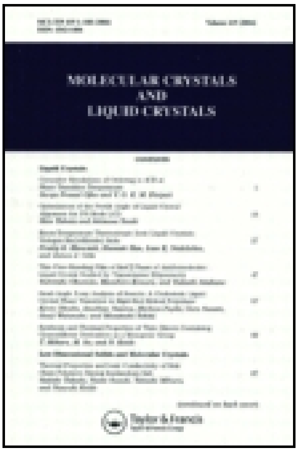

Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl20

Polyaniline-Poly(Vinyl Alcohol) Composite: Spectroscopic Characterization and Diffraction Grating Recording

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Version of record first published: 29 Oct 2010

Mol. Cryst. Liq. Cryst., Vol. 374, pp. 173-178

1058-725X/02 $12.00 + .00

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Diffraction gratings were recorded both optically and interferometrically in dichromated poly(vinyl alcohol) (DCPVA) films by means of dichromate photoreduction. Aniline was used as a chemical developer, through in situ polymerization in the unreduced parts of the film. The resulting composite material shows the optical and chemical properties of polyaniline and the mechanical resistance of PVA. Characterization of the gratings gave a line width of 12.2 μm and a diffraction efficiency of 32 %. Uv-vis spectroscopy was used to study dichromate photoreduction and the optical properties of the composite..

Keywords: polyaniline; image recording; diffraction grating.

1. INTRODUCTION

Conducting polymers have been intensively investigated in the last two decades because of their fundamental physical properties and potential applicability in advanced technologies. In particular, polyaniline (PAni) has attracted intense interest because it presents an easy route of synthesis, good environmental and thermal stability and also due to the fact that its physical properties can be reversibly controlled both by oxidative and by protonic doping [1].

However, a major drawback of conducting polymers has been their non-processability. One of the many approaches to overcome this problem is combining the conducting polymer with other processable polymers [2]. Poly(vinyl alcohol) (PVA), a water soluble polymer used in many industrial applications [3], is one of these polymers that can be combined with PAni to form a very stable composite [4]. Among several important applications, PVA has been used as an optical recording medium for holography. This system, known as dichromated PVA (DCPVA), has been carefully studied and its recording mechanism is now quite well established [5, 6].

In the search for active, functionalized images, with tunable properties, much research have been done on image formation with conducting polymers [7]. Polyaniline itself has been thoroughly studied in both chemically modified and/or electrochemically prepared single films, combined with electrochromic dopants and so on. Its unique physical and electrochemical properties make PAni suitable for several applications, and some encouraging results have already been obtained [7].

In this work we report the results of diffraction grating recording using optical and interferometrical techniques in DCPVA films using aniline as a chemical developer. The optical technique used resembles photolithography in the sense that we use masks to spatially control photoreduction of dichromate, but without any etching step.

2. EXPERIMENTAL

DCPVA films were prepared by casting aqueous solutions of PVA, containing ammonium dichromate, in petri dishes or flat glass plates. Image recording was carried out optically or interferometrically. In the first case, a commercial Ronchi ruling (1000 lines per inch) was used as a mask, placed on the film surface and then illuminated by a conventional slide projector lamp. In the latter case, an interference pattern was generated by two laser beams directly on the film surface.

Image development was done by treating the exposed film with an aniline 0.5 M / HCl 1.0 M aqueous solution, previously diluted with ethanol, for approximately five minutes. Polymerization was seen to occur by the drastic color change on the unexposed areas, from orange-yellowish due to dichromate, to green, characteristic of doped PAni. After polymerization, the film was washed with alcohol and left to dry.

The recorded image can be turned to blue or back to green several times by treating the films with alkaline or acid solutions, respectively.

The uv-visible spectroscopic characterization was carried out by a Perkin Elmer model Lambda 6 spectrometer. Before measurements, the films were peeled off from their plates and placed in the optical path of the spectrometer. In order to determine the resolution of the recorded gratings (in term of line width), we measured the light diffracted from a He-Ne laser (632.8 nm) passing through the film, with a photodetector mounted in a linear translating support.

3. RESULTS AND DISCUSSION

Figure 1 shows the absorption spectra of DCPVA film before (full line) and after (dashed line) light exposure. The spectrum of the unexposed DCPVA film has two bands centered at 270 and 366 nm and a shoulder around 440 nm, in good agreement with the literature [6]. In the exposed films, these bands are strongly reduced, indicating bleaching of the film.

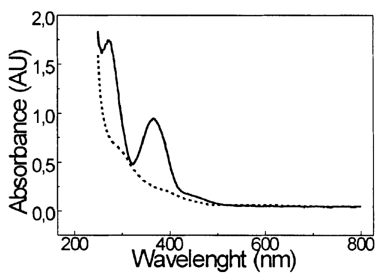

FIGURE 1. Uv-vis spectra of unexposed DCPVA film (——), and same film after 1 h light exposure (------).

Figure 2 shows the progress of photoreduction with the exposure time, accompanied by the decrease absorption band of dichromate at 366 nm. The light source was the slide projector lamp, distant about 10 cm from the film. Most of the decrease at 366 nm takes place within the first minutes of illumination, being progressively less pronounced after about 20 minutes. Total photoreduction may take approximately 1 h, but a good contrast can be obtained with substantially less time. When using a laser light, photoreduction takes much less time. Hence, the interferometric recording can be done efficiently within very few minutes.

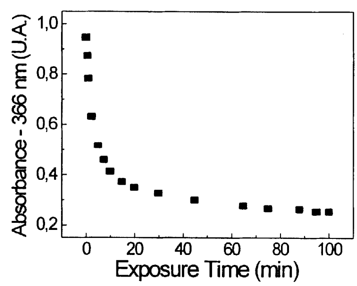

FIGURE 2. Progress of dichromate photoreduction with the exposure time. .

Figure 3 shows the absorption spectra of the PAni-PVA composite, before and after treatment with NH_4OH solution. The absorption bands for the acid and the base forms of PAni are very similar to those reported in the literature [8]. There is also an additional band at around 280 nm, which we ascribed to unreduced dichromate. We can see that PAni remains optically active in the composite. Also, conversion to base and acid forms can be done several times without appreciable degradation of the composite film.

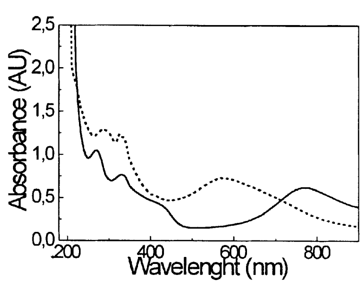

FIGURE 1. Uv-vis spectra of PAni-PVA composite before (——) and after (------) treatment with NH_4OH solution.

Figure 4 shows the diffraction pattern for one of the optically recorded gratings, as a function of the photodetector perpendicular displacement. The separation between the lines was calculated from the diffraction equation, knowing the distance between the composite film and the detector, and the orders separation. Line width for this grating was found to be 12.2 μm.

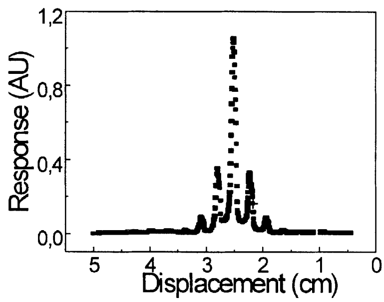

FIGURE 4. Intensity along the diffraction pattern generated from a beam of 632.8 nm light passed through the composite film

This line width is equivalent to about 1045 lines per inch, in a good agreement with the number of lines for the commercial grating used as a mask. The diffraction efficiency (DE) for this grating was determined using the ratio between the intensities of the first order beam and of the zero order beam [9]. For this grating, DE was found to be about 32 %.

The interferometrically recorded grating gave similar results. Further work is in progress to improve such results.

4. CONCLUSION

We have demonstrated the possibility of using PAni-PVA composite for permanent image recording. DCPVA films were used as the recording media, and polyaniline was the chemical developing agent, with the image being developed through in situ polymerization of aniline. The composite retains the optical and chemical properties of polyaniline and the mechanical resistance of poly(vinyl alcohol).

The method allows to pattern the conducting polymer into any desired shape on the PVA film and reversibly change its doping state, thus controlling the net properties of the material. The system exhibits good resolution, in the scale of micrometers, and is suitable for both optical and interferometrical recording..

ACKNOWLEDGEMENTS

The authors wish to thank to CNPq and PADCT for financial support.

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