HYDROPHILIC / HYDROPHOBIC CHARACTER OF SOME BIOPOLYMER BASED THIN FILMS

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In the last period, in the electronics, optoelectronics and other industries, more and more materials based on biopolymers have been developed, especially using DNA as matrix. One of the problems often encountered is related to the hydrophilicity of the material. In this paper are presented results on the hydrophilic/hydrophobic character of thin films based on biomaterials (DNA, DNA-CTMA, Collagen) functionalized with various chromophores. This study is particularly important for applications in the electronics/ photonics, where the properties of these materials may be influenced by the amount of adsorbed/absorbed water.

Keywords: biopolymer, thin films, hydrophilic-hydrophobic character, contact angle

1. Introduction

In order to valorize the renewable sources, recent researches were turned towards biomaterials extracted from waste materials.

Deoxyribonucleic acid (DNA) is certainly one of the most interesting materials, due to its special properties determined by the construction of the double helix discovered and described in 1953 by James Watson and Francis Crick [1]. At the same time, DNA is biodegradable and usually is extracted from the waste resulted in the food processing industry. In our days, DNA materials and some surfactants are used for many interesting applications like organic light emitting diodes (OLED) [2, 3, 4], lasers [5] or in nonlinear optics field [6, 7, 8].

An intrinsic property of biomaterials, and in particular of DNA, is the strong affinity to water. Naturally, DNA exists in aqueous medium and contains an important amount of bound water. Because the water evaporates slowly and it has high surface tension, its utilization as a solvent in thin films preparation is quite difficult.

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In order to improve thermal and mechanical properties of DNA based materials is necessary to functionalize DNA with a surfactant [9]. In this way, a complex which is stable up 220 ^{o}C, insoluble in water and soluble in organic solvents, particularly alcohols, with good mechanical properties and film formation ability is obtained. This functionalization is realized by replacing sodium Na^{+} counter ion of DNA, which is a negatively charged anionic polyelectrolyte [10], by ionic liquids [11] or amphiphile cations [12]. In the second case, Ogata and coworkers from Chitose Institute of Technology [12] used several cationic surfactants which react with DNA by electrostatic forces and they succeeded in making several stable complexes using surfactants, such as: cetyltrimetylammonium (CTMA) [13] and benzyldimethylammonium (CBDA) [14].

Materials used in electronic and photonic industries must be in form of thin films of micron or nano thickness.

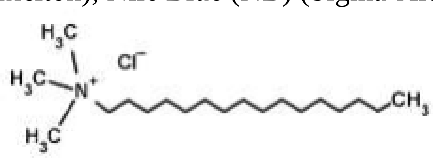
In this context this paper aims at studying the surface characteristics of thin films quantified by hydrophilic / hydrophobic balance, which can provide useful information about quality and stability evaluation of thin films for different applicative conditions of optical devices in which they are used.

2. Materials and methods

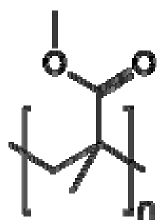
By spin-coating technique DNA, DNA-CTMA, Collagen and PMMA based thin films were prepared on very clean glass substrate [15], by varing the rotation speed, type and chromophore concentration, molar mass of biopolymer, matrix and concentration of solutions.

Deoxyribonucleic acid, purity of 96%, was purchased from Ogata Research Laboratory, LTD., Chitose, Japan. Collagen was obtained from bovine derma in National R&D Institute for Textile and Leather, Division ICPI – Collagen Dept., Romania and poly(methyl metacrylate) (PMMA) was acquired from Sigma-Aldrich.

In order to obtain a material soluble in organic solvents, DNA was functionalized with cetyltrimetylammonium (CTMA) (Fig. 1) of purity 99%, purchased from Acros, Organics. The chromophores used, with chemical structures presented in fig. 1, were: Disperse Red (DR1) (Sigma-Aldrich), Rhodamine 590 (Rh) (Exciton), Nile Blue (NB) (Sigma-Aldrich).



(a)



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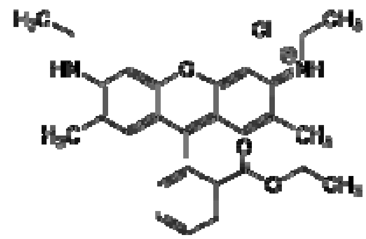

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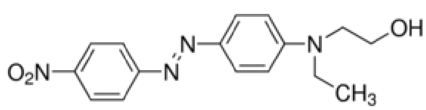

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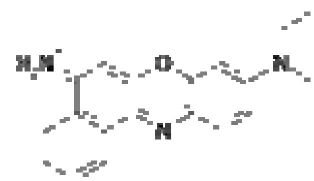

(e)

Fig. 1 Chemical structures of CTMA (a), PMMA (b), Rhodamine 590 (c), Disperse Red 1 (d), Nile Blue (e)

A series of thin films based on DNA, DNA-CTMA, Collagen and PMMA was analyzed in terms of hydrophilic/hydrophobic balance variation depending on the film composition and the nature and the concentration of the chromophore used.

The hydrophilic/hydrophobic character was determined by measuring the contact angle with a KSV Instruments commercial apparatus, model CAM 100.

3. Results and discussion

The surface properties, adherence/adhesion and wettability of thin films prepared are quantified by measuring the contact angle.

The contact angle is obtained as the result of adhesive and cohesive forces. As the tendency of a drop to spread out over a flat, solid surface increases, the contact angle decreases. Thus, the contact angle provides an inverse measure of wettability.

Table 1 presents the obtaining conditions for thin films preparation for DNA – Rh (Rhodamine) 5% and DNA-CTMA-NB (Nile Blue) 5% materials and the contact angle values measured for these thin films.

One may consider that the deviation value represents a measure of film homogeneity. In most cases were obtained deviation values below ± 3 degrees. High values were observed in the case of thin films DNA-Rh 5% obtained at higher rotation speed. It could be concluded that all the other films exhibit relatively homogeneous surfaces, with a good optical quality.

DNA-Rh based thin films analysis leads to the conclusion that there are two ranges of contact angle: one at about 58 degrees for the first two working speeds and another at about 63 degrees for higher working speeds.

In the case of DNA-CTMA –NB 5% thin films the average values of contact angle are between 51 and 55 degrees, suggesting that, for this system, the working speed does not significantly influence the surface properties.

Table 1

Average values of contact angle for thin films prepared by spin-coating at different rotation speeds in both steps (spreading and drying)

Sample	Working conditions for obtaining thin films	Contact angle, degrees
DNA -Rh5%	40s x 500rpm + 60s x 1000rpm	58.86 ± 3.99
	40s x 1000rpm + 60s x 1500rpm	58.54 ± 1.91
	40s x 1500rpm + 60s x 2000rpm	63.22 ±0.92
	40s x 2000rpm + 60s x 2500rpm	63.97 ± 8.98
	40s x 2500rpm + 60s x 3000rpm	63.85 ± 5.46
DNA -CTMA-NB 5%	40s x 500rpm + 60s x 1000rpm	52.75 ± 1.31
	40s x 1000rpm + 60s x 1500rpm	51.61 ± 0.78
	40s x 1500rpm + 60s x 2000rpm	54.76 ± 1.82
	40s x 2000rpm + 60s x 2500rpm	54.31 ± 0.29
	40s x 2500rpm + 60s x 3000rpm	52.99 ± 1.02

Figures 2-4 presents the results obtained for some thin films. These figures reveal information about the nature of intermolecular interactions between the matrix and the dopant. It can be observed that the largest contact angle is registered in the case of thin films DNA – CTMA – Rh 20% (fig. 2).

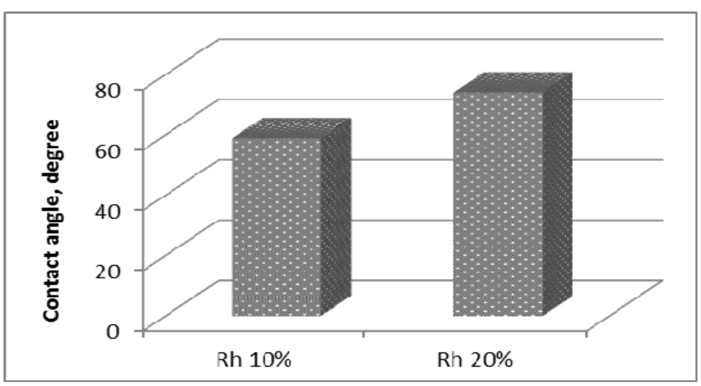

Fig. 2 Contact angle results for DNA-CTMA thin films doped with Rhodamine (Rh)

At the same time, the contact angle depends on the chromophore concentration for the films with Rhodamine (Rh), while variation of contact angle for materials obtained by doping with Disperse Red 1 (DR1) is almost independent of the chromophore concentration, for a given matrix [16] (fig. 3).

Replacing DNA with another biopolymer leads to smaller values of contact angles, these materials being more hydrophilic. This could be explained by the fact that DNA-CTMA is more hydrophobic than collagen (fig. 3).

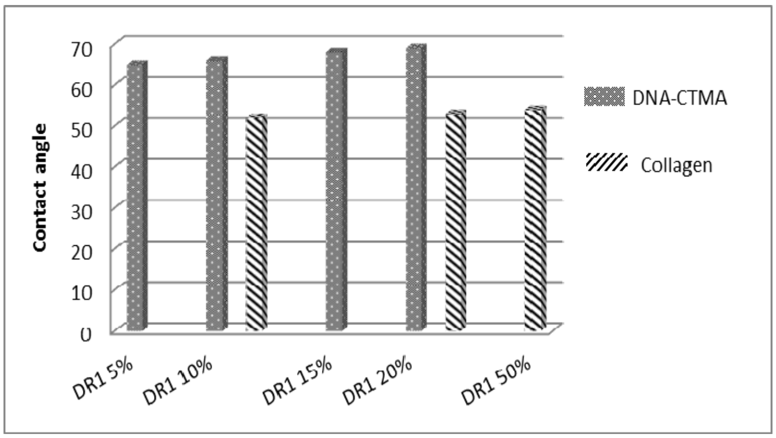

Fig. 3 Contact angle results for DNA-CTMA and Collagen thin films doped with Disperse Red 1 (DR1)

Fig. 4 presents the results obtained for the DNA, DNA-CTMA and Collagen thin films doped with Nile Blue (NB) by comparing with those obtained for thin films based on a synthetic polymer (PMMA). As expected, films based on DNA reveal low contact angle values as DNA and NB are both hydrophilic.

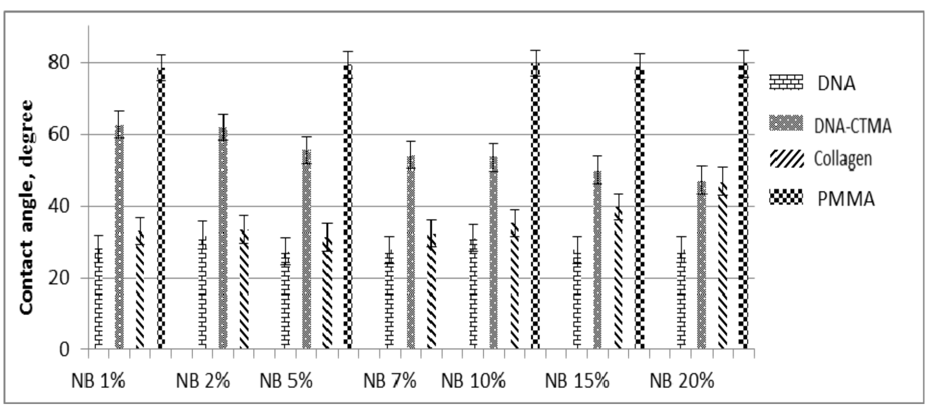

Fig. 4 Contact angle results for DNA, DNA-CTMA, Collagen and PMMA thin films doped with Nile Blue (NB)

The increasing hydrophilic character of DNA-CTMA based thin films with the increase of NB concentration is due to ionic characteristics of chromophore, which favors the water molecules retention. It is worth to notice that in all cases the relative standard deviation is less than 3 degrees, suggesting a good uniformity of surface films and the fact that chromophore concentration has no influence on the contact angle values (fig. 4).

In the case of Collagen-NB (fig. 4) it can be also observed a good homogeneity of the surface. The contact angle value is maintained at relatively low values, 31-33 degrees, showing the hydrophilic character up to a concentration of NB 7%. Dopant concentration higher than 7% leads to an increase of contact angle.

The highest values of contact angle were obtained in the case of PMMA – NB thin films (fig. 4) (78 and 79 degrees), showing a hydrophobic character for these materials. This character is given by the matrix and the chromophore concentration does not significantly influence it.

In all cases, for a given matrix, the contact angle values were similarly when NB or DR1 was used as dopant. Dependence on the chromophore concentration was observed in the case of Rhodamine. This behavior could be explained by the dopant dimension. Small molecules like DR1 and NB, up to a certain concentration, could intercalate within DNA or semi intercalate in DNA-CTMA [16, 17], reducing in this way the probability of chromophore aggregation. Increasing the dopant concentration (> 10% NB for DNA-CTMA), the chromophores have no more space to intercalate, thus they form aggregates and since NB is hydrophilic, the hydrophilic character is increased.

Bigger chromophores like Rhodamine have no room to intercalate and even at low concentration they form aggregates which have hydrophobic character.

4. Conclusions

By comparing the values obtained on contact angle for all systems studied it can be noticed that, as expected, the lowest hydrophilic character was registered for synthetic polymer (PMMA), while the most powerful hydrophilic character was observed for DNA – NB and Collagen – NB.

Generally, DNA-CTMA based materials lead to more hydrophobic thin films as compared to DNA and Collagen based thin films.

DNA – CTMA – NB thin films presents a less hydrophilic character, especially at low concentrations and this is the area of interest for optical applications, because at concentrations of the chromophore over 5% the aggregation phenomenon could appear.

In conclusion, it could be appreciated that the optimum system selected for obtaining thin films with relatively better stability and appropriate optical properties is DNA – CTMA – NB 1-2%.

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