recognized as important materials for polymer fillers and reinforcements. Polymers properly filled with carbon nanofibers have shown improved electrical, thermal, and mechanical properties with little property tradeoffs.[7–10] For example, polypropylene isotropically filled with carbon nanofibers has shown enhanced thermal stability and as much as a 350% increase in dynamic modulus.[11] Epoxy filled with 1 wt% carbon nanotube has shown a 125% increase in thermal conductivity.[12] For these emerging nanocomposite materials, micro/nano fabrication techniques need to be developed to meet the requirements of precise device manufacturing.[13,14]

In this letter, we demonstrate a laser-based, photothermal imprinting method for direct patterning of carbon nanofiber-reinforced, high density polyethylene (HDPE) nanocomposite. Pulsed laser beams of UV and visible wavelengths (10 ns, 355 nm, and 532 nm) are used to heat the nanofibers in the polymer matrix. Heat is conducted from the nanofibers to the polymer and imprinting is realized when a quartz mold is pressed against the softened/melted polymer composite. Simple heat conduction simulation is carried out to calculate the temperature evolution of both the nanofibers and surrounding polymer matrix.

Carbon nanofibers called Pyrograf-III™ (Applied Sciences, Inc.) were produced by a catalytic process of hydrocarbons in a vapor state. Vapor-grown carbon fiber (VGCFs) have a circular cross-section with diameters ranging from 20 to 200 nm and a central hollow core usually called filaments with diameters of tens of nanometers. Results of scanning electron microscope (SEM) analysis showed that the VGCFs were highly clustered and contained dispersed amorphous carbon and metal catalysts. The preparation of HDPE filled with VGCF was reported by Lozano *et al.*[11] VGCFs were mixed with the HDPE matrix (10% w/w) in an internal mixer where high shear rates were required to overcome the nanofiber agglomerates. After mixing, the material was compression molded at temperatures ranging from 170 to 200 °C between two dust-free parallel silicon wafers to form thin sheets.

To make the quartz mold, a piece of fused quartz plate of surface roughness less than a few nanometers was sputter-coated with a 100 nm chrome layer. Subsequently, an *e*-beam resist of 500 nm thickness was spin-coated onto the chrome layer. A pattern was directly written onto the resist by electron beam lithography. The exposed resist was developed and the underlying chrome was removed by wet etching to reveal the quartz. The quartz was dry-etched by reactive ion etching (RIE) and the residual resist/chrome was removed using an acetone/chrome etch. Finally, the quartz was treated with (tridecafluoro-l, 1, 2, 2,-tetrahydro-octyl)-l-trichlorosilane vapor to create a surface with low interfacial free energy.

A schematic of the experimental setup is shown in Fig. 1. A Nd:YAG laser of 10 ns pulse width and 355 and 532 nm wavelengths were used for the imprinting process. The quartz mold shown in Fig. 2(a) was pressed against the polymer substrate. A single pulse from the laser was passed through the quartz mold, softening or partially melting the top layer of the polymer composite substrate. The relief pattern of the mold was thus imprinted into the substrate and the
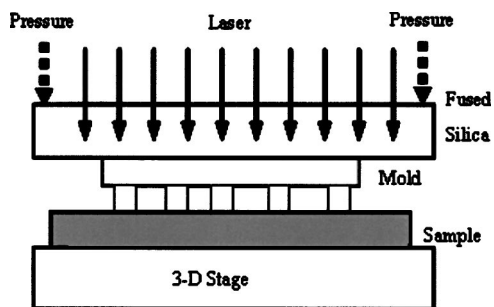
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FIG. 1. Schematic setup of the laser-assisted photothermal imprinting process.

FIG. 3. SEM image of imprinted surface of polymer composite using 355 nm laser. Scale bars indicate 2 μm.

quartz mold was released after the resolidification of substrate.

The imprinted pattern on the polymer nanocomposite showed high fidelity after being exposed to both the 355 and 532 nm laser beams. The imprinted pattern [Fig. 2(b)] had vertical sidewalls and flat smooth top and bottom surfaces, which were identical to the geometry of the quartz mold. As shown in Fig. 3 after a single 355 nm laser pulse at a fluence of 0.3 J/cm^2, the pattern was completely transferred to the polymer. As illustrated in Fig. 4, successful pattern transfer was also achieved with a 532 nm laser pulse of the same fluence. However, the surfaces appeared to be porous with noticeable clusters of tangled nanofibers. Since the nanocomposite absorbs the 532 nm laser more strongly, the fluence was closer to the ablation threshold. Therefore, the top surface layer of HDPE was evaporated, leaving the thermally stable carbon nanofibers. By lowering the fluence, we obtained patterns identical to that of a 355 nm laser. Observable defects on the imprinted pattern were a result of ambient dust and nonuniformity of the nanocomposite.
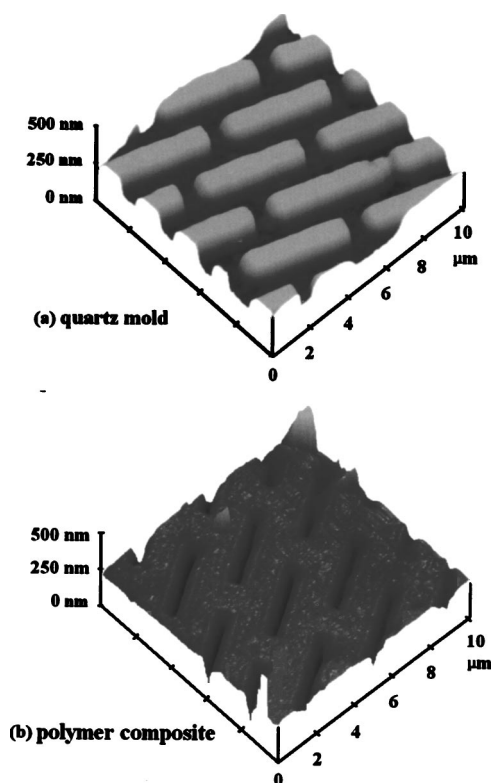
We have measured the absorption coefficients of the pristine HDPE as 0.45 mm^{-1} at 355 nm and 0.33 mm^{-1} at 532 nm. Due to weak absorption, melting the surface layer of pristine HDPE was difficult. Although the HDPE may absorb radiation in the deep UV spectrum more strongly (e.g., $\alpha \sim 50$ mm^{-1} at 193 nm solely on the basis of carbonyl groups),[15] it may be directly ablated due to due to photochemical reaction.[16] By adding a small amount of carbon nanofibers to the HDPE matrix we obtained absorption coefficients of 5.71 mm^{-1} at 355 nm and 8.98 mm^{-1} at 532 nm. The highly absorbent carbon nanofibers absorbed the laser radiation and the phonon energy produced by nonradiative decay was responsible for the melting of surrounding polymer. It has been reported that the VGCF filled polymer composites have a much higher thermal conductivity,[12] making it possible to produce deeper patterns.

To help understand the photothermal effect that facilitates the imprinting process, a simple numerical study was conducted using the Fourier heat conduction model, and this model is still valid for nanosecond laser heating processes.[17] The heat conduction model consists of two parts, the carbon nanofiber which absorbs the laser radiation and the polymer matrix part that surrounds the nanofiber. The two parts are connected by heat conduction through the interface. All material properties except the specific heat of the nanofiber were obtained from the manufacturer and the handbook.[18,19] The specific heat of nanofiber was approximated as that of graphite due to lack of information. Although the thermal conductivity of an isolated carbon nanofiber was estimated as 1900 W/mK, the effective thermal conductivity of the composite is much smaller than expected due to the interfacial conduction resistance. It was found that the interfacial thermal resistance introduces considerable error in the pure conduction model for nanocomposite materials.[20] Results of
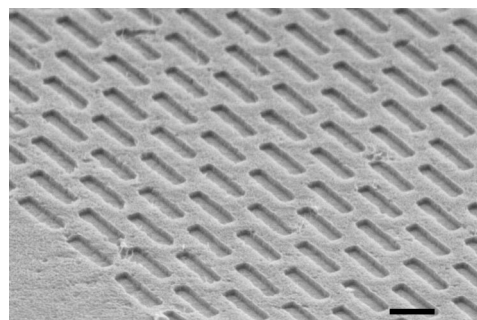

FIG. 2. AFM images of (a) the quartz mold and (b) the imprinted polymer composite.

FIG. 4. SEM image of imprinted surface of polymer composite using 532 nm laser. Scale bars indicate 2 μm.
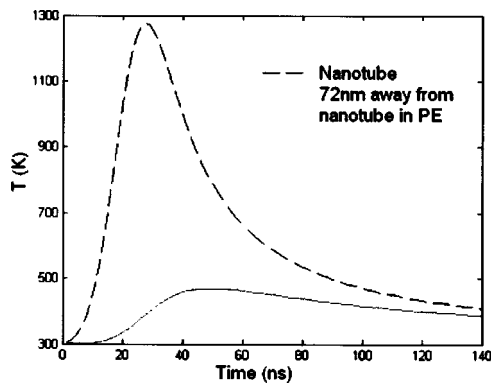
FIG. 5. Simulation results of temperature evolution in the carbon nanofiber and surrounding polymer matrix after the incidence of a single laser pulse. The melting temperature of the polymer matrix is about 390 K.

molecular dynamics simulation have shown that the energy transfer between the carbon nanofiber and the polymer can be characterized by low-frequency phonon vibration.[21] The high frequency mode phonons resulting from the photothermal effect have to first transfer to a low frequency mode and thus energy transfer is significantly hampered. An interfacial conductance of 5 MW/m^2 K was incorporated into the model to account for the interfacial heat conduction effect. From the simulation, it is shown that the nanofiber reached temperatures as high as ~1000 K while the temperature in the surrounding HDPE was much lower during the process. Figure 5 shows the temperature profile of a nanofiber of 120 nm in diameter and the surrounding HDPE matrix. The results indicate that the HDPE was partially melted both in time and space.

In summary, laser-assisted photothermal imprinting is capable of directly patterning microfeatures onto polymeric nanocomposites in a massively parallel fashion. By adding carbon nanofibers to the polymer matrix, higher optical absorption levels for a wide bandwidth and higher heat conductance levels can be obtained, dramatically enhancing the imprinting process. We expect nanoscale features are achievable when using a quartz mold with nanorelief structures. This method could be used to fabricate micro/nanosystems using polymeric nanocomposites with enhanced mechanical, thermal, and optical properties.

[1]S. Y. Chou, P. R. Krauss, and P. J. Renstrom, Science **272**, 85 (1996).

[2]S. Y. Chou, P. R. Krauss, W. Zhang, L. Guo, and L. Zhaung, J. Vac. Sci. Technol. B **15**, 2897 (1997).

[3]D. K. Armani and C. Liu, J. Micromech. Microeng. **10**, 80 (2000).

[4]C. Miller, H. Shanks, A. Witt, G. Rutkowski, and S. Mallapragada, Biomaterials **22**, 1263 (2001).

[5]S. Y. Chou, P. R. Krauss, and P. J. Renstrom, Appl. Phys. Lett. **67**, 3114 (1995).

[6]Q. Xia, C. Keimel, H. Ge, Z. Yu, W. Wu, and S. Y. Chou, Appl. Phys. Lett. **83**, 4417 (2003).

[7]B. J. Ash, D. F. Rogers, C. J. Wiegand, L. S. Schadler, R. W. Siegel, B. C. Benicewicz, and T. Apple, Polym. Compos. **23**, 1014 (2002).

[8]R. Ramasubramaniam, J. Chen, and H. Liu, Appl. Phys. Lett. **83**, 2928 (2003).

[9]M. Sennett, E. Welsh, J. B. Wright, W. Z. Li, J. G. Wen, and Z. F. Ren, Appl. Phys. A: Mater. Sci. Process. **76**, 111 (2003).

[10]X. Wang and T. J. Pinnavaia, Chem. Mater. **10**, 1820 (1998).

[11]K. Lozano and E. V. Barrera, J. Appl. Polym. Sci. **79**, 125 (2001).

[12]M. J. Biercuk, M. C. Llaguno, M. Radosavljevic, J. K. Hyun, A. T. Johnson, and J. E. Fischer, Appl. Phys. Lett. **80**, 2767 (2002).

[13]P. Fournet, J. N. Coleman, B. Lahr, A. Drury, W. J. Blau, D. F. O'Brien, and H. H. Horhold, J. Appl. Phys. **90**, 969 (2001).

[14]G. B. Blanchet, C. R. Fincher, and F. Gao, Appl. Phys. Lett. **82**, 1290 (2003).

[15]P. E. Dyer and D. M. Karnakis, Appl. Phys. Lett. **61**, 1344 (1994).

[16]S. C. Chen., V. Kancharla, and Y. Lu, Int. J. Mater. Prod. Technol. **18**, 457 (2003).

[17]G. Chen and C. L. Tien, J. Heat Transfer **116**, 311 (1994).

[18]Physical properties of Pyrograf-III were found on the Applied Sciences, website: www.apsci.com.

[19]*Industrial Polymers Handbook: Products, Processes, Applications*, edited by E. S. Wilks (Wiley-VCH, New York, 2001), p. 647.

[20]M. Hu, X. Wang, G. V. Hartland, V. Salgueirin~o-Maceira, and L. M. Liz-Marzan, Chem. Phys. Lett. **372**, 767 (2003).

[21]S. T. Huxtable, D. G. Cahill, S. Shenogin, L. Xue, R. Ozisik, P. Barone, M. Usrey, M. S. Strano, G. Siddons, M. Shim, and P Keblinski, Nat. Mater. **2**, 731 (2003).