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# Enhancement of the optical response in a biodegradable polymer/azo-dye film by the addition of carbon nanotubes*

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**Abstract**

A new biodegradable photoresponsive material was developed using poly(lactic acid) (PLA) as the matrix material and Disperse Orange 3 (DO3) as photoisomerizable azo-dye. It was observed that the addition of multi-walled carbon nanotubes (MWCNTs) leads to a new phenomenon consisting of an enhancement of the optical anisotropy in a wide range of temperatures. In particular, the optical anisotropy increases 100% at room temperature. Moreover, the material containing MWCNTs shows a faster optical response that is evidenced as an increase in the growth rate of optical anisotropy. Spectroscopic data is provided to study the interaction among DO3, MWCNTs and PLA. The enhancement of optical anisotropy obtained with the addition of MWCNTs was related to the glass transition temperature ($T_g$) of each material. Maximum optical anisotropy was obtained 15 °C below the $T_g$ for both materials. Results are interpreted in terms of the interactions among DO3, MWCNTs and PLA and the packing density of the dye into the polymer chains.

Keywords: optical properties, photosensitive material, biodegradable material, azo-dye, carbon nanotubes

(Some figures may appear in colour only in the online journal)

## 1. Introduction

The specific response of azo-dyes to visible light makes them perfect candidates for the development of a broad kind of optical devices. The addition of these azo-dyes chromophores into different polymers allows the development of new materials with applications to waveguides, optical memories, optical information storage and optical processing devices [1–7]. In all cases, the characteristic photoisomerization process of azo-dyes plays a prominent role. The azo-dye molecules successively change from *trans* to *cis* configurations when they are irradiated with light of the proper wavelength. If the light is linearly polarized, molecules having some component of their dipole moment in a direction parallel to the polarization axis will undergo the photoisomerization process. As a result, molecules will gradually accumulate in the *trans* form in the normal direction of the light polarization axis. This gradual accumulation of molecules in their *trans* state leads to optical anisotropy. In general, the development of devices containing azo-dyes involves the study of their optical response. This optical response is generally understood as the optical anisotropy that can be photoinduced in the material as well as the rate at which this occurs. One important feature of polymeric devices containing azo-dyes is the fact that the polymer host is transparent to visible light whereas their optical properties are entirely given by the azo-dyes. From a practical point of view, availability and easy manipulation of the polymer host are also important factors to consider. In this study poly(lactic acid) (PLA) was chosen as the polymer host as it combines the mentioned physical characteristics and also

* In memory of Professor Iñaki Mondragon.

 

biodegradability [8]. PLA is one of the most studied materials for applications in the packaging industry because of its biodegradability and its mechanical properties. In this sense, the idea was to look for an additional functionality (optical properties) when developing the photosensitive composites. Even though the $T_g$ of the PLA is around 50 °C, many sensors are used in frozen products or products at a temperature below room temperature and then the value of the $T_g$ would not be a problem for these applications. Also, the idea is to develop materials with optical properties that can be manipulated at room temperature (that they are not fragile), since this is a great problem for industrial applications. These features render PLA as a promising host for photoresponsive devices since international agreements encourage the use of biodegradable materials as a replacement for petroleum-based polymers.

Otherwise, the combination of carbon nanotubes, azo-dyes and polymer has been used for different applications from photodeformable materials to optical memories [9–14]. In particular; it has been recently shown that the addition of carbon nanotubes into azo-containing polymers eventually improves the optical response of the hybrid material when compared to its parent polymer at room temperature [14]. In azo-containing polymers the azo moieties are covalently bonded to the polymer backbone to form side-chain systems. Thus, this kind of system is more complex to prepare than guest–host systems. In addition, the optical response of materials containing azo-dyes depends on temperature. Some reports explored the temperature effect on the optical response of photoresponsive materials without filler and explained the results in terms of the free volume concept [3, 15].

As reported by our group, multi-walled carbon nanotubes (MWCNTs) can efficiently interact with a specific azo-dye, Disperse Orange 3 (DO3) by means of $\pi$–$\pi$ stacking interactions [16]. The interaction between MWCNTs and the azo-dye led to good stable dispersions in tetrahydrofuran (THF). Considering these results, it could be expected that the addition of MWCNTs into a photoresponsive polymer (PLA with DO3) generates some interaction with the azo-dye modifying the optical response. To the best of the authors' knowledge, the effect of carbon nanotubes addition in polymer/azo-dye guest–host systems has not been reported previously. Moreover, there are no reports of the temperature effect on the optical response of photoresponsive materials that contains MWCNTs.

The aim of this work is to show that the addition of a small amount of MWCNTs into a photoresponsive polymer (PLA with DO3) improves the optical response of the material in a wide temperature range. The improvement of the optical response is obtained as an enhancement of the degree of photoinduced optical anisotropy and as an increment in the rate at which this effect occurs. It should be remarked that this work presents the first experimental research on the optical response of a biodegradable polymer/azo-dye film. Moreover, low concentrations of MWCNTs and DO3 were used in order to avoid disrupting the biodegradable character of PLA. The obtained results show that these materials are promising for the development of optical storage of information devices that could be applied, for instance, in environmentally friendly photosensitive secondary packaging.

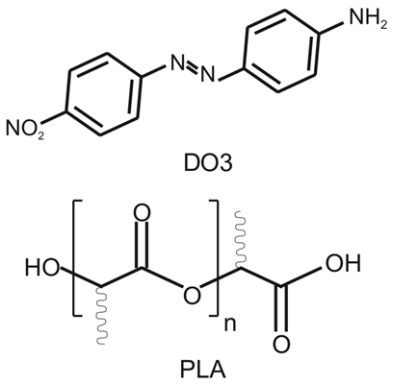


**Figure 1.** Chemical structure of DO3 and PLA.

## 2. Experimental

Two different kinds of biodegradable polymer/azo-dye films were prepared in order to study the optical anisotropy as a function of temperature: PLA containing an azo-dye, DO3, and PLA containing DO3 and MWCNTs.

### *2.1. Materials*

Pellets of PLA (10% D-Lactide, 90% L-Lactide), manufactured by Shenzhen Bright China Industrial Co. Ltd (Wuhan, China), were used as the matrix material in this study. The weight and number averaged molecular weight of the polymer are 67.600 g mol$^{-1}$ and 49.900 g mol$^{-1}$, respectively. DO3 dye is an azobenzene derivative that has the appearance of orange powder and it was used as received from Sigma-Aldrich. The chemical structures of the polymer and the dye are shown in figure 1. MWCNTs were purchased from Nanocyl (NC3100). Their length is about 1.5 $\mu$m and their diameter is around 20–40 nm [17]. The MWCNTs were dried in a vacuum oven at 120° C during 3 h (to remove adsorbed water) and they were left in vacuum at room temperature until use. Chloroform was chosen as solvent for the following reasons: because DO3 and PLA are soluble in it and because a good stable dispersion of MWCNTs in a DO3/chloroform solution can be obtained. Reagent grade chloroform from Biopack (Argentina) was used.

### *2.2. Preparation of films*

*Photoresponsive PLA.* Photoresponsive PLA was prepared by the following protocol: the calculated amount of DO3 in order to have a final concentration of 0.25 wt% was dispersed in 50 mL of chloroform using a bath sonicator. After 60 min, 1 g of PLA was added to the solution and sonication continued for other 60 min. Immediately after that, the final solution was cast into flat-bottom glass Petri dishes. The solution was dried for 24 h at room temperature. Finally, the films were oven dried under vacuum at 40 °C for two days and then at 60 °C for 24 h. The complete removal of residual solvent was confirmed by proton nuclear magnetic resonance ($^1$H-NMR) dissolving the film in dimethyl sulfoxide (DMSO).

*Photoresponsive nano-composite.* A similar protocol to that one previously described was used to prepare the nano-composites. The only difference is that in this case 0.0005 g

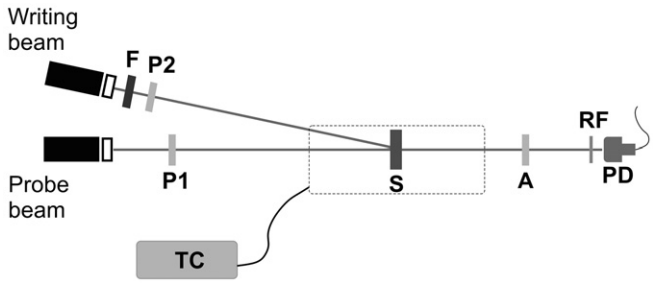


**Figure 2.** Experimental setup used to induce and measure optical anisotropy in the materials at different temperatures.

of MWCNTs were put together with 0.0025 g of DO3 in 50 ml of chloroform and then sonicated for 60 min. It should be mentioned that a good dispersion of MWCNTs in PLA was obtained.

A neat PLA matrix without DO3 or MWCNT was also prepared using the same protocol as for the other materials, including the drying process. The neat PLA film is transparent to visible light and it is not photoresponsive since it does not contain any azo-dye. However, neat PLA was prepared in order to evaluate changes in the physical properties distribution introduced by the addition of DO3 and MWCNTs. Five different films of each kind of sample were prepared. The mean thickness of each set of five samples was 75 $\mu$m with a dispersion of 2 $\mu$m. The thickness of each sample was determined using a digital micrometre with a precision of 0.1 $\mu$m. Thicknesses variations within a single sample were below 0.2 $\mu$m. It should be mentioned that developing thick films ($\mu$m) allows obtaining films that can be self-supported (in contrast to spin-coated films, for example, where a coverglass is needed). Moreover, a film that preserves its shape without any additional substrate becomes useful from both sides, which allows broadening its applications. For instance, it could be used as a sensor in a secondary packaging (not in contact with eatables).

### *2.3. Characterization*

Dynamic mechanical characterization of all films was performed using a dynamic mechanical thermal analyser (DMTA IV Rheometrics) working in rectangular tension mode at 1 Hz, in the temperature range between 30 and 90 °C, at a heating rate of 2 °C min$^{-1}$. Glass transition temperatures ($T_g$) were determined as the maximum of the loss tangent curve (Tan $\delta$). The $T_g$ for all films was also determined by differential scanning calorimetry (DSC) at a heating rate of 10 °C min$^{-1}$ (DSC-60 Shimadzu). Fourier transform infrared (FTIR) spectroscopy by attenuated total reflectance (ATR) using a Nicolet 8700 spectrometer was performed for all materials. The spectra were recorded by the average of 512 scans in the wavenumber range of 4000–525 cm$^{-1}$. Ultraviolet–visible (UV–Vis) spectroscopy measurements were performed using a HP 8453 spectrophotometer. All measurements were done at room temperature.

The successive photoisomerization processes were characterized by measuring the time dependence of the transmittance. Figure 2 shows the experimental setup used for these measurements. This arrangement is similar to experimental configurations that were previously discussed in the literature [18]. Taking into account the absorption wavelengths of the dye, optical anisotropy was induced using a solid state laser (writing beam) at 473 nm. The power of the writing beam was set to 1 mW in all experiments using a neutral filter (F). The response was monitored using a He–Ne laser (probe beam) at 633 nm in a configuration of polarizer/sample/analyser (P1, S and A in figure 1). P1 was oriented with its axis normal to the incident plane (s polarization) and A was oriented with its axis parallel to the incident plane (p polarization). The writing beam was also linearly polarized after passing through a polarizer (P2) which axis was set to 45° with respect to the polarizer/analyser orientation in order to measure maximum response. A red filter (RF) was placed right before the photodiode (PD) to avoid detecting light from the writing beam. The temperature of all films was controlled with a hollow cylindrical-shaped oven drawn with a dotted line in figure 2. The main axis of the oven was placed in the direction of the optical axis. 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 photoinduced optical anisotropy was monitored at different temperatures. Each measurement began after 15 min of temperature stabilization. The temperature was varied in steps of 5 °C from 20 to 75 °C for photoresponsive PLA and from 20 to 45 °C for photoresponsive nano-composite. It is known that for temperatures near the $T_g$ of the material, thermal agitation becomes more relevant and competes with the photoalignment of the azo-dye molecules. In particular, beyond the $T_g$ the optical anisotropy strongly decreases. The temperature was determined with variations less than 1 °C using a temperature controller (TC). For each temperature, films were exposed to linearly polarized light for 1.5 h. After 1.5 h of photoinducing anisotropy, the writing beam was turned off and measurements of the transmittance continued for 30 min.

All the experiments were performed over five different films of each kind of sample in order to ensure the reproducibility of the results. Moreover, the optical response of the films was also evaluated in different regions of each single sample leading to similar results. As the different experiments over each set of five samples did not show significant differences, in the following section the results are shown for one sample only.

## 3. Results and discussion

Figure 3 shows the loss tangent, Tan $\delta$, as a function of temperature, for neat PLA, photoresponsive PLA and for the photoresponsive nano-composite. For neat PLA, the $T_g$ was 54 °C, for photoresponsive PLA the $T_g$ was 59 °C (increasing 5 °C) while for the photoresponsive nano-composite the $T_g$ was 40 °C. It is well known that an increment in the $T_g$ is associated to a decrease in the free volume. The differences in $T_g$ between the photoresponsive PLA and the neat PLA can be explained in terms of the packing density of the azo-dye molecules in the polymer. According to the literature, the ester group of the

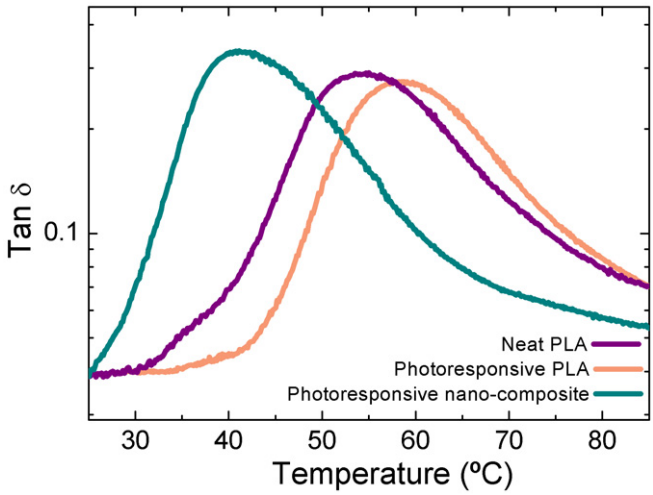


**Figure 3.** Loss tangent as a function of temperature for neat PLA, photoresponsive PLA and photoresponsive nano-composite.

PLA interacts with the amino terminal group of DO3 molecules [19]. Then the addition of DO3 into PLA might correspond to a more compact arrangement, reducing the free volume and giving rise to an increment in the $T_g$ value. In the case of the photoresponsive nano-composite, the addition of MWCNTs introduces two different processes. One of them could be associated to an increment in the free volume (i.e. a decrease in the $T_g$ of the material) due to the steric hindrance generated by the MWCNTs in the PLA chains arrangement. The other process is due to the $\pi$–$\pi$ stacking interaction between the MWCNTs and the azo-dye molecules [16]. The result of this interaction leads to a different organization of the azo-dye molecules within the free volume holes as a consequence of the preparation process of the photoresponsive nano-composite. As MWCNTs will be non-covalently functionalized with the DO3 molecules it could be expected that a lower amount of DO3 molecules were available to interact with the PLA chains. Thus, this second process also increases the free volume of the material with respect to photoresponsive PLA.

The relative differences between the $T_g$ values of the three materials (neat PLA, photoresponsive PLA and photoresponsive nano-composite) obtained from DMTA measurements were confirmed by DSC study.

As mentioned previously, the results of the DMTA analysis suggest that the addition of DO3 into PLA would reduce the mean value in the free volume size distribution. Therefore, it could be expected that DO3 molecules affect the characteristic vibrations of PLA in some way. However, the situation is quite different when adding MWCNTs because there is no physical chemistry reason for which MWCNTs should interact with PLA. In the case of adding MWCNTs, there is a new spatial distribution of PLA chains. First, the $\pi$–$\pi$ interaction of DO3 and MWCNTs prevails on the PLA and DO3 interaction decreasing the number of interactions between PLA and DO3. Second, MWCNTs increase the PLA free volume. Therefore, the addition of MWCNTs might turn back the changes produced in the PLA vibration modes due to the inclusion of DO3. This idea is supported by the FTIR study.

Figure 4 shows four regions of the FTIR spectra in order to visualize the more meaningful changes which are introduced by the addition of only DO3 or both DO3 and MWCNTs into the PLA. For each region, the spectra of neat PLA, photoresponsive PLA and photoresponsive nano-composite are shown. The transmittance in arbitrary units is plotted against the wavenumber. Figure 4(*a*) shows the spectra in the range 1320–1270 $cm^{-1}$. The band around 1300 $cm^{-1}$ in neat PLA, associated to the CH bending mode, is narrowed for photoresponsive PLA [8]. Besides, in this last spectrum a new band appears around 1294 $cm^{-1}$. This new band in photoresponsive PLA can be assigned to the C–N stretching mode of C–$NH_2$ of DO3 [18]. Having in mind that the $NH_2$ group of DO3 can interact with the PLA ester group [18], the region around the frequencies corresponding to the vibration of the carbonyl group (C=O) in neat PLA spectrum should be modified. This effect is shown in figure 4(*b*). As it can be seen in this figure, neat PLA has a band assigned to the C=O around 1750 $cm^{-1}$ which is modified in the photoresponsive PLA spectrum. Moreover, the addition of DO3 into PLA also modifies the band around 1452 $cm^{-1}$ assigned to the asymmetric bending of PLA methyl group (figure 4(*c*)). For photoresponsive PLA this band looks narrower when compared to neat PLA and it also loses the shoulder around 1460 $cm^{-1}$. At last, figure 4(*d*) shows the spectra in the range 800–600 $cm^{-1}$.The wide band around 700 $cm^{-1}$ assigned to the C=O out of plane bending in neat PLA is strongly modified in photoresponsive PLA. This is probably due to the fact that DO3 has a strong absorption in 690 $cm^{-1}$ (assigned to C=C–H bending) [20]. As shown in figure 4, the spectrum of photoresponsive nano-composite does not substantially differ from that of neat PLA. This result suggests that the addition of both MWCNTs and DO3 would turn back the effects of the addition of only DO3. Moreover, the fact that the DO3 bands are not observed in the photoresponsive nano-composite spectrum suggests that the interaction DO3-MWCNT limits the intrinsic vibration modes of the dye.

According to previous reports [16], the interaction between MWCNTs and DO3 can also be detected by UV–Vis spectroscopy. In figure 5 the UV–Vis absorption spectra for neat PLA, photoresponsive PLA and photoresponsive nano-composite are shown. As it can be seen from these curves, PLA has an absorption band in the UV range, around 231 nm. As expected, this band appears in all the spectra. In the absorption spectra of photoresponsive PLA and photoresponsive nano-composite two new bands appear: one around 273 nm and the other around 428 nm. It should be noted that the relative intensity of the band around 273 nm with respect to the band at 428 nm is lower for photoresponsive nano-composite. Both bands (273 and 428 nm) are characteristic of DO3 molecules. The one at lower wavelengths corresponds to a $\pi$–$\pi^*$ electronic transition assigned to the benzene ring of the dye and the other at 428 nm corresponds to the stronger $\pi$–$\pi^*$ electronic transition of the azo group [16]. DO3 molecules interact with MWCNTs via $\pi$–$\pi$ stacking [16]. This interaction occurs by the stacking of the rings of the outer surface of MWCNTs with the DO3 benzene ring. The results shown in figure 5 indicate that the addition of MWCNTs modifies the

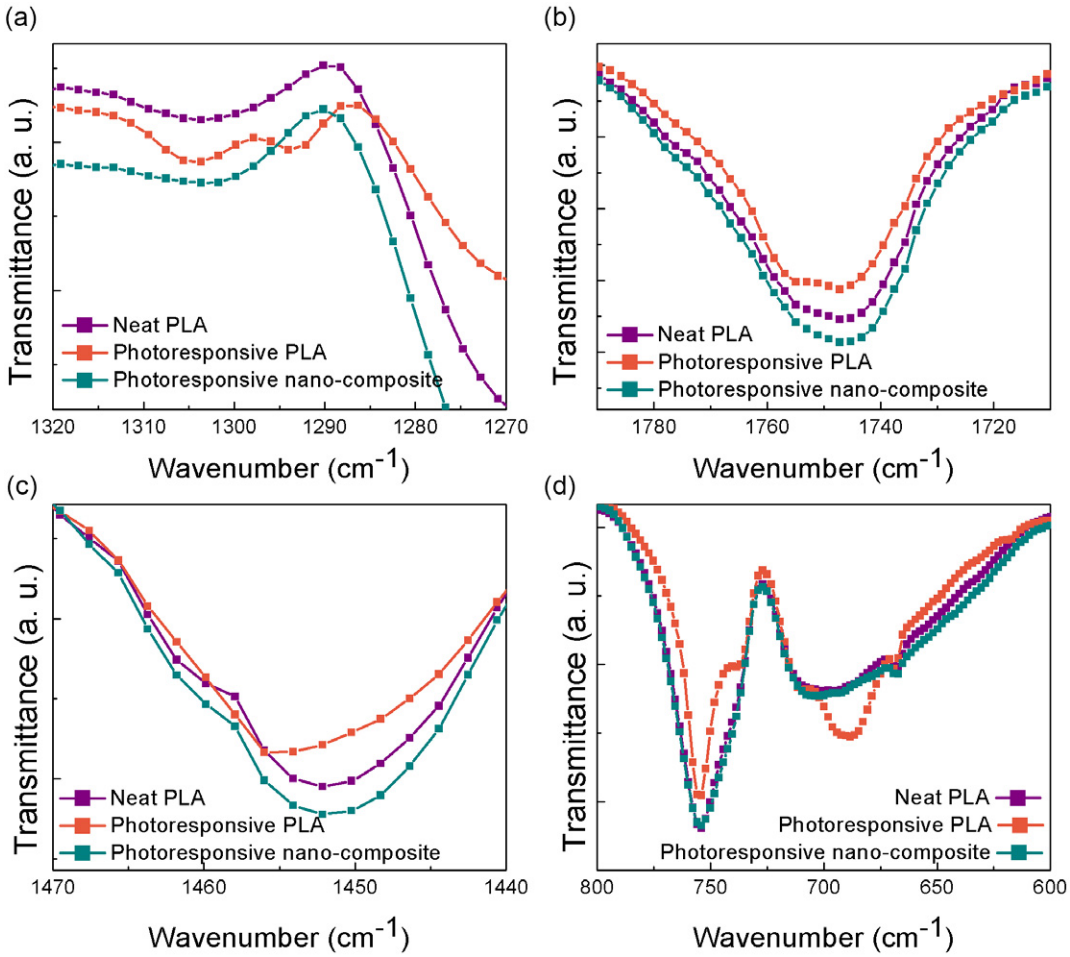


**Figure 4.** FTIR spectra of neat PLA, photoresponsive PLA and photoresponsive nano-composite: (*a*) from 1320 to 1270 $cm^{-1}$ (*b*) from 1790 to 1710 $cm^{-1}$ (*c*) from 1470 to 1440 $cm^{-1}$ and (*d*) from 800 to 600 $cm^{-1}$.

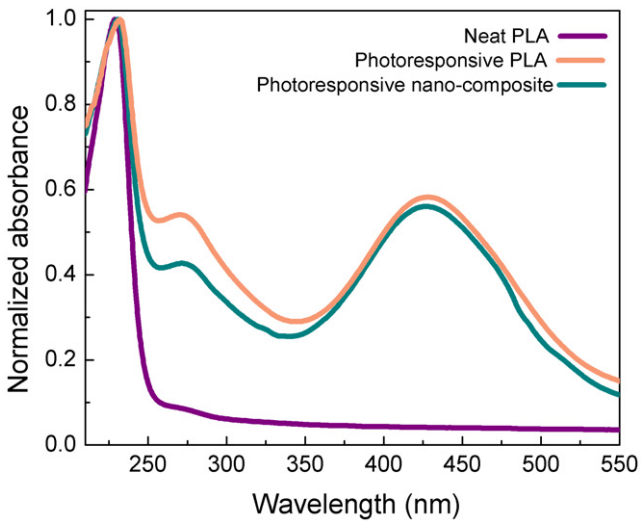


**Figure 5.** UV–Vis absorption spectra for neat PLA, photoresponsive PLA and photoresponsive nano-composite.

spectrum of photoresponsive PLA in the region around 273 nm evidencing the interaction MWCNTs-DO3.

As it was previously mentioned in the introduction section, from a thermodynamically point of view the *trans* isomer is the most stable. Successive *trans-cis-trans* configurations can be photoinduced when irradiating them with light of the proper wavelength. If the light is linearly polarized, all molecules having some component of their dipole moment in a direction parallel to the polarization axis will undergo the photoisomerization process. As a consequence, after exposing a film with an azo-dye to linearly polarized light, the molecules will gradually accumulate in the *trans* isomer with its dipole moment perpendicular to the polarization axis of the light. In this way, optical anisotropy can be photoinduced. When the light is turned off, thermal relaxation occurs and some degree of the anisotropy previously achieved is lost. The optical anisotropy, denoted as $\Delta n$, was derived from the equation:

$$I = I_0 \sin^2(\pi \Delta n d/\lambda), \quad (1)$$

where $I$ is the registered signal during the measurement, $I_0$ is the signal in the configuration of parallel polarizer/analyser (without a sample), $d$ is the thickness of the film and $\lambda$ is the wavelength of the probe beam.

Figure 6 shows curves of the induction and relaxation of the optical anisotropy behaviour with temperature for photoresponsive PLA (figure 6(*a*)) and photoresponsive nano-composite (figure 6(*b*)). In both cases, the response of the optical anisotropy at three different temperatures is

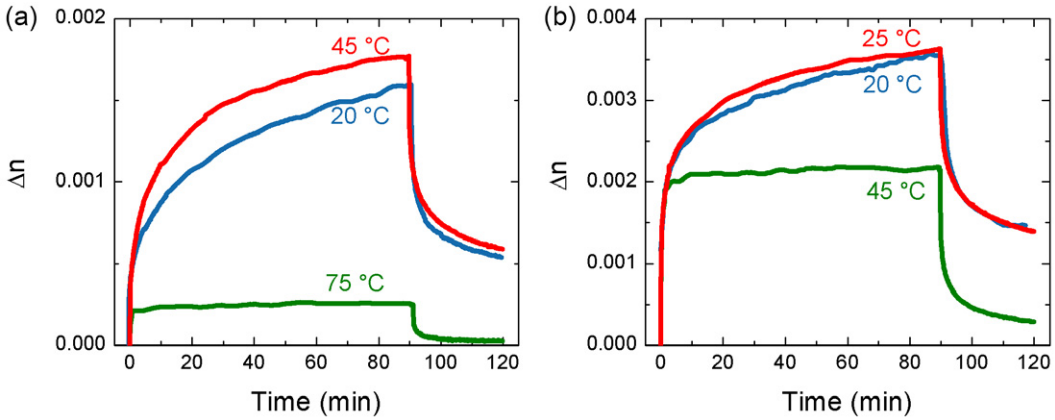


**Figure 6.** Photoinduced anisotropy curves at different temperatures for: (*a*) photoresponsive PLA at 20, 45 and 75 °C and (*b*) photoresponsive nano-composite at 20, 25 and 45 °C.

shown: the curve at the minimum measured temperature (room temperature), the curve at which there was maximum response and the curve at the maximum temperature beyond which no optical anisotropy could be detected. For all measurements, the pumping laser was initially turned on and the photoinduced anisotropy appears. Light exposure time was kept fixed for all measurements in order to avoid extra physical factors that could interfere with the present analysis. After 90 min of exposure, the laser was turned off and thermal relaxation occurred.

As it can be observed from figure 6, photoinduced anisotropy strongly depends on temperature. Moreover, the presence of MWCNTs modifies the rate at which the anisotropy grows as well as the maximum degree of reached optical anisotropy. In order to quantify this rate, a biexponential function was used to fit the growth in the anisotropy [21]:

$$\Delta n = A[1 - \exp(-k_f t)] + B]\,1 - \exp(-k_s t)]. \qquad (2)$$

In (2) the variable $t$ is the irradiation time and $A$ and $B$ are amplitudes related to two different processes characterized with rate constants $k_f$ and $k_s$, respectively. The 'fast' process, with rate constant $k_f$, is related to the photoalignment of azo-dye molecules and the 'slow' process, with rate constant $k_s$, is related to the accommodation of polymer chains. When comparing the curves for a given temperature results show that the addition of MWCNTs fastens the alignment of DO3 molecules [14]. Results are summarized in table 1; the values of $k_f$ for both materials are shown at two different temperatures. In the table, $T_{mr}$ is defined as the temperature at which the induced optical anisotropy is maximum and $T_{lim}$ is defined as the maximum temperature beyond which no optical anisotropy could be detected. Particularly, at the temperature at which each material presents the highest photoinduced anisotropy, the rate constant $k_f$ for photoresponsive nano-composite is twice larger (0.74 $min^{-1}$) than that for photoresponsive PLA (0.37 $min^{-1}$).

In figure 7(*a*) the maximum degree of photoinduced anisotropy as a function of temperature for both materials is shown: photoresponsive PLA and photoresponsive nano-composite. Usually, many polymer properties and its dependence with temperature are visualized as a function of the difference between the temperature of the experiment and the $T_g$ of the material. Taking this into account, in figure 7(*b*) the maximum degree of photoinduced anisotropy is plotted against the temperature difference $T - T_g$.

**Table 1.** Values of $k_f$ for photoresponsive PLA and photoresponsive nano-composite at $T_{mr}$ and $T_{lim}$.

| | $k_f$ for photoresponsive PLA ($min^{-1}$) | $k_f$ for photoresponsive nano-composite ($min^{-1}$) |
|---|---|---|
| $T_{mr}$ | 0.37 | 0.74 |
| $T_{lim}$ | 1.85 | 2 |

As can be seen from figure 7, photoresponsive PLA exhibits two different behaviours for the range of explored temperatures: the optical anisotropy grows to a maximum value and then it decreases. This can be understood if one considers that there are two competing processes involved in the photoalignment of azo-dyes doped polymers. On one hand, successive photoisomerization processes lead to the alignment of azo-dye molecules. On the other hand, thermal relaxation has an opposite effect, leading to the misalignment of molecules [22]. These two competing effects may explain the fact that the maximum degree of photoinduced optical anisotropy was reached at 45 °C for photoresponsive PLA. It is already known that a minimum size of the local free volume is needed for photoisomerization to occur [23, 24]. As temperature increases from 25 to 45 °C the volume in which the azo-dye molecules may undergo photo-orientation processes also increases until reaching a distribution of free volumes in which the degree of optical anisotropy becomes maximum. After 45 °C, the free volume of photoresponsive PLA dramatically increases ($T_g \sim 59$ °C) and so DO3 molecules have higher mobility. Additionally, thermal agitation increases and some degree of anisotropy is lost. As a result, thermal agitation dominates over the alignment of DO3 molecules for temperatures above 45 °C in photoresponsive PLA.

For the photoresponsive nano-composite the behaviour of its maximum optical anisotropy versus temperature is similar to photoresponsive PLA: there is a maximum optical response for a given value of temperature. This behaviour could be

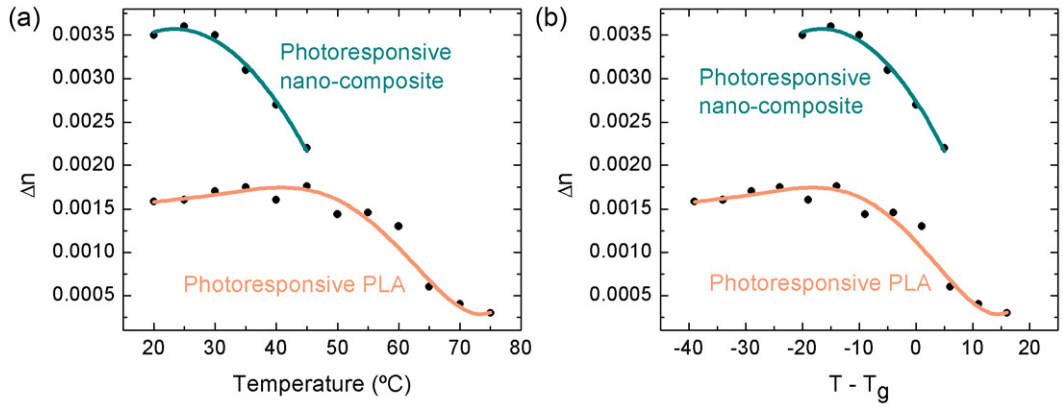


**Figure 7.** Temperature dependence for the optical anisotropy reached after 90 min of irradiation. The upper curves correspond to photoresponsive nano-composite and the lower to photoresponsive PLA. Solid lines are for guiding the eye. (*a*) Optical anisotropy versus temperature. (*b*) Optical anisotropy versus temperature difference with the $T_g$ of each material.

explained taking in mind the existence of the already mentioned competing processes. Moreover, the results can be compared considering the $T_g$ of each material. As observed from figure 7(*b*) the maximum of the optical anisotropy was obtained 15 °C below their $T_g$ for both photoresponsive materials. For both materials, the photoinduced optical anisotropy decreases for temperatures above their respective $T_g - 15$ °C.

When comparing the curves for the different photoresponsive materials depicted in figure 7 it can be observed that the degree of optical anisotropy for photoresponsive nano-composite was higher than for photoresponsive PLA for all the temperature range. Particularly, the addition MWCNTs increased the optical anisotropy at room temperature in a 100%. In photoresponsive nano-composite, the explanation of its higher degree of photoinduced anisotropy can be understood as a combination of two effects. On one hand, due to their electronic structure, both MWCNTs and DO3 molecules interact via $\pi$–$\pi$ stacking [16]. This interaction would keep DO3 molecules in the neighbourhoods of MWCNTs preventing them from being confined within the PLA chains and thus changing the packing density of azo-dye molecules [14]. On the other hand, the presence of MWCNTs introduces steric hindrance changing the PLA chains arrangement and generating a larger mean value in the free volume size distribution. This can be related to the fact that photoresponsive nano-composite has a lower $T_g$ with respect to photoresponsive PLA, which enables DO3 molecules to increase their mobility. As a consequence, an increment in the optical anisotropy and its growth rate (as mentioned in the description of figure 6) is obtained. Another point to note about the results shown in figure 7 is that the photoresponsive nano-composite reaches its maximum optical anisotropy around room temperature.

## 4. Conclusions

The optical response of a biodegradable matrix (PLA) containing an azo-dye (DO3) can be remarkably enhanced by the addition of a small amount of MWCNTs. This behaviour occurs for all the studied temperature range. In particular, at room temperature, the optical anisotropy for the photoresponsive nano-composite was 100% larger than that obtained for the material without carbon nanotubes. In both materials, photoresponsive PLA and photoresponsive nano-composite, the temperatures at which the maximum optical anisotropy occurs are around 15 °C below their respective glass transition temperatures. Moreover, when the photoinduced anisotropy curves are compared, the growth rate of the optical anisotropy for the material with MWCNTs is twice higher than the one for the material without MWCNTs. These results were discussed considering the interactions among DO3, MWCNTs and PLA and the packing density of the dye into the polymer chains. The enhancement of the optical anisotropy and its growth rate render the photoresponsive nano-composite a very attractive material for the future development of biodegradable photonic devices.

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