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In this work we report on the formation of microchannels on dye-polymethacrylic acid films using a cw-laser. A focalized beam of a He-Ne laser (632.8 nm emission line) was used to form microchannels on the films. It was found that there exists a laser power density threshold for a pit formation that depends on the dye concentration. The dimensions of the laser-induced channels are dependent on the laser power density. Microchannel formation in the transparent polymethacrylic acid films was not observed. Green colored films were obtained by the spin coating technique from a polymethacrylic acid solution mixed with commercial dye. All the films obtained presented four absorption bands at 607, 636, 677 and 713 nm. These results show that this material could be applied in microfluidic devices.

Keywords: Laser-induced; microchannels; dye-polymers.

In este trabajo reportamos la fabricación de microcanales en capas de poliácido metacrilico (PMAA) pigmentado, usando un láser de He-Ne (emisión en 632.8 nm). Se encontró un umbral en la densidad de potencia láser dependiente de la concentración del colorante y que las dimensiones del canal dependen de la densidad de potencia láser. En las capas de PMAA (sin colorante) no fue posible formar canales. Las capas de PMAA pigmentadas se obtuvieron por la técnica de depósito por giro, a partir de una solución de PMAA con tinta verde de bolígrafo. Estas capas presentaron cuatro bandas de absorción centradas en 607, 636, 677 y 713 nm. Los resultados muestran que este material podría tener aplicaciones en el campo de los dispositivos usados para el transporte de microfluidos.

Descriptores: Procesos inducidos por laser; microcanales; polímeros pigmentados.

PACS: 78.20.-e; 78.40.-q; 78.40.Me

1. Introduction

The local modification of materials induced by laser is an effect known for a variety of materials as: metals [1], metal oxides [2], chalcogenide glasses [3], metal doped glasses [4], dye-polymers [5], among others. The local modification implies changes in their chemical or physical properties. In chalcogenide films, the change of the optical properties is due to a transition from the amorphous state to the crystalline one [6]. In the case of metal oxides, it has been reported that changes in the optical properties are related to changes in composition (laser oxidation) [7]. Dye-doped polymers technology is used in CD-R product; in that case, laser recording is due to the modification of the surface morphology [8]. Polymers are attractive for the fabrication of channels by laser since they have a lower threshold to induce changes compared with other materials, such as glass or metals. For transparent materials, pulsed lasers are used to change chemical and physical properties. D. Day and M. Gu [9] have recently reported the microchannel formation in PMMA using femtosecond laser pulses. However, cw-lasers can be used to induce changes in materials by thermal effects. E. Haro-Poniatowski et al. [10] have reported the crystallization of MoO3 glasses using an Argon cw-laser.

The aim of this paper is to present evidence about the formation of channels in dye-doped PMAA films using a CW-laser at a low power level ~ 2 mW. The optical absorption properties of pure PMAA were modified by the addition of a green dye. The modified PMMA presents four absorption bands within the 500-800 nm range, one of them at 636 nm.

In this case, the mechanism of the channel formation is the heating of the surface of the polymeric material by the absorption at the 633 nm laser line.

2. Experimental

2.1. Preparation of the PMAA films

Polymethacrylic acid (PMAA) was synthesized from metacrylic acid monomer (Aldrich 99.9%), purified and characterized by FT-IR spectroscopy. A home made spin coater was used to deposit the films at 1200 rpm onto 2×2.5×0.3 cm2 clean glass substrates. Films from a solution of PMAA in methanol were prepared and characterized by UV/Vis spectroscopy. Colored films were obtained by the addition of commercial green pen ink (dye) to the PMAA solution. Since the pen ink is a patented product, we are not able to present the chemical composition; however, we carried out some essential characterization in order to compare the properties of initial and final compounds. The PMAA films at three different dye concentrations (weight percent) were deposited: 9.6, 21.0 and 34.8%.

2.2. Structural and Optical Characterization of the PMAA films

A spectrophotometer FT-IR (Nicolet, Avatar 360) was used to characterize pure PMAA and dye-PMAA. Optical absorption of the films was obtained by UV-Vis spectrometry (Varian, Cary 5000 spectrometer). The film thicknesses and the
fabricated channels were measured by Scanning Electron Microscopy (SEM) with a Jeol, JSM-5900LV Microscope.

2.3. Microchannel formation

Films with and without dye were irradiated with a He-Ne laser (632.8 nm) focalized on the surface through a 100 X microscope objective. The dye-PMAA films were mounted on \( x - y \) translation stage. Displacements in one direction were carried out manually to fabricate the channels. The laser spot was 5 \( \mu \text{m} \) in diameter and the power at the surface was varied between 0.65 to 5.6 mW using neutral density filters. Under these conditions, the laser power density (LPD) at the sample was between 3.3 and 28.5 kW / cm\(^2\). The irradiated area was monitored in-situ using a CCD camera coupled to an optical microscope (Olympus BX-41). To estimate the laser power density threshold (LPDT, minimum laser power density to induce a pit on the film) we varied the laser power density to measure the transmitted light intensity before and after the pit formation. For a laser power density higher than the PLDT, pits and channels can be recorded.

3. Results and discussion

PMAA gave transparent and homogeneous films on glass substrates. It allowed a very good miscibility with the commercial dye at several concentrations in polar solvents, as methanol and the dye-doped films had a very good optical quality.

The thicknesses of the films measured by SEM were 2.05, 2.20 and 2.40 \( \mu \text{m} \). By FT-IR spectroscopy, we have identified the vibrations corresponding to the main functional groups of the polymer: 3500-2700 \( \text{cm}^{-1} \) (O-H), 2932 \( \text{cm}^{-1} \) (CH\(_3\)), 1697 \( \text{cm}^{-1} \) (C=O), 1280 and 1180 \( \text{cm}^{-1} \) (C-O), as it is shown in the transmission spectrum, Fig. 1a. Figure 1b shows the spectrum of the dye-doped PMAA. This spectrum is a superposition of the PMAA and dye vibrational features. In addition to the PMAA signals, two bands, one at 3440 (O-H) and the other at 1640 \( \text{cm}^{-1} \) (C=C), are present.

![Figure 1. FT-IR spectra: a) PMAA and b) Dye-PMAA.](image)

![Figure 2. Optical absorption spectrum of a Dye-PMAA film.](image)

![Figure 3. Temporal evolution of transmitted laser intensity during pit formation; curves a,b,c,d were obtained at 3.3, 6.6, 14.7 and 28.5 kW/cm\(^2\) respectively.](image)

Figure 2 shows the absorption spectrum in the range 500-800 nm. Four absorption bands centered at 607, 636, 677 and 713 nm were obtained after deconvolution of the spectrum. In order to change some properties in a given material with a cw-laser, the local temperature must increase to induce material changes by thermal effects. In this case, the role of the dye is to induce the absorption in the PMAA. In this way, light at 632.8 nm (He-Ne laser) can be used to change the material properties. The Vis-NIR spectra feature also shows that the absorbance increases by increasing the dye concentration (not shown here). The absorption intensity is the result of a combining effect of both the dye-concentration and the film thickness.

To determine the LPDT, we have varied the laser power density on the film. In this experiment, we measured the transmitted light during the pit formation. Figure 3 shows a plot of the laser power of the transmitted light as a function of time. The arrow indicates the time of the turn on of laser in the experiment. The curves (a), (b), (c) and (d) correspond to 3.3, 6.6, 14.7 and 28.5 kW / cm\(^2\), respectively. For
3.3 kW/cm$^2$, transmitted light is quite constant, as it can be seen in Figure 3a. In this case, we did not find a mark (point) in the optical image. However, for 6.6 kW/cm$^2$ transmitted light starts to increase in the time until it reaches a constant value. This constant value indicates that laser radiation has produced a pit of maximum depth in which transmitted light intensity is practically constant, Fig. 3b. Assuming a constant absorption coefficient, the change in the transmittance would be due to a change in the thickness of the film. According to expected results, a similar behavior was observed for 14.7 and 28.5 kW/cm$^2$, where transmitted light intensity increases with increasing LPD Figs. 3c-3d. These results can be used to define the LPDT, which produces a pit on dye-PMAA surface, being 6.6 kW/cm$^2$ for this film. Additionally, we have found that the LPDT is lower for the dye-PMAA films at higher concentrations. This indicates that the local heating of the polymer is more efficient for higher dye concentrations.

Figure 4a shows an optical image of three channels recorded at various laser power densities on the surface of a dye-PMAA film. Channel I was fabricated at 6.6, channel II at 14.7, and channel III at 28.5 kW/cm$^2$. Channel I is not well defined in the optical image. Figure 4b shows the SEM image corresponding to the channels II and III that appears in Fig. 4a. The width of these channels is not uniform, but were 0.95 (channel II) and 1.2 $\mu$m (channel III) on average. As it can be seen, the channel size depends on the LPD and the speed of surface scanning.

4. Conclusions

In this work we demonstrated that a cw-laser can be used to fabricate channels in dye-PMAA films using a low laser power level. We have found that the PLDT depends on the dye concentration of the film. The size of the channels can be controlled simply by changing the laser power density and the scanning speed. We think that the channel formation mechanism is related to a change in the density of the dye-PMAA film by the local heating of the laser irradiated area.

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