NANOPARTICLE-ENHANCED LASER MICROMACHINING OF POLYMERIC NANOCOMPOSITES

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KEYWORDS

Laser, micromachining, carbon nanofiber, nanocomposite.

ABSTRACT

Nanocomposites are emerging materials with unique mechanical, thermal, electrical, and optical properties. We report direct laser ablation of high-density polyethylene (HDPE) filled with carbon nanofibers using a pulsed Nd:YAG laser. Both 532 nm and 355 nm wavelengths with a spot size of 40 μm were used for the study. The laser fluence was varied from 0.8 μJ/cm^2 to 3.8 μJ/cm^2. Material pop-up occurred near the threshold energy, while open holes were achieved with higher laser energy. The etching depth increased linearly with the number of pulses. Although polyethylene was transparent to the laser beam, the carbon nanofibers added to the polymer matrix absorbed the laser energy and converted it into heat. Numerical heat conduction simulation shown the HDPE matrix was partially melted or evaporated, due to pyrolytic decomposition.

INTRODUCTION

The essence of nanotechnology is the ability to work at the molecular level to create large structures with fundamentally new molecular organization. Although polymers have been widely used in the defense industry and in commercial applications, devices made of polymers are mechanically weak. It is the goal of composite techniques to improve the mechanical, thermal, and electrical properties of polymers by filling the polymer matrix with another material. Nanofillers like nanoparticles (zero-dimensional), nanofibers (one-dimensional), and nanolayers (two-dimensional) have been properly dispersed throughout the polymer matrix creating much more surface area for a polymer/filler interaction than do conventional composites [Ash et al, 2002, Ramasubramaniam et al, 2003, Sennet. et al, 2003]. Another unique aspect of nanocomposites is the lack of property trade-offs. It is possible to design materials without compromises typically found in conventionally filled polymer composites. For example, the moduli of polypropylene and nylon 6 nanocomposites have been reported to increase from 1.1 to 2.1 GPa (91%) and from 1.98 to 3.12 GPa (58%), respectively, by the addition of 2-8 wt% of layered silicate nanoparticles [Wang X. et al, 1998]. Lozano et al. showed that enhanced thermal stability and an increased dynamic modulus resulted from carbon nanofiber-reinforced thermoplastic composites [Lozano et al, 2001]. Emerging applications of nanocomposites can be found in the automotive, aerospace, and tissue engineering

fields [Giannelis, 1998, Lee et al, 2003, Waid et al, 2004].

Micromolding and microimprinting techniques have been used to fabricate surface relief structures on polymer substrates [Xia et al, 1998]. However, utility of these techniques are often limited by contamination from chemical solvents, tensile stresses, and the availability of appropriate masters. Laser micromachining has been used to pattern polymers for micro/meso-device fabrication [Lu et al, 2004, Kancharla et al, 2002]. Photons of the laser light act as "clean particles." Additionally, the laser irradiation is essentially non-invasive and laser micromachining is a single-step process. The most popular lasers used for machining polymers are UV lasers. The small wavelengths allow strong interactions of the beam with a variety of materials. Laser micromachining with nanosecond green or infrared lasers have strong thermal effects when materials are heated rapidly beyond the level responsible for the onset of pyrolytic decomposition resulting in a chain depolymerization reaction [Blanchet et al, 1994]. UV lasers can remove material through direct solid-vapor ablation. However, the incident photon energy has to be high enough to break the chemical bonds of the target material directly. The material is then dissociated into its chemical components and no liquid phase transition occurs in this process.

Despite extensive work on the laser micromachining of polymers and semiconductors [Mao et al, 2001, Wu et al, 2003], little work has been done on laser ablation of polymeric nanocomposites [Wen et al, 1994]. Although a pristine polymer may have little absorption of the incident laser energy, incorporating a small amount of metallic nanoparticles (e.g., gold nanoparticles) into the polymer matrix may enhance laser absorption and lead to laser-induced optical breakdown at a much lower threshold [Ye et al, 2002]. Similar work has also been carried out for laser processing of polymer-based silver nanocomposites and fabricating polymer/carbon nanocomposite thin-films for chemical sensing applications [Zeng et al, 2002, Bubb et al, 2001].

In this work, we report direct laser ablation of a high density polyethylene nanocomposite filled with carbon nanofibers. Both the 2nd and 3rd harmonic wavelengths (532 nm and 355 nm) of a Nd:YAG laser were used to ablate the nanocomposite. Although HDPE is transparent to visible and far UV wavelengths, absorption by carbon nanofibers in the polymer matrix was expected during material removal since the method of laser ablation of graphite has been used for producing carbon nanotubes [Labazan et al, 2003, Maser et al, 1998]. We used scanning electron microscopy (SEM) and energy dispersive spectroscopy (EDS) to characterize the surface morphology and chemistry.

EXPERIMENTAL DETAILS

The preparation of HDPE filled with vapor-grown carbon fibers (VGCF) was reported by Lozano et al [Lozano et al, 2001]. VGCFs were mixed with the HDPE matrix (10% w/w) in an internal mixer where the application of high shear rates was required to overcome the nanofiber agglomerates. After mixing, the material was compression molded at a temperature of 170-200°C to form thin sheets. Carbon nanofibers called Pyrograf-III[TM] (Applied Sciences, Inc.) were produced by a catalytic process of hydrocarbons in a vapor state. 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 tenths of nanometers. An SEM analysis showed that the VGCFs were highly tangled having dispersed amorphous carbon and metal catalysts.

The laser ablation setup consisted of four main parts: a laser system, a beam delivery system, a micrometer-resolution x-y-z sample stage, and an on-line monitoring system (Fig. 1). The second (532 nm) and third (355 nm) harmonic laser beams from a solid-state Nd:YAG laser with a pulse duration of 12 ns (full width at half maximum) were used for material ablation. The repetition rate was 2 Hz and the fluence was varied from 0.8 $\mu J/cm^2$ to 3.8 $\mu J/cm^2$. The focusing length of the lens was 50 mm yielding a laser spot size of approximately 40 μm on the sample surface. To measure the monochromatic transmissivity of the HDPE nanocomposite and pristine HDPE at wavelengths of 532 nm and 355 nm we measured the laser energy before and after the sample using a pyroelectric energy detector (PE 10, Ophir Optronics Inc.). A series of holes was ablated from the top surface and the edge of the composite sheet. The number of laser pulses was varied from a single pulse to 5, 20, and 50

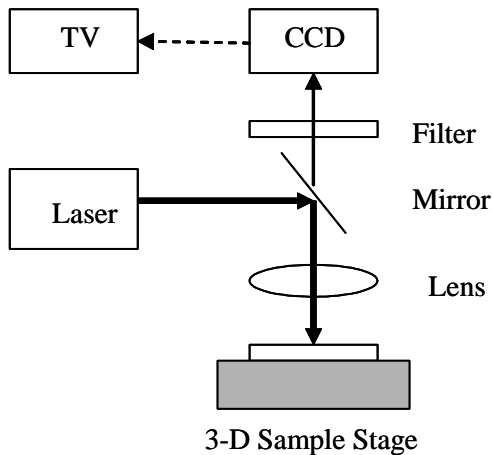pulses in order to help us investigate the relationship between pulse number and the etching depth.

FIG. 1. A SCHEMATIC DIAGRAM OF THE EXPERIMENTAL SETUP FOR LASER ABLATION.

The ablated holes were observed using an SEM (LEO 1530). A thin layer of gold was coated on the surface of the composite to improve the conductivity. We also used EDS for elemental analysis and the mapping of the laser-processed sample.

RESULTS AND DISCUSSION

Fig. 2 shows SEM images of a series of holes ablated on an HDPE VGCF composite under different laser energies. At the energy just above the laser ablation threshold, which is 0.8 $\mu J/cm^2$ for 355 nm (Fig 2A), volumetric expansion, "pop-up", was observed. The diameter and depth of the ablated holes increased as energy increased. EDS elemental analysis showed the same chemical composition in the popped-up area and nearby non-irradiated area. By carefully inspecting the surface we noticed that ablation was initiated in the bulk of the composite instead of on the surface. It indicated the typical volumetric effect that occurs in photothermal laser ablation. In other words, the absorption of the incident laser light and accumulation of the heat require a certain volume in the sample. The resulting monomer or oligomer was in gas form producing a high pressure that induced the volumetric expansion in the bulk of the composite. As the laser energy increased open holes were ablated (Fig. 2B-D).
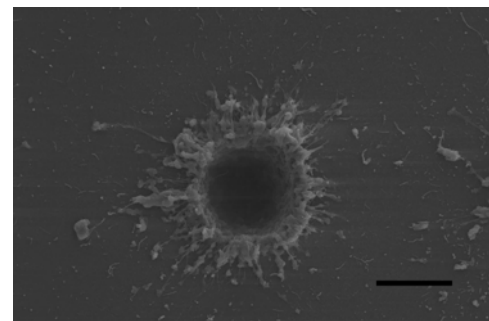
We noticed that the top layer softened and had splashed around the holes.
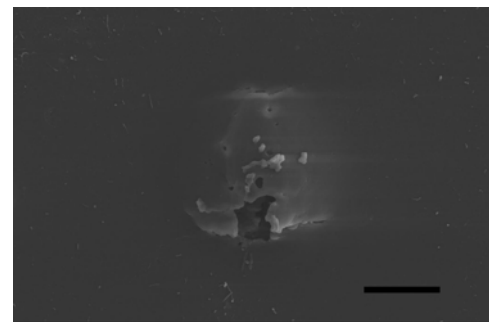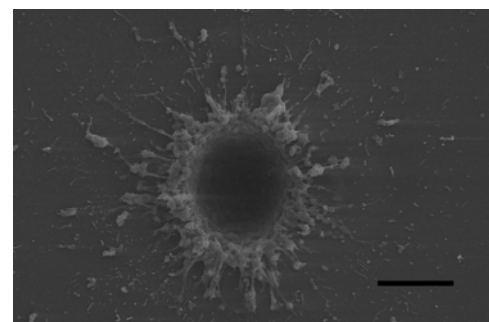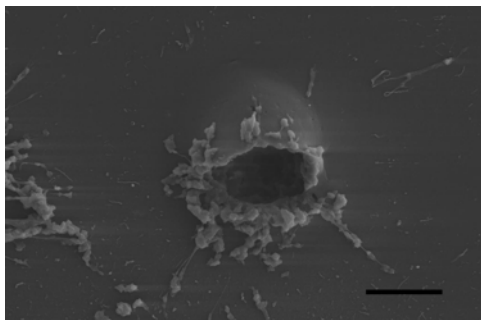

(A)
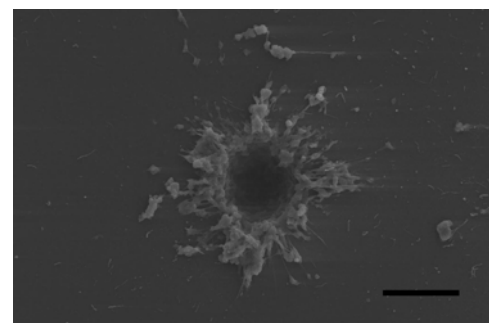
(B)

(C)

(D)
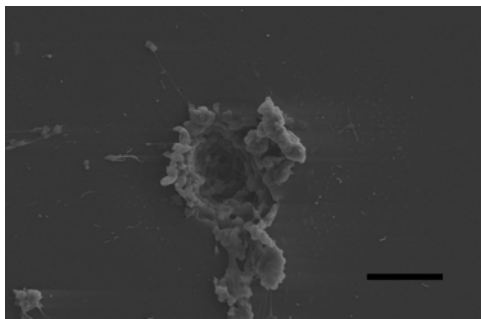
FIG. 2. SEM PICTURES OF THE HDPE VGCF COMPOSITE UPON 20 PULSE IRRADIATION USING A 355 nm LASER. THE LASER FLUENCES

USED WERE 0.8 μJ/cm² (A), 1.3 μJ/cm² (B), 1.8 μJ/cm² (C), AND 2.5 μJ/cm² (D). THE SCALE BARS INDICATE 20 μm.

Similar results were obtained for the 532 nm laser as shown in Fig. 3. The laser ablation threshold for the 532 nm laser was ~1.6 μJ/cm² (Fig. 3A). The volumetric expansion effect can be clearly seen. The success of using both the 532 nm and 355 nm lasers suggests that the laser ablation process was less wavelength dependent. Therefore, a wide variety of lasers ranging from UV to visible could be used for micromachining nanocomposites.
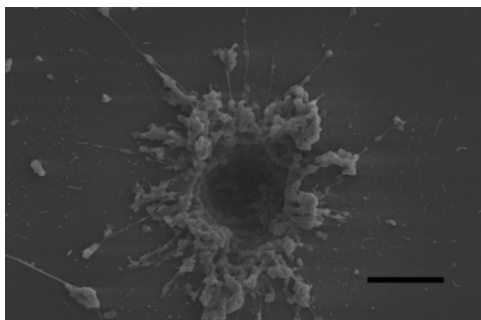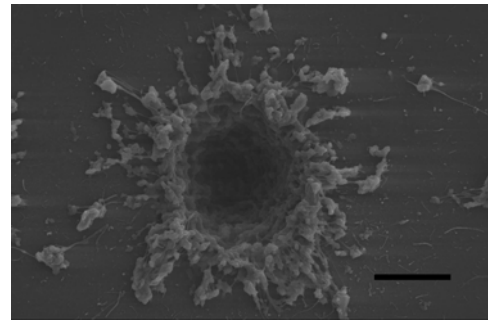

(D)

FIG. 3. SEM PICTURES OF THE HDPE VGCF COMPOSITE UPON 20 PULSE ABLATION USING A 532 nm LASER. THE LASER FLUENCES USED WERE 1.6 μJ/cm² (A), 2.3 μJ/cm² (B), 3.2 μJ/cm² (C), and 3.8 μJ/cm² (D). THE SCALE BARS INDICATE 20 μm.

(A)

(B)

(C)

Experiments were also conducted with different number of pulses. The etching depth increased linearly with the number of laser pulses as shown in Fig. 4. We believed that the ablation plume dissipated completely before blocking the next laser pulse and heat did not accumulate on the ablated surface between the pulse intervals.
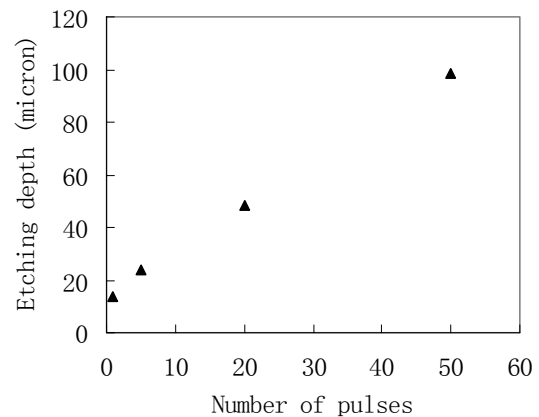

FIG. 4. ETCHING DEPTH VS NUMBER OF PULSES USING A 355 nm LASER AT A LASER FLUENCE OF 1.8 μJ/cm².

Laser pulses were also delivered on the edge of the nanocomposite sheet with half the beam targeted on the surface and another half outside the sample. This allowed us to have a closer look at the topography and cross-sectional view of the ablated holes (Fig. 5). A detailed view of the sidewall of the hole is shown in Fig. 6. We noticed that the nanocomposite

was melted at the ablation site with resolidified molten flow and deposited ablated materials. This result clearly indicated the photothermal effect during the ablation process.
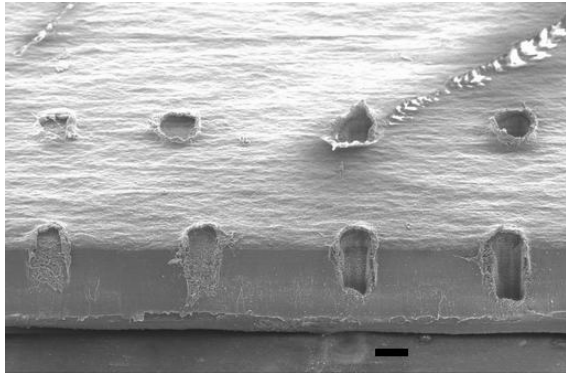

FIG. 5. SEM PICTURES OF HOLES ABLATED IN THE COMPOSITE MATERIAL SHEET USING A 355 nm LASER AT A FLUENCE OF 1.8 µJ/cm^2 WITH MULTIPLE PULSES. ON THE SAMPLE FROM LEFT TO RIGHT FOR BOTH ROWS, THE NUMBER OF PULSES IS 1, 5, 20, AND 50, RESPECTIVELY. THE SCALE BAR INDICATES 40 µm.
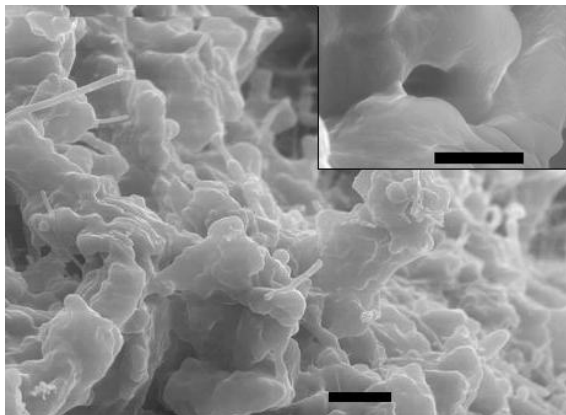

FIG. 6. AN SEM PICTURE OF THE SIDEWALL OF THE HOLE ABLATED BY A 355 nm LASER.

The measured absorption coefficient of the pristine HDPE was 0.42 mm^{-1} at 355 nm and 0.33 mm^{-1} at 532 nm. The C-C bonding energy of the HDPE was about 3.62 eV. Therefore, it was difficult to ablate the pristine HDPE using the same laser energy as used for ablating the HDPE nanocomposite by the photothermal effect or the photochemical effect [Srinivasan et al, 1986]. By adding a small amount of carbon nanofibers into the HDPE matrix we obtained absorption coefficients of 5.71 mm^{-1} at 355 nm and 8.98 mm^{-1} at 532 nm.

In an EDS elemental analysis, Nb and Pb, which were components of the metal catalysts, were more concentrated on the ablated surfaces than they were on the original surface. Since the metal catalysts coexisted with the carbon nanofiber, more carbon nanofibers appeared on the ablated surfaces than on the original surface. We believed that the carbon nanofibers were more thermally stable than the HDPE under the high temperature.

To help understand the photothermal effect that induces the ablation process, a simple numerical study was conducted using the Fourier heat conduction model, and this model is still valid for nanosecond laser heating processes [Chen et al, 1994]. Our 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 (Applied Sciences, www.apsci.com) and the handbook [Wilks, 2001]. The specific heat of nanofiber was approximated as that of graphite due to lack of information. Although the thermal conductivity of an isolated multi-wall 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 [Hu et al, 2003]. Results of molecular dynamics simulation have shown that the energy transfer between the carbon nanofiber and the polymer can be characterized by low-frequency phonon vibration [Huxtable et al, 2003]. 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 ~1800 K while the temperature in the surrounding HDPE was much lower during the process. Figure 7 shows the temperature profile of a nanofiber of 120 nm in diameter and the surrounding HDPE matrix at a laser fluence of 0.8 µJ/cm^2. The results indicate that an extremely high temperature was formed in the

polymer matrix surrounding the nanofibers resulting in the melting or evaporation of the HDPE matrix.
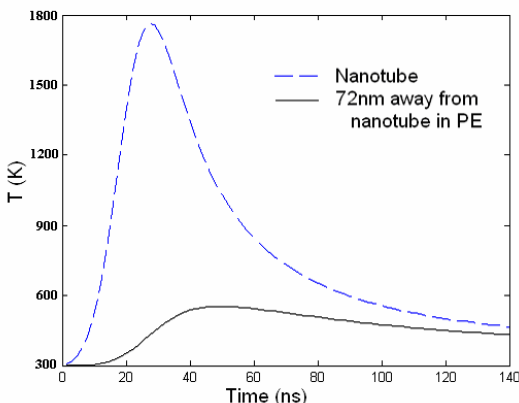

FIGURE 5. SIMULATION RESULTS OF TEMPERATURE EVOLUTION IN THE CARBON NANOFIBER AND SURROUNDING POLYMER MATRIX AFTER THE INCIDENCE OF A SINGLE LASER PULSE. THE MELTING TEMPERATURE OF THE POLYMER MATRIX IS ABOUT 390 K.

CONCLUSION

We have demonstrated direct laser ablation of an HDPE nanocomposite using a pulsed laser of UV and visible wavelengths. Removal of materials was induced by the photothermal effect, which accompanied volumetric effects causing ablation in the bulk of the composite. The mixed carbon nanofibers dramatically enhanced the absorption of the incident light in the matrix polymer and turned the photon energy to heat, which decomposed the matrix polymer into small molecules. The ablation process had no significant wavelength dependence, which allowed the flexible choice of lasers for patterning polymeric nanocomposites.

ACKNOWLEDGEMENTS

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