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Why does poly(acrylic acid) addition improve the quality of holograms recorded in dichromated poly(vinyl alcohol)?

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ABSTRACT

Holographic measurements have shown that the addition of 0.5% of poly(acrylic acid) (PAA) can improve the quality of holograms recorded in poly(vinyl alcohol) (PVA) doped with ammonium dichromate (ADC). The purpose of this paper is to explain this improvement. First, an analytical approach investigated the structural and architectural modification of the polymeric matrix and the fate of the various chromium species within PVA/PAA/ADC films. The addition of PAA in dichromated PVA led to a pre-reticulation of the polymeric matrix. This process increased with the amount of PAA.

Second, an analytical approach focused on the evolution of PVA/PAA/ADC films upon irradiation at 365 nm, which is representative of hologram formation. The improvement brought by the presence of 0.5% of PAA in PVA/ADC was assigned to an additional source of crosslinking through the formation of covalent bonds. This process paralleled the crosslinking through coordination bonds involving Cr(V) and PVA units. At 0.5% of PAA, the mobility of the medium before exposure was sufficient to allow the migration of the species involved in the reticulation process during hologram formation, whereas higher concentrations of PAA inhibited this migration.

1. Introduction

Holography is a laser beam technique that has found potential applications in optical data storage [1–4], art [5], medical imaging [6–7], electrochemistry [8] and structures on an atomic scale [9–10]. The oldest material, dichromated gelatin (DCG), still remains the best photosensitive recording material used in holography, leading to high quality holograms and high signal/noise ratios [11]. However, a major DCG drawback is the need for development after exposure. Thus, to avoid this additional treatment, research has been extended to self-developing materials allowing for real-time holographic recording. Among all the investigated systems, a large number of studies have been devoted to polymers whose the repetition units contain only one functional group of gelatin especially dichromated poly(vinyl alcohol) (DCPVA) and dichromated poly(acrylic acid) (DCPAA) [12–18].

In holographic experiments, the addition of a certain percentage of PAA can improve the quality of holograms recorded in DCPVA, evidenced by the increase of the diffraction efficiency. Indeed, the higher the diffraction efficiency is, the higher the quality of hologram is. The optimal composition is 0.5% PAA with 4% PVA and 0.5% ADC also present, which corresponds to a [PVA–PAA unit]/[Cr(VI)] molar ratio of 24.5 [19]. The explanation for this experimental observation is not trivial. Indeed, holograms recorded in DCPVA and DCPAA separately showed similarities, but also large differences, as evidenced by the implementation of analytical approaches combining investigation of the structural modification of the polymeric matrix, the fate of the various chromium species and the correlation between the two sets of results [17–18].

- The irradiation of these two dichromated systems was shown to provoke a two-step reduction of Cr(VI) into Cr(V) and then into Cr(III). The oxidation and the

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crosslinking of the host polymer occur in parallel. Finally, it was established that Cr(V) is at the origin of the quality of the hologram [15].

- The reduction process was shown to be strongly influenced by the nature of the polymeric matrix. Differences between DCPVA and DCPAA are connected to various parameters: the nature of the excited state, the kinetics, the stability of Cr(V), the reticulation process and the oxidation species formed along the macromolecular chains. Indeed:
    1. Cr(VI) reduction took place in two successive and well-separated steps in DCPVA, Cr(VI) → Cr(V) → Cr(III), with only the involvement of photo-redox processes [17]. On the contrary, an acido-basic reaction first occurred in DCPAA between Cr(VI) in its excited state and COOH groups followed by an intramolecular charge transfer reaction. This yields the formation of Cr(V) which is followed by the very fast formation of the final Cr(III) [18].
    2. Cr(V) formed under irradiation is stable in DCPVA and unstable in DCPAA.
    3. In the two matrixes, the formation of the carboxylate groups, which parallels the reaction producing Cr(III), depends on the nature of the polymeric matrix. In DCPVA, the carboxylate groups are secondary photoproducts. They are obtained from the oxidation of the polymer corresponding to the slow step of the reduction, Cr(V) → Cr(III) [17]. In DCPAA, the carboxylates are formed from the beginning of the exposure and result from a reaction between Cr(III) and the initial COOH groups. In parallel to the reduction of Cr(VI) into Cr(V), a decarboxylation process of the polymer occurs with the formation of carbon dioxide trapped in the matrix [18]. So, COOH groups leads to the formation of both carboxylate groups and carbon dioxide.
    4. In DCPVA, the reticulation was shown to involve a complexation reaction of Cr(V), which acts as a bridge between the macromolecular chains, and of Cr(III) at longer exposure times [17]. By contrast in DCPAA, the crosslinking proceeded through covalent bonds between the PAA units. The initial rate of crosslinking in the case of DCPVA is quite higher than the one observed in DCPAA, this difference is in the same order of magnitude as the one observed for the reduction of Cr(VI) [18].

In order to understand the improvement in the diffraction efficiency due to the addition of PAA in DCPVA, three types of films containing various concentrations of PAA (0.5%, 1% and 6%) and constant concentrations of PVA (4%) and ADC (0.5%) have been prepared. First, the thermal evolution of the PVA/PAA/ADC films in the dark was analyzed. Then, the PVA/PAA/ADC films were exposed at 365 nm and at ambient temperature, irradiation conditions which are representative of hologram recording [17]. The formation of the characteristic "markers" of oxidation of PVA and PAA in DCPVA and DCPAA was evidenced in previous papers [17,18]: ketones for PVA resulting from the oxidation of the OH functions and formed during the first step of Cr(VI) reduction, carboxylate groups and carbon dioxide formed from the beginning of exposure for PAA. Thus, the phototransformation in the three types of PVA/PAA/ADC films was respectively followed throughout exposure by evidencing ketones, carboxylate groups, carbon dioxide and by monitoring the kinetics of formation of these markers. In addition, the influence of PAA addition on Cr(VI) reduction and on the crosslinking process was examined. The chemical modifications were analyzed by UV–visible and infrared spectroscopy, and the structural changes were monitored by insoluble fraction measurements.

2. Experimental

2.1. Materials and film preparation

Poly(vinyl alcohol) (PVA) (98% hydrolyzed, weight-averaged molecular weight $\approx 16{,}000\ \mathrm{g\,mol^{-1}}$) and poly(acrylic acid) (PAA) (aqueous solution, 24.89% in water, weight-averaged molecular weight $\approx 240{,}000\ \mathrm{g\,mol^{-1}}$) were purchased from Interchim. Ammonium dichromate $(NH_4)_2Cr_2O_7$ (ADC) was supplied by Fluka (purum pro analysis). All the compounds were used without further purification. All the starting solutions were prepared in water purified by a Millipore Milli-Q system.

The dichromated films were prepared by the evaporation of a polymer dichromate aqueous solution. The dissolution of the required amount of PVA in deionized, ultrapure water led to a PVA solution, which had a 4% wt PVA composition. An exact weight (0.5 wt%) of ADC and a given amount of PAA (varying from 0% to 6%) were then added to obtain the desired mixtures of DCPVA and DCPAA reported in Table 1. The mixture was stirred to obtain a homogeneous solution that was poured onto a carefully cleaned Petri dish (diameter = 5.5 cm). The samples were dried in a dark chamber under normal laboratory conditions (20 °C and 30–40% relative humidity) for approximately 15 h. After water evaporation, the dry films were peeled off. The films were designed as PVA/PAA/ADC films characterized by their percentage in weight of PAA (Table 1).

To prevent a heterogeneous phototransformation in the bulk of the doped polymer film, the incident radiation does not have to be totally absorbed when crossing the whole sample. To meet this condition, the thickness of all the studied samples corresponded to an absorbance of less than or equal to 1.6 at the irradiation wavelength (365 nm).

2.2. Apparatus and procedure

A 125 W high-pressure mercury lamp (HPW type, Philips) mainly supplied radiation at $\lambda = 365$ nm (93% at 365 nm and 7% at 334 nm). The source was located along the focal axis of a cylinder with an elliptical base. At the other focal axis, the samples were fixed on a rotating carousel that could hold 15 samples. To absorb the infrared component of the source not filtered by the glass envelope of the lamp, a water Pyrex wall 1.8 cm thick was located