

Direct Patterning of Polystyrene–Polymethyl Methacrylate Copolymer by Means of Laser Interference Lithography Using UV Laser Irradiation

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The fabrication of functionalized surfaces on polymeric substrates is of importance in chemistry, biology, physics, and material science. Examples of functional surfaces are micro/nano periodic arrays that can be fabricated using different methods. However, many of these techniques require several fabrication steps. In this communication, we report the fabrication of advanced architectures in poly(methylmethacrylate)–polystyrene (PMMA–PS) copolymers using direct laser interference patterning. Because of the mixed optical properties of the copolymers, a different type of periodic architectures could be fabricated when compared with traditional pure polymers. This new type of periodic structures results from the local swelling of the copolymer due to the formation of gaseous products induced by the laser radiation. Additionally, relatively low laser fluences are necessary to initiate the ablation process of the copolymers. POLYM. ENG. SCI., 48:2367–2372, 2008. © 2008 Society of Plastics Engineers

INTRODUCTION

The fabrication of functionalized surfaces of polymers is of relevant importance in chemistry, biology, physics, and material science. Examples of functional surfaces are micro/nano periodic arrays that can be fabricated using different methods. However, many of these techniques require

several fabrication steps. Particularly, laser techniques permit the treatment of macroscopic surfaces in a short time scale. Apart from the technological aspects, the behavior of the polymers when interacting with laser light must also be considered. Poly(methylmethacrylate)–polystyrene copolymers (PMMA–PS) offer special characteristics due to their mixed optical properties. When these substrates interact with laser radiation, the swelling of the polymeric surface is observed. This interesting characteristic can be used for the fabrication of new surface architectures.

Methods for micro- and nanopatterning of polymeric materials using laser ablation mechanisms has been object of growing interest due to potential applications in the field of bioengineering and microelectronics [1–3]. In general, ablation of polymeric materials can be described by two typical mechanisms: photochemical [4] and photothermal ablation [5]. In photochemical ablation, bond-breaking and material ejection take place directly from the excited electronic state. Alternatively, in the photothermal process, the electronic energy is converted via radiationless transitions into heat. For processes in which both thermal and nonthermal mechanisms contribute to the overall ablation rate, one calls these as a photophysical ablation.

The process of patterning is commonly referred as lithography, which involves a flow of information that typically begins with the design of a pattern in the form of a dataset and ends as a patterned array of features on the surface of a substrate [6]. In particular, the direct laser interference patterning (DLIP) method [7–9] permits the fabrication of repetitive 1D and 2D patterns and microstructures by direct irradiation of the sample surface with coherent beams of light. Moreover, no additional process steps (i.e., etching, development of photoresist, and mask fabrication) are required.

In [10], it was demonstrated that different architectures could be fabricated using DLIP in commercial polymeric substrates including polycarbonate (PC), poly(etherimide) (PEI), poly(imide) (PI), and poly(etheretherketone) (PEEK).

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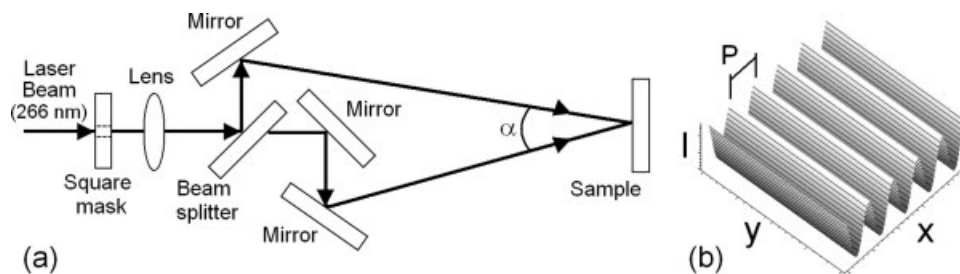


FIG. 1. (a) Interference experimental setup showing the optical elements and (b) calculated intensity distribution of the two-beam interference pattern. The period of the pattern can be changed by varying the angle (α) between the incident beams.

For two-laser beams configuration, a periodical line-type pattern is obtained (see Fig. 1), while when three-laser beams arranged in a symmetrical form are used, a dot-type interference pattern with a hexagonal intensity distribution is obtained [11]. The results of this previous work indicated that the photomachinability of polymers is highly influenced by laser wavelength and the polymer's own optical properties (absorption coefficient). Furthermore, PMMA substrates could not be structured using DLIP at 266 and 355 nm of wavelength at high laser intensities using one single pulse because of the extremely low absorption coefficient of the polymer. Consequently, alternatively routes must be utilized to fabricate periodical arrays in PMMA at moderate laser flux densities.

One possible method was previously described in [12] and consists of adding a doping agent into the polymeric matrix (up to 0.25 wt%) that increases absorption of the laser radiation at the utilized laser wavelength. A second alternative, and the objective of this study, is to demonstrate that the incorporation of a second monomer with a higher absorption coefficient (e.g., styrene monomer units) into a PMMA polymer backbone using copolymerization can increase the absorption coefficient of the material to make the ablation effective and permitting to fabricate well-defined micro/nano structures. This fabrication method is simple and does not require expensive monomers or dopants, which makes the method more useful for practical applications than other alternatives.

In this work, we report preliminary experimental results on the driven ablation patterning of polystyrene (PS), PMMA, and a PMMA/PS copolymer (60%:40%) substrates using DLIP. The surface topography of the irradiated copolymers was investigated using white light interferometry (WLI), scanning electron microscopy (SEM) and cross-sectional investigations using focus ion beam technique (FIB).

EXPERIMENTAL

Substrates Preparation

Polymethylmethacrylate was purchased from Sp2 Scientific Polymer Products (M_w 75,000, 99%). Polystyrene ($M_w = 120,000$) and poly(methylmethacrylate-*co*-styrene)

(PMMA-PS, $M_w = 100,000$ – $150,000$, 40% styrene) were purchased from Aldrich. The polymers PMMA, PS, and PMMA-PS were dissolved in acetone at a concentration of 5 wt/v. Fifteen milliliters of the solution was poured into a glass dish of 4.5 cm in diameter, with a bottom plate of good planarity. The solvent was allowed to evaporate for 24 h. The film was then cut out of the dish and dried in vacuum for 24 h. The final thickness of the substrates was between 200 and 300 μm .

Interference Experiments

A high-power pulsed Nd:YAG laser (Quanta-Ray PRO 290, Spectra Physics) was employed for the laser interference experiments. For the laser induced patterning experiments, we used a wavelength (λ) of 266 nm (TEM00), which is the 4th harmonic of the fundamental wavelength (1064 nm). The frequency of the laser was 10 Hz and the pulse duration was 10 ns. The primary laser beam was split into two or three coherent beams to interfere with each other on the sample surface as shown in Fig. 1a. One pulse was chosen for each experiment. The laser beam was focused onto the targets by a fused silica lens with focal distance of 2000 mm. The treated area per pulse was 10.3 mm². In the case of two-beam interference experiments, the period (P) of the periodic line-like pattern can be controlled by changing the angle between the laser beams (α) and the wavelength of the laser light as indicated in Eq. 1 [11]:

$$P = \frac{\lambda}{2 \sin \alpha} \quad (1)$$

Using an incident angle of 3.14°, a structure period of 4.85 μm was realized.

If three-beams laser interference experiments are conducted, a dot-type interference pattern with a hexagonal intensity distribution is obtained [11], and the period is given by:

$$P = \frac{\lambda}{\sqrt{3} \sin(\alpha)} \quad (2)$$

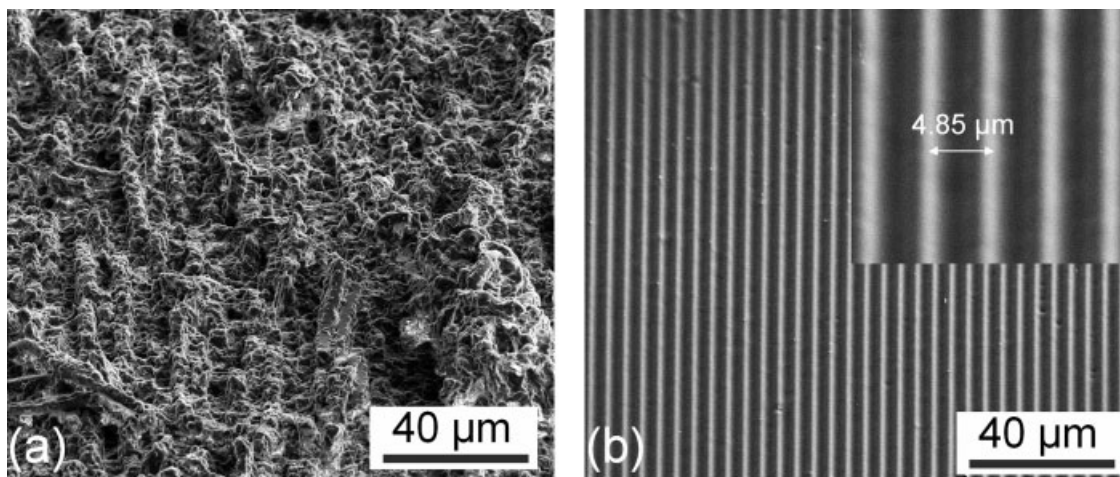


FIG. 2. Irradiated PMMA and PS samples using two-laser beams configuration. (a) PMMA, laser fluence = 2.88 J cm^{-2} ; (b) PS, laser fluence = 1.80 J cm^{-2} .

Sample Characterization

All samples were imaged with a high-resolution SEM equipped with a field emission gun (FEI Strata DB 235) at 5 kV acceleration voltage. Cross-sectional analyzes were performed with the aid of a dual beam workstation (FEI Strata DB 235) using the electron beam for imaging and the focused ion beam (Ga) for milling of the sample and Pt deposition. A protective layer of Pt is deposited over the area of investigation. The Pt layer serves to protect the sample during milling and suppressing curtaining effects, improving the quality of the cuts, and providing a sharp interface to the sample material.

Surface topography was measured using a white light interferometer (Zygo New View 3D Imaging Surface Structure Analyzer) with a vertical and lateral resolution of 0.3 nm and $0.73 \mu\text{m}$, respectively.

RESULTS AND DISCUSSION

Figure 2a and b shows the surface topography of irradiated PMMA and PS substrates using one single laser pulse. In the case of PMMA (Fig. 2a), the surface of the polymer is only ablated at high laser fluences (2.88 J cm^{-2}) and its surface topography is completely different from PS (Fig. 2b). This is due to the weak absorption of the PMMA at the utilized wavelength (250 cm^{-1} at 266 nm) [13]. PMMA ablates through sub-surface superheating meaning that the material heats above its softening point below the surface producing acoustic waves due to material's inherent elasticity [14]. These waves may lead to the development, aggregation, and subsequent bursting of microscopic bubbles resulting in the violent removal of surface material. This mechanism of ablation produces the overall destruction of the polymeric surface into a cratered structure with significant debris formation. Additionally, in weakly absorbing polymers (PMMA), there is a different phenomenon associated

with ablation. Prior to ablation, there is an incubation period in which the polymer absorbs energy that is followed by side-chain scission resulting in a less saturated backbone and stronger UV absorber [15, 16]. Therefore, no periodical structures in this energy range were induced using single-pulse exposure (Fig. 2a). Moreover, at high intensities all of the steps needed for significant material removal through volume bubble formation can take place even using a single irradiation pulse [14].

On the other hand, for strongly absorbing polymers such as PS (Fig. 2b), the ablation rate is directly related to the laser fluence and pulse duration [17]. The PS backbone has pendants phenyl groups. Those aromatic moieties have π -conjugated orbitals where electronic transitions occur at lower energies (large wavelengths) than in methacrylate monomer units. For example, ethylbenzene has absorption bands at 209 nm (molar absorptivity (ϵ) = $31,600 \text{ l mol}^{-1} \text{ cm}^{-1}$) and 259 nm ($\epsilon = 158 \text{ l mol}^{-1} \text{ cm}^{-1}$), whereas ethyl acetate shows a band only at 209 nm ($\epsilon = 72 \text{ l mol}^{-1} \text{ cm}^{-1}$) [18]. Consequently, relative low laser fluences are necessary to ablate the polymer surface. The periodical intensity modulation produced by the interference pattern results in a local and periodical removal of material obtaining a quite regular surface topography as indicated in (Fig. 2b). Thus, the obtained topography is equivalent to the inverse of the laser interference intensity distribution [10]. This behavior is also observed at high laser intensities.

A different behavior is observed for the PS-PMMA copolymers. Figure 3 shows the evolution of the surface topography for the copolymer PS-PMMA at three different laser fluence values (0.36 , 0.91 , and 1.81 J cm^{-2}). Figure 3a indicates that a very good homogeneity of the periodical structure is obtained on a large area. The results also indicate that the copolymer PMMA-PS can be structured using the same laser fluence range of PS due to the addition of styrene monomer units with a high absorption coefficient. As it can be observed in Fig. 3b,

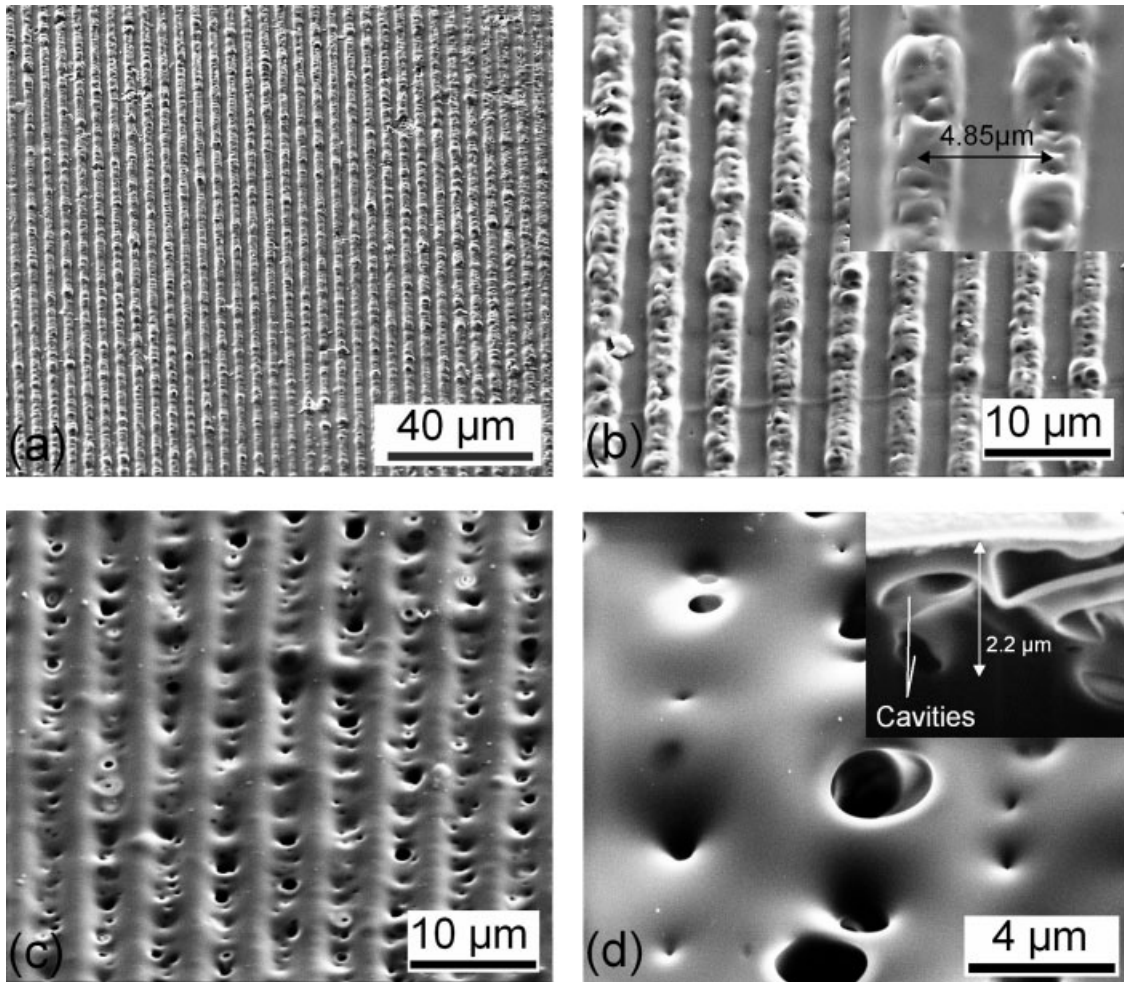


FIG. 3. Irradiated (60:40) PMMA/PS copolymer surfaces using two-laser beam interference setup. (a) A quite well-homogeneous structure is obtained in a large area (laser fluence = 0.36 J cm^{-2}); (b) inflated line-like structures at low laser fluences (laser fluence = 0.36 J cm^{-2}), the period of the pattern was $4.85 \mu\text{m}$; (c, d) crater-like structures obtained at relative large laser fluences (0.91 and 1.81 J cm^{-2} for (c) and (d), respectively). The insert in (d) shows the cross-section of the structure.

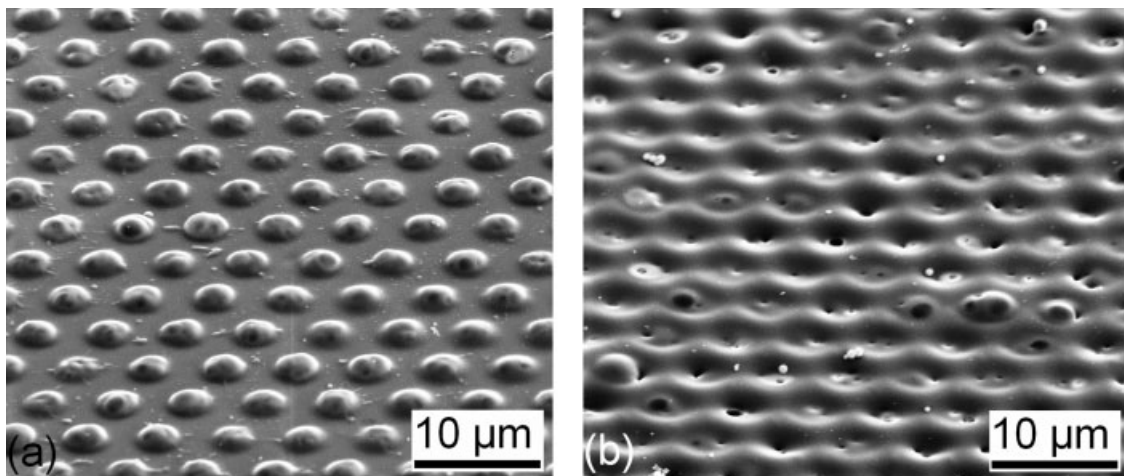


FIG. 4. Irradiated (60:40) PMMA/PS copolymer surfaces using three-laser beam interference setup. (a) Microbumps ordered in a hexagonal arrangement fabricated at low laser intensities (laser fluence = 0.28 J cm^{-2}); (b) crater-like structure observed at higher laser fluences (0.75 J cm^{-2}).

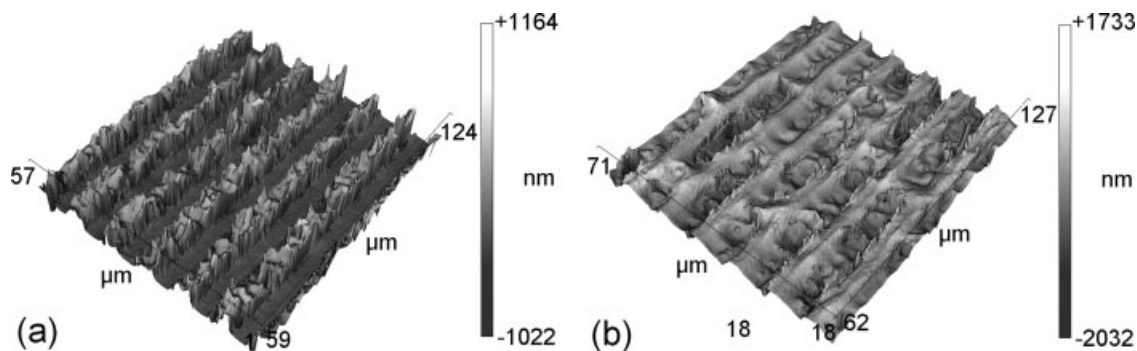


FIG. 5. White light interferometer images of PMMA/PS copolymer irradiated at (a) 0.36 and (b) 1.35 J cm⁻² laser fluences, respectively.

when PMMA-PS is irradiated with relative low laser fluences (~ 0.36 J cm⁻²), the regions at interference maxima inflate obtaining bubbles that cannot release from the material's surface due to the low local gas pressure [19]. The degradation of PMMA through photochemical reactions into methanol, carbon monoxide, and methyl formate was confirmed by Krajnovich [15, 17]. Photochemical decomposition of the ester group ($-\text{COOCH}_3$), which absorbs most photon energy in this ultraviolet-light range, causes bond breakages and vaporous ablation products (CO and CO₂) that are responsible for the inflation of the polymer. Additionally, solid fragments (MMA-monomers) tend to be formed. However, according to [20], photothermal reactions also occur at a wavelength of 266 nm, which produces the pyrolytic decomposition of the polymer. Thus, both photothermal and photochemical effects contribute to the ablation mechanism.

As shown in Fig. 4a, similar results are observed if three-laser beam configuration is used in the lower laser intensity range. In this case, the regions which correspond to the laser interference maxima positions inflate, obtaining microbumps ordered in a hexagonal arrange with a very high homogeneity on an area of several mm². These topographies are very different when compared with irradiated PC, PEEK, PEI, PI [10], and PS polymers. In the last case, the material is directly ablated at the interference maxima producing a surface topography that is equivalent to the inverse of the laser interference intensity distribution (Fig. 1b) as shown in Fig. 2b.

According to WLI investigations, (Fig. 5a), the height of the inflated regions is about 2 μm for a laser fluence of 0.36 J cm⁻². If the laser fluence is increased at 0.91 J cm⁻², the subsurface bubbles have sufficient energy to rise to the surface and burst, resulting in a cratered structure with a long-range order in the lateral scale given by the periodical intensity distribution of the laser beams (Fig. 3c). Higher laser fluences will induce larger bubbles, and thus larger craters as shown in Fig. 3d. However, a fraction of the produced bubbles remains under the polymer's surface as indicated in the insert of Fig. 3d (cavities). According to WLI investigations, the depth of the

“open craters” varies from ~ 1 to 2 μm (Fig. 5b). These values are in agreement with the depth at which microbubbles are observed according to the cross-sectional analyses (Fig. 2d).

CONCLUSIONS

In summary, we have shown that applying interference patterns on PMMA-PS copolymers is possible to fabricate complex surface architectures which result from the mixed properties of the individual components. Additionally, due to the contribution of the polymer with high absorption coefficient, lower laser fluences comparable to that of pure PS are necessary for the local and periodic ablation process. The following topographies were observed according to the used laser intensity: (1) at low fluences, the irradiated surface swells up due to the formation of microbubbles that are the results of the degradation of PMMA; (2) for high laser intensities (~ 1 J cm⁻²), the bubbles release from the surface forming a periodic micropored structure with a long-range order. Further studies about the effect of the copolymer composition on the surface topographies will be realized in the future.

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