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On the Stability and Degradation of DNA Based Thin Films

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In this paper recent studies showing the influence of light, temperature and chemical environments on the stability of pure and functionalized collagen and DNA based thin films are presented and discussed. The results are compared with similar studies performed on synthetic polymers.

Keywords Biopolymers; chemical degradation; DNA; kinetics parameters; photodegradation

Introduction

Recently an important accent in material research is put on the use of ecofriendly, and renewable materials, such as DNA and collagen. These two biopolymers are extracted from biological waste and their resources are practically unlimited. Several electro – optic devices based on these biopolymers were already demonstrated. They represent an attractive alternative to common, synthetic organic polymers used presently in photonics [1–4]. However the practical use of these materials as active or passive elements requires extensive material and optical characterization of DNA and collagen as well as their functionalization with active molecules to get the properties required for practical applications: linear optical, thermal, photoconducting, nonlinear optical properties. Before being applied they need to undergo a careful and appropriate characterization of their physical and chemical properties. One of the important parameter is the photo-, thermal and chemical stability. Also in view of the targeted applications many additional processing techniques are to be used to made DNA and collagen of sufficient optical quality suitable for photonic and biotronics devices. Collagen and DNA are molecules with relatively weak π electron conjugation, thus limited NLO properties. Therefore they require to be

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functionalized with appropriate molecules in order to become photosensitive in visible and in infrared, as it is currently done with synthetic polymers for application in photonics. Therefore not only the stability of DNA and collagen, considered as matrix for active molecules, is important, but also that of functionalizing, photoactive molecules embedded in. In this paper we describe the results of our studies of the photo- and thermal stability of DNA and collagen films doped with organic dyes and compare them with that of synthetic polymers, doped with the same molecules. The photostability of these materials in UV range is also studied.

Materials and Methods

The thermal and photo degradation studies were performed on DNA-CTMA complex, doped with Rhodamine 590 (Rh) and disperse red (DR1). The chemical structures of these chromophores are shown in Figure 1. Rhodamine 590 is a well known photoluminescent dye, used in dye lasers and in organic light emitting diodes (OLED's) [5], while DR1 is a quasi 1D charge transfer (CT) dye used in electro-optic devices [6,7].

The spectroscopic UV-VIS studies were performed with the JASCO UV-VIS-NIR spectrophotometer, model V 670.

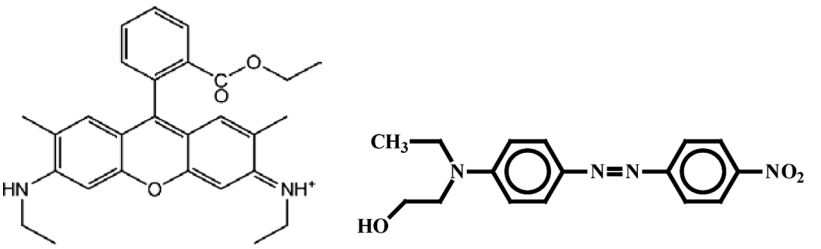
Thin films of studied compounds were obtained by spin coating of solutions on the carefully cleaned glass substrates. Spectroscopic grade solvents were used. The spin coating machine was Laurell – Model WS – 400B –6NPP/LITE. The dyes were commercially available once: Rhodamine 590 from Exciton and DR1 from Aldrich. They were additionally purified by recrystallization and liquid chromatography. DNA was obtained from Chitose Institute of Science & Technology, Japan, where it was extracted from the salmon waste.

The guest-host systems at different concentrations of dye molecules were prepared in buthanol. The kinetic parameters were calculated following the procedure described in Ref. [8].

Results and Discussion

Room Temperature Chemical Degradation

The degradation studies were performed on thin films, deposited on very clean glass substrates. Figure 2 shows, the variation of the thin film optical absorption spectrum with time t for a thin film of DNA CTMA, doped with Rh at 20%. The observed



(a) (b)

Figure 1. Chemical structures of Rhodamine 590 (a) and Disperse Red 1 (b).

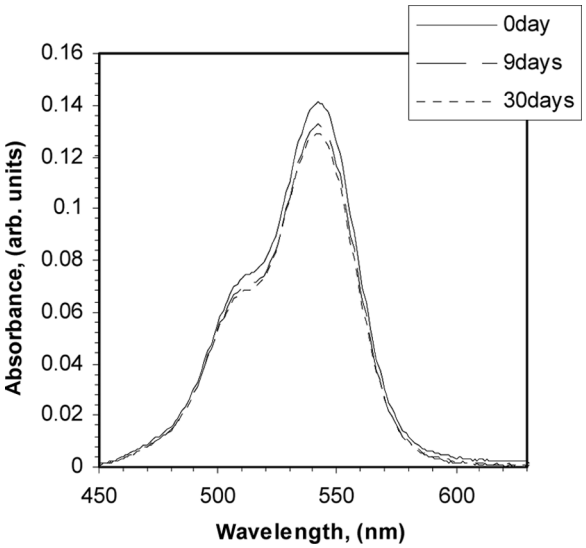


Figure 2. Variation of the optical absorption spectrum of DNA – CTMA – Rhodamine 20% thin film as function of time (in days).

decrease of the optical density A(t) is caused by the degradation. The data were fitted using the following equation:

$$\ln A(t) = -kt + \text{const} \tag{1}$$

It results from the assumption that the degradation follows the single exponential first order kinetic law. In Eq. (1) A is the optical density at the maximum absorption wavelength λ_{max}, t is the time and k is the kinetic constant. The fitted results for k parameter for the studied films are collected in Table 1.

Table 1. Room and high (85°C) temperature kinetic degradation constant of Rhodamine 590 at different matrices

Host material	Kinetic degradation constant ($mins^{-1}$) at room temperature	Kinetic degradation constant ($mins^{-1}$) at 85°C
DNA	2.78×10^{-6} (5% Rh)	6.68×10^{-6} (5% Rh)
DNA + CTMA	1.11×10^{-6} (20% Rh) (540 nm)	5.0×10^{-6} (20% Rh)
	1.18×10^{-6} (510 nm)	13.3×10^{-6}
	2.78×10^{-6} (10% Rh) (540 nm)	40.0×10^{-6} (10% Rh)
	2.57×10^{-6} (510 nm)	36.6×10^{-6}
	15.4×10^{-6} (10% DR1)	55×10^{-6} (10% DR1)
	17.2×10^{-6} (20% DR1)	63×10^{-6} (20% DR1)
DNA + PEG	5.57×10^{-6} (5% Rh)	51.7×10^{-6} (5% Rh)
Collagen	2.09×10^{-6} (5% Rh)	35×10^{-6} (5% Rh)
Collagen + PEG	1.05×10^{-6} (5% Rh)	55×10^{-6} (5% Rh)
PC	3.13×10^{-6} (5% Rh)	11000×10^{-6} (5% Rh)
PEG	9.03×10^{-6} (5% Rh)	89000×10^{-6} (5% Rh)

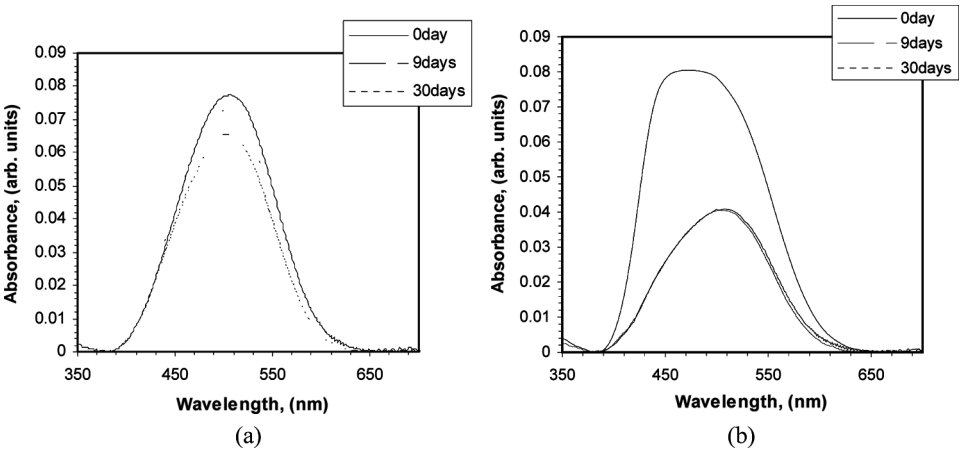


Figure 3. Variation of the optical absorption spectrum of DNA – CTMA – DR1 (10% – a; 20% – b) thin film as function of time (in days).

The degradation kinetics of DNA-CTMA based thin films, doped with DR1 chrmophore depends on the chromophore concentration due to the possible intercalation of the chromophore (for more details see Popescu *et al.* [9]). The study shows that the DR1 molecules which are not intercalated degraded faster (cf. Fig. 3) than the intercalated ones.

Chemical Degradation at Elevated Temperature (85°C)

We have also studied the degradation of doped thin films at elevated temperature (85°C), below the DNA degradation temperature (230°C), in order to check the influence of heating on the stability of doping chromophores. The studied films were heated to 85°C, kept at this temperature and the absorption spectra were monitored as function of time. They are shown in Figures 4 and 5 for the studied thin films. The temporal variation of the absorbance A(t) for a given material was also fitted with Eq. (1) and the obtained kinetic degradation constants are listed in Table 1 too and compared with the room temperature data.

The data show that:

1. In all matrices the Rhodamine 590 dye is unstable at room temperature;
2. The kinetic constants at 85°C are larger than at room temperature, as expected. A one order increase is observed. Anyway this increase is smaller than in case of the two synthetic polymers studied (almost four orders of magnitude, cf. Table 1)
3. The increase of the Rhodamine concentration in DNA – CTMA based thin films leads to the decrease of the degradability while the stability of DNA – CTMA – DR1 thin films does not depend on concentration.

Room Temperature Photo Degradation (Under UV Illumination)

The photodegradation measurements were performed using a commercial Vilber Urmat apparatus with two irradiation sources: UVA at 365 nm and UVB at 312 nm. The illumination intensity was of 5.5 mW/cm^2 for UVA and 2.5 mW/cm^2

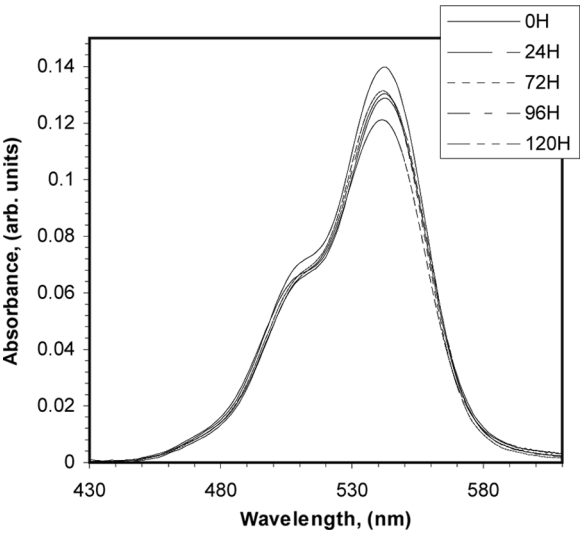


Figure 4. Variation of the optical absorption spectrum of DNA – CTMA – Rhodamine 20% thin films as function of time (in hours) at 85°C.

for UVB. It means that the ratio of photons illuminating the sample at UVA to that at UVB $n_{UVA}/n_{UVB} \approx 2.6$.

In the beginning the thin films degradation at 312 nm was measured. Then, for another set of thin films the degradation at 365 nm in order to see the difference. The observed variations of optical absorption spectra are shown in Figures 6 and 7. We present only the absorption spectra variations for the case when illuminating at 312 nm. The variations are very similar for the other case (at 365 nm). The measured kinetic photodegradation parameters are listed in Table 2.

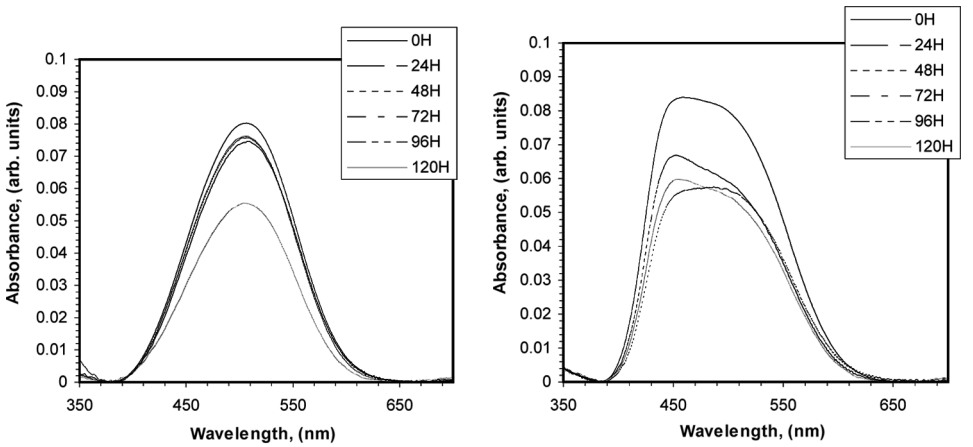


Figure 5. Variation of the optical absorption spectrum of DNA – CTMA – DR1 (10% – a; 20% – b) thin films as function of time (in hours) at 85°C.

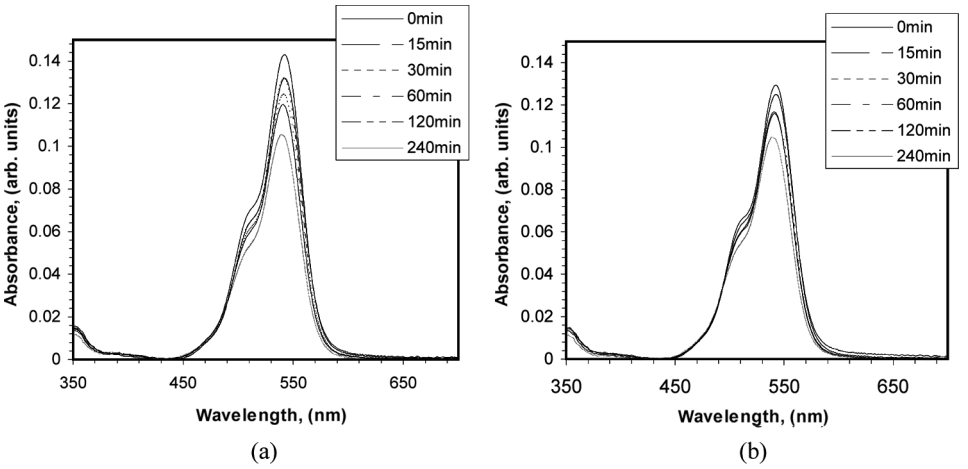


Figure 6. Room temperature variation of the optical absorption spectrum of DNA – CTMA – Rhodamine (10% – a; 20% – b) thin film as function of time (in mins) under UV irradiation (312 nm).

First of all, when one looks at the variation of the optical absorption spectra one observes not only a decrease of thin films optical density but also a shift of the Rhodamine absorption band towards the higher energies (blue shift). It means that the optical gap is increasing and the π electron conjugation decreases, probably due to the opening of the C=C double bonds. It shows that the mechanism behind photodegradation is different than in the case of thermal degradation, described previously. The photodegradation is much faster than the thermal degradation: the corresponding kinetic degradation parameters are about three orders of

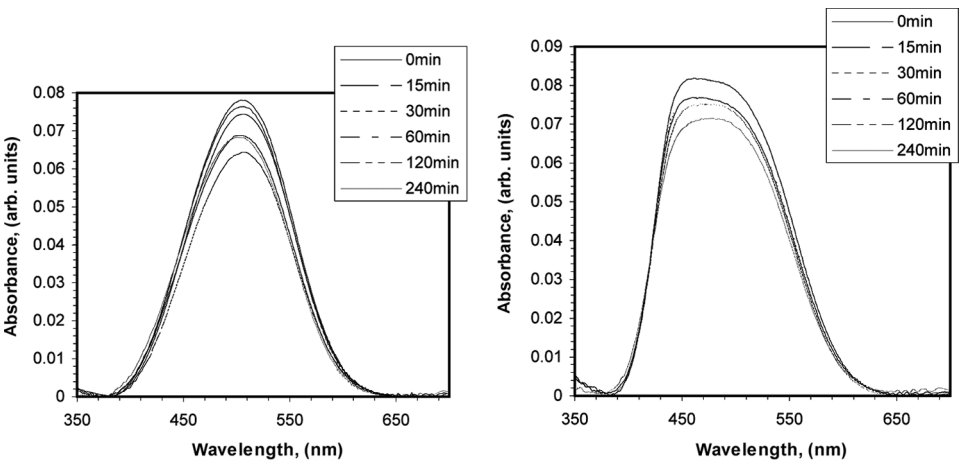


Figure 7. Room temperature variation of the optical absorption spectrum of DNA – CTMA – DR 1 (10% – a; 20% – b) thin film as function of time (in mins) under UV irradiation (312 nm).

Table 2. Room temperature kinetic degradation constant of Rhodamine 590 at different matrices and under UV illumination

Host material	k ($mins^{-1}$) at room temp. (under illum. of 312 nm)	k ($mins^{-1}$) at room temp. (under illum. of 365 nm)	k ($mins^{-1}$) at room temp. (under illum. of both UV sources 312 and 365 nm)
DNA	3800×10^{-6} (5% Rh)	2000×10^{-6} (5% Rh)	3400×10^{-6} (5% Rh)
DNA + CTMA	1000×10^{-6} (10% Rh) (540 nm)	2300×10^{-6} (10% Rh)	
	1100×10^{-6} (510 nm)	2000×10^{-6}	
	800×10^{-6} (20% Rh) (540 nm)	1900×10^{-6} (20% Rh)	
	900×10^{-6} (510 nm)	1900×10^{-6}	
	880×10^{-6} (10%DR1)	2200×10^{-6} (10%DR1)	
	1000×10^{-6} (20%DR1)	1800×10^{-6} (20%DR1)	
DNA + PEG	6100×10^{-6} (5% Rh)	4100×10^{-6} (5% Rh)	5000×10^{-6} (5% Rh)
Collagen	1600×10^{-6} (5% Rh)	2200×10^{-6} (5% Rh)	3300×10^{-6} (5% Rh)
Collagen + PEG	3330×10^{-6} (5% Rh)	2100×10^{-6} (5% Rh)	2290×10^{-6} (5% Rh)
PC	$8900^{1} \times 10^{-6}$ (5% Rh)	2800×10^{-6} (5% Rh)	4500×10^{-6} (5% Rh)
	$1900^{2} \times 10^{-6}$	1000×10^{-6}	
PEG	5000×10^{-6} (5% Rh)	4500×10^{-6} (5% Rh)	4600×10^{-6} (5% Rh)

magnitude larger than at room temperature. The kinetic photodegradation constants are of the same order of magnitude for all studied matrices. We observe also that in the case of PC (Poly bis(phenol A carbonate)) matrix there are two degradation processes described by two parameters k_1 and k_2.

Conclusions

From the present study the following conclusions can be drawn:

- In all matrices the Rhodamine 590 dye is unstable at room temperature;
- The kinetic degradation depends on the composition:
  - the decay is the slowest one in DNA matrix and the fastest in PC;
  - addition of PEG (poly ethylene glycol) to DNA decreases the chromophore stability but increases in the case of collagen;
- The kinetic constants at 85°C are larger than at room temperature, as expected. A one order increase is observed in the case of DNA – CTMA based thin films. Anyway this increase is smaller than in he case of two synthetic polymers studied (almost four orders of magnitude);
- There is a possible thermal and/or photo crosslinking between collagen, PEG and Rhodamine;
- The degradation is faster under UVB illumination than under UVA illumination;
- The photodegradation is much faster than the thermal degradation: the corresponding kinetic degradation parameters are about three orders of magnitude larger than the corresponding parameters for the room temperature degradation;
- The contact angle measurements (for more details see R. Popescu *et al.* [9]) corroborated with the constant rate calculus show that the degradation is slower for the hydrophobic films. This may be due to the protective role of such surface against moisture (ambient water present in air);
- It seems also that under the UV illumination a chemical reaction between collagen, PEG and rhodamine takes place. Here PEG acts as a cross-linking agent. A thermal cross linking process in collagen was observed by Zimmermann *et al.* [10] a time ago already.

Acknowledgments

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