Photobleaching effect in azo-dye containing epoxy resin films: the potentiality of carbon nanotubes as azo-dye dispensers

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Abstract. Azo-dye molecules may suffer from bleaching under certain illumination conditions. When this photoinduced process occurs, it generates an irreversible effect that is characterized by the loss of absorption of the dye molecule. Moreover, the well-known isomerization of azo-dye molecules does not occur anymore. In this work it is shown how the addition of a small amount of multi-walled carbon nanotubes (MWCNTs) helps to decrease the bleaching effect in a photosensitive guest-host azo-polymer film. Two different systems were fabricated using an epoxy resin as polymer matrix. An azo-dye, Disperse Orange 3, was used as photosensitive material in both systems and MWCNTs were added into one of them. The optical response of the polymeric systems was studied considering the degree of photoinduced birefringence. Photobleaching of the azo-dye was observed in all cases however, the effect is lower for the composite material containing 0.2 wt % MWCNTs. The weak interaction between MWCNTs and dye molecules is less favorable when the material is heated. The optical behavior of the heated composite material suggests that carbon nanotubes can be potentially used as azo dye dispensers. The results are interpreted in terms of the non-covalent interaction between azo-dye molecules and MWCNTs.

1. Introduction

The combination of carbon nanotubes and azo-dye chromophores has recently arisen as a new nanoarchitecture for optoelectronics applications. Particularly, the electronic structure of carbon nanotubes and azo-dye chromophores allows them to weakly interact via a non-covalent binding [1, 2].

Among the many possible ways of working with carbon nanotubes and azo-dye chromophores, one alternative turns out from the addition of both carbon nanotubes and azo-dye molecules into a polymeric matrix [3, 4]. As a result, this nanocomposite material can exhibit new properties given by the presence of the dye and the nanotubes. Particularly, azo-dye molecules are well-known for their light-triggered behavior, the photoisomerization: azo-dye molecules have two isomers, trans and cis, being the trans state the energetically most stable one. Exposure to light of the proper wavelength photoinduces cis isomers and that then relax to trans isomers. Azo-dye molecules photoisomerize if their dipole moment has a non-vanishing component in the direction of the light polarization. Therefore, azo-dye chromophores accumulate in the direction perpendicular to the polarization axis of light giving rise to some degree of birefringence in the host material. Since the photoisomerization process is reversible and sensitive to the light polarization, azo-dyes have been used for the fabrication

of a broad class of photosensitive materials with varied applications including waveguiding [5], optical switching [6] and optical information storage and processing [7, 8]. However, irreversible photoinduced bleaching (photobleaching) can be suffered by the azo-dye molecules [9, 10]. If this occurs, it means that the molecule loses absorption intensity and thus the activity of the chromophore is lost. Even though it has been demonstrated that this effect can be useful for the development of waveguide devices [10], for most practical purposes photobleaching is usually an undesired effect.

The aim of this work is to demonstrate that the addition of a small quantity of multi-walled carbon nanotubes (MWCNTs) into a photosensitive guest-host azo-polymer system helps to decrease the photobleaching effect. In order to show this, the optical behavior of a nanocomposite material using an epoxy resin as matrix, Disperse Orange 3 as azo-dye and MWCNTs as filler was compared to the behavior of a material with only azo-dye. In both materials the photoinduced birefringence was explored. Successive photoinduced processes led to decreasing birefringence that can be related to photobleaching in the both photosensitive materials. The systematic study of the photoinduced birefringence reveals that the photobleaching process is diminished in the material with MWCNTs and that temperature could be used as an external trigger to modify its optical response. Results suggest that MWCNTs may work as azo-dye dispensers that can be activated by heating the material.

2. Materials and methods

2.1. Materials

One of the most common epoxy-based materials is epoxy resin and at the same time, the most important class of epoxy resins is diglycidyl ether of bisphenol A (DGEBA). DGEBA resins are transparent to visible light. The epoxy pre-polymer and curing agent used in this work were DGEBA LY 556 and IPDA HY 2962, both from Ciba Geigy. The employed azo-dye was Disperse Orange 3 (DO3) from Sigma-Aldrich. Its chemical structure is shown in figure 1. Commercially available MWCNTs were purchased from Nanocyl (NC3100). Their length is about 1.5 μm and their diameter is around 20-40 nm [1]. MWCNTs were dried in a vacuum oven at 120° C during 3 h (in order to remove adsorbed water) and they were storage in vacuum at room temperature until used. Reagent grade tetrahydrofuran (THF) from Biopack (Argentina) was used as solvent.
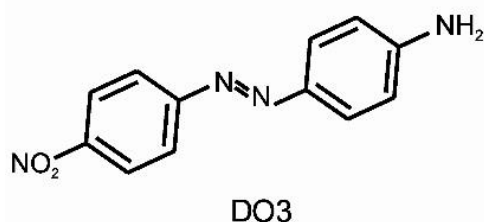

Figure 1. Chemical structure of the azo-dye chromophore Disperse Orange 3 (DO3).

2.2. Preparations of films

Two different kinds of films were prepared: films of epoxy resin and DO3 (DO3 epoxy film) and films of epoxy resin, DO3 and MWCNTs (DO3-MWCNTs epoxy film). For both kinds of films, a stoichiometric ratio (aminohydrogen/epoxy) of 1 was used. The followed protocol was used in order to prepare the photosensitive films: 0.05 g of DO3 were dissolved in 1 mL of THF and incorporated into 0.8 g of the pre-polymer DGEBA. The mixture was stirred at room temperature during 5 min. Then, 0.2 g of hardener were added and mixed again during 5 min. Immediately after that, the DO3 films were prepared by spin-coating technique. DO3 films were first storage at room temperature for 20 h and then were dried at 120 ºC for 3 h in an air flow conventional oven.

DO3-MWCNTs films were done following the same protocol as for the DO3 films. In this case, 0.002 g of MWCNTs were bath sonicated together with the DO3 and THF during 30 min in order to have a stable dispersion of MWCNTs. Then, this dispersion was mixed with the pre-polymer DGEBA at room temperature. The following steps were the same as for DO3 films. After these processes, DO3 films with 5 wt % dye concentration and DO3-MWCNTs films with 5 wt % dye and 0.2 wt % carbon nanotubes concentration were obtained.

2.3. Characterization

The photosensitive materials were characterized by measuring the time dependence of the transmittance. The experimental setup for this kind of measurements is shown in figure 2. Taking into account the absorption wavelength of the dye, birefringence was induced with a writing laser beam at 473 nm. The incidence was almost normal to the sample (about 5°) in order to avoid asymmetries in the spot. The response was monitored using a probe laser beam at 633 nm in a configuration of polarizer/sample/analyzer (P1, S and A in figure 1). The writing beam was also linearly polarized (s polarization) after passing through a polarizer (P2) which axis was set to 45° with respect to the polarizer/analyzer orientation in order to measure maximum response. Even though there are some phenomena, for instance mass transport, that are dependent on the state of polarization of the writing beam, enough general results are expected for the bleaching phenomenon from a linear polarization state. The power of the writing beam was set to 75 mW/cm^2 in all experiments and it was controlled using a neutral filter (F). A red filter (RF) was placed right before the photodiode (PD) to avoid detecting light from the writing beam. Misalignment of dye molecules can be photoinduced by irradiating the sample with circularly polarized light. To do this, a quarter wave plate was placed after P2 when necessary. For both kinds of samples, DO3 epoxy films and DO3-MWCNTs epoxy films, seven cycles to induce and erase birefringence were done successively on the same area of each film. After 60 min of photoinducing birefringence, the erasing process was done for five minutes, in order to ensure that the birefringence turns to its minimum value and then the re-writing process began again. For experiments done at a temperature other than room temperature, a hollow cylindrical-shaped oven was used as it is drawn with a dotted line in figure 2. The main axis of the oven was placed in the direction of the optical axis. The temperature was set to 85 ℃ for photoresponsive nano-composite. Films were placed inside the oven with a film holder specially designed for this purpose. The oven plateau was 5 cm guaranteeing thermal stability in that region where the film was placed. The temperature was determined with variations less than 1 ℃ using a temperature controller (TC). The experiment was done as follows. First, birefringence, relaxation and erasure of birefringence were induced for a total of 70 min at room temperature (25 ℃). Immediately after that, temperature was raised up to 85 ℃ until thermal stabilization occurred. Once the stabilization was reached, the same process for inducing, relaxing and erasing birefringence was repeated on the same area of the sample.
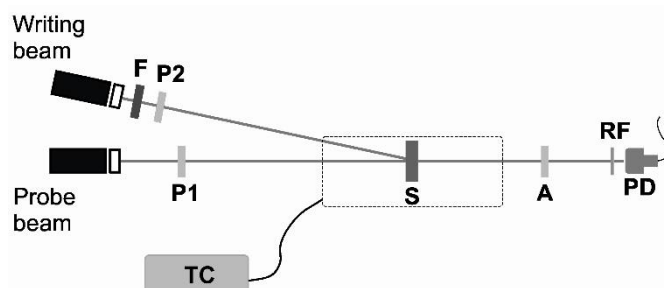

Figure 2. Experimental setup used to induce and measure birefringence in the materials. The writing beam, first attenuated by filter F and polarized by P$_2$, impinges on the sample S; the probe beam, polarized by P$_1$, impinges on the sample S, is then polarized by A and finally collected by the photodetector PD. RF is a red filter and then dotted line indicates the cylindrical oven.

3. Results and discussion

Figure 3 shows the birefringence curves for DO3 epoxy films (Figure 3a) and for DO3-MWCNTs epoxy films (Figure 3b). For both kinds of materials, inducing and erasing cycles of birefringence were done successively on the same area of the film. In order to easily appreciate the obtained effect, only three curves of inducing birefringence corresponding to cycles 1, 3 and 7, were plotted in each figures 3a and 3b, respectively. For both materials the final value of birefringence decreases with the successive cycles indicating that during each cycle there are some dye molecules that lose their optical response. This behavior can be explained in terms of photobleaching effects. Moreover, it is clear that the growth of the signal for the first cycle for DO3 films and for DO3-MWCNTs films is quite different: the detected signal for DO3-MWCNTs film is slower. This suggests that the process to photoinduce birefringence is affected by the addition of MWCNTs. In particular, the change in the rate at which birefringence is photoinduced could be due to an increment in the steric hindrance introduced by the addition of MWCNTs [3].
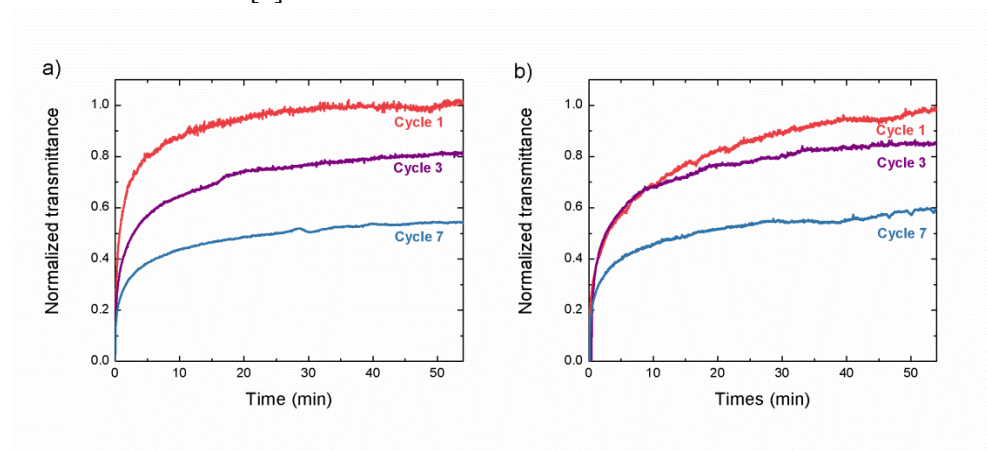

Figure 3. Photoinduced birefringence for (a) DO3 film and (b) DO3-MWCNTs film.

The maximum levels of birefringence for all the measured cycles are plotted in Figure 3 for both kinds of films: DO3 films and DO3-MWCNTs films. In figure 4a the asymptotic values of the signal were plotted as a function of the number of cycles. These values of birefringence seem to follow a linear trend for both kinds of samples. Of course, negative slopes are expected to be found in both cases as it reflects the losses in the values of birefringence. The asymptotic values belonging to the DO3 films and to the DO3-MWCNTs films were fitted with linear functions in order to quantify the losses rate for successive cycles. First, it should be noted that the maximum transmittance values for DO3-MWCNTs films is always lower than those for DO3 films. Second, the slope obtained is 10 times smaller for DO3-MWCNTs films than for DO3 films. In figure 4b the same values of maximum reached birefringence were normalized to the highest level of birefringence reached in the first cycle. This could be interpreted as a normalization to the dye molecules initially available to undergo photoisomerization. When the results are plotted in this way, the normalized maximum signal for both kinds of samples follows a similar trend. This reflects that if there were initially the same amount of available DO3 molecules, then the response for both materials would be similar.
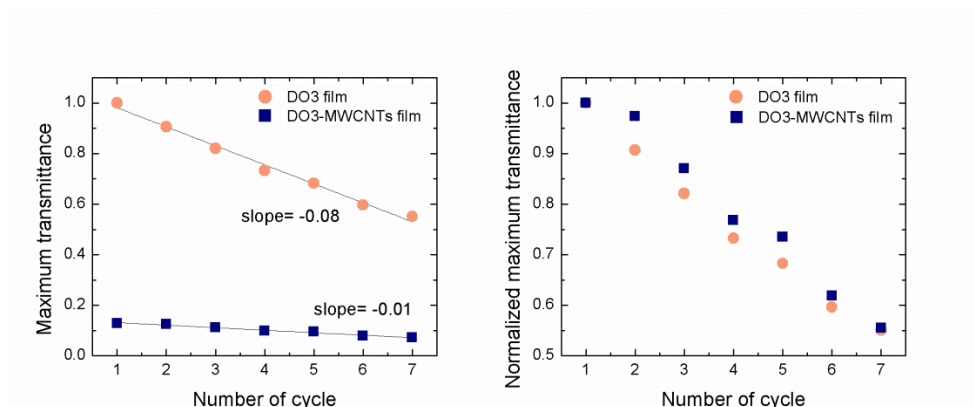
Figure 4. (4a) Maximum level of birefringence reached for the successive cycles on both films. Solid lines are fitted linear functions. (4b) The same values normalized to the maximum level of birefringence of the first cycle.

The progressive losses in the optical response of the materials can be related to the morphological changes observed with naked eye. In fact, DO3 epoxy films and DO3-MWCNTs epoxy films showed photobleaching effects after exposure to light at 473 nm. Picture in figure 5 is showed in order to illustrate the bleaching process in a DO3 film. This image was obtained after irradiation of the sample at 473 nm (75 mW/cm^2) during 6 h. The circular shape of the bleached spot ($\sim$ 2 mm) follows the beam shape.
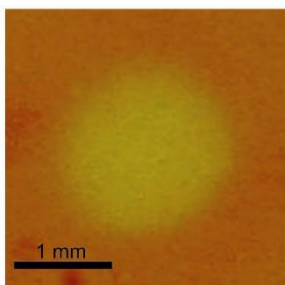

Figure 5. Illustrative picture of a photobleached effect in a DO3 epoxy film.

According to the previous results, the material with MWCNTs presents a different behavior with respect to the DO3 film reflecting that the presence of MWCNTs plays an important role in the optical response. In fact, the two observations previously mentioned in the description of Figure 3a could be explained in terms of the π-π interaction between DO3 molecules and MWCNTs [1, 4]. This interaction generates that some fraction of DO3 molecules are preferentially in the vicinities of MWCNTs and less molecules are available for photoisomerization and thus for photobleaching.

A birefringence experiment at higher temperature was performed in order to create an environment where the weak, non-covalent π-π interaction between MWCNTs and dye molecules is less favorable. Figure 6 shows two curves of induction, relaxation and erasure of birefringence for DO3-MWCNTs epoxy film at two different temperatures: the first one at 25 °C and the second one at 85 °C. The sample was kept fixed between consecutive measurements in order to irradiate the same area of the film. The time interval between each measurement corresponds to the required time to increase and stabilize the temperature. As it can be seen from figure 6 the measurement at 85 °C presents a similar temporal behaviour to the previous measurement at room temperature. Moreover, biexponential functions were used to fit each measurement (dotted line in Fig 6) and the asymptotic values for both curves are similar. Contrary to what happens when two successive cycles are done at room

temperature, in this case there is no decrease in the transmittance for the second cycle. This result indicates that some dye molecules can be activated by heating the material. A plausible explanation for this effect to occur is that thermal agitation could increase the number of available azo-dye molecules as it overcomes the non-covalent interaction between the azo-dye molecules and MWCNTs. Presumably, these dye molecules initially do not participate in the photoisomerization and photobleaching process for being in the vicinities of the carbon nanotubes. This characteristic of the DO3-MWCNTs epoxy films suggest that carbon nanotubes could be used as DO3 dispensers that can be activated by increasing temperature.
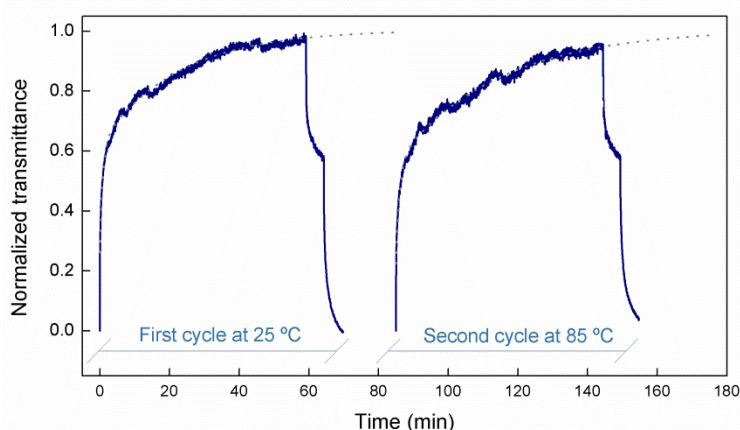

Figure 6. Curves of the induction, relaxation and erasure of the birefringence for DO3-MWCNTs films performed for two successive cycles: first at 25 °C and second 85 °C.

4. Conclusions
The study of the induced birefringence at room temperature in guest-host azo-epoxy resin materials reveals that the addition of a low concentration of MWCNTs decreases the photobleaching effect suffered by the azo molecules. The bleaching effect, which can be seen with the naked eye, can be detected by successively measure the photoinduced birefringence. Successive measurements for DO3 epoxy films and DO3-MWCNTs epoxy films revealed that some azo-dye molecules lost their absorption. However, MWCNTs epoxy films showed that the rate at which the material photobleaches is 10 times slower than for the materials without MWCNTs. Measurements of photoinduced birefringence at higher temperature were done in order to evaluate if the rate at which the DO3-MWCNTs epoxy film photobleaches was the same. As revealed by the experiments, not only the asymptotic value did not decrease but it was the same after successive cycles. A possible explanation for this behavior could be that the non-covalent interaction between MWCNTs and azo-dye molecules keeps azo molecules in the vicinities of the nanotubes preventing the azo molecules from bleaching. The fact that a higher level of birefringence was obtained by heating the sample indicates that there exist more azo-dye molecules contributing to the final birefringence. Thermal agitation could be responsible for a higher availability of azo-dye molecules overcoming the non-covalent interaction between azo-dye molecules and MWCNTs. These results suggest that MWCNTs may work as azo-dye dispensers that can be activated by heating the material.

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