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OPTICAL AND SPECTRAL PROPERTIES OF SOME POLYMERIC MATERIALS WITH POTENTIAL APPLICATIONS IN BIOMEDICAL FIELD

- Thesis abstract -

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INTRODUCTION

Due to the special physical properties, the polymeric materials are used in many of high technology, the interest of researchers are currently giving rise not only in the industry (for the realization of optoelectronic devices or membranes), but also in medicine and pharmacology. In the majority of the applications, the macromolecular compounds come into contact with some external factors which may affect their characteristics and their stability with time. Thus, depending on the structure and chemical composition, the polymers can interact differently with electromagnetic radiation, which is why it requires a careful research of its optical and spectral properties.

The use of the polymeric materials in certain medical purposes (bacteria or cell cultures) requires the fulfillment of certain criteria regarding the color, clarity, transparency and refractive index. In addition, the assessment of the biocompatibility, cytotoxicity or of the antimicrobial character is a prerequisite to the application of polymers in biomedicine and biotechnology. For this reason, it is necessary the compatibilization of the characteristics induced by the supramolecular structure of the polymers with those of the physiological environments by considering the reactions at the cellular level and the reactions of acceptance / rejection and the damages on the biological environment they come in contact with. In addition to the structural complexity, the polymers involves the presence in their structure of some functional groups which allow the formation of hydrogen bonds and which, in turn, determines the geometrical conformation of the macromolecule (statistically ball, co-planar chain in zig - zag, helically chain) capable of forming ordered structures. In cases where ordering is not achieved, it can be interfered by modifying the surface through techniques that could assure the anisotropic character (e.g. friction with textile materials, laser irradiation or other lithographical methods). The transparent polymer films with oriented surfaces are used in tissue engineering for guided cell growth. Also, such materials are useful as the alignment layers of the liquid crystal having direct implication in the implementation of the liquid crystal displays (LCD).

On the other hand, in the release of medication the chirality is an important factor. Taking into account that the optical activity depends on the concentration of the active substance, it can be monitored either the kinetics of the drug release from one matrix without chirality, or the

dissolution / biodegradation dissolution of the chiral polymer allowed to distribute an active substance which does not rotate the polarization plane.

Based on these considerations, the paper highlights the importance of the spectral and optical properties in presetting the structure – properties correlation, referring in particular to the new polymer architectures, both in solid state and in solution, which were the subject of my own researches.

In this context, the thesis was focused on the analysis of optical and spectral properties of new polymeric materials, pursuing two lines of research:

- obtaining polyimide films having suitable transparence for applications as alignment layers for nematic liquid crystals, cell growth media or coatings with antibacterial activity;
- the development of some delivery systems stable to UV radiations and monitoring the active substance through the optical activity of the polymeric matrix.

Chapter 1 is a summary of the literature data on the basics of optical and spectral characteristics of the macromolecular compounds of importance for the two directions of investigation concerned:

- a description of the current state of research is made, related to the adaptation techniques of the polymeric materials morphology for biomedical purposes, either by structuring (UV irradiation or ion beam fascicle, laser ablation, textile friction), or by functionalization (chemical treatment or in plasma);
- are shown some aspects related to the biocompatibility and optical activity of some materials intended for drug release.

In **Chapter 2** are presented the methods of obtaining and processing the synthesized materials, establishing the experimental conditions for their characterization by various physical methods. Two classes of polymers were selected for study. In the first category are the polyimides due to their thermo-mechanical resistance, transparency, allowing easy adjustment of the morphology and facile viewing of the cells / micro-organisms in contact with the sample. In the second category are included the cellulosic derivatives due to their optical characteristics (transparency and optical activity) and their good biocompatibility, which recommends those as matrices for active substances release. It have been used a variety of techniques for surface modification of polymeric films, and the characterization methods used allowed the determination of the optical, spectral, mechanical, morphological, rheological and biological characteristics.

The studies shown in **Chapter 3** are based on a series of semi-aliphatic amorphous polyimides pursuing the structure effect over the absorption limits and over the morphology and trying a correlation in order to determine their impact over the cytotoxicity. Thus, it has been shown that:

- By combining the units of dianhydride with small polarizability and the flexible groups of aromatic diamines is reduced the base chain conjugation of the samples and are decreased the refractive index, the extinction coefficient and the dielectric constant;
- the transparency of the samples containing methylene and ethylene groups into the diamine fragments is about 90% in the visible and near-infrared;
- the reducing of the complex with charge transfer is generating the increasing of forbidden band energy of the optical processes of over 3.26 eV;
- the structural disorder in the studied polyimides increases with the rigidity of the diamine segment and it determines the increase of Urbach and Tauc energies;
- the cytotoxicity was determined by polarizing microscope observations (for different incubation periods), but also by using the standard spectral method MTT. For all the experimental conditions applied, the polyimide film comprising ethylene groups in the diamine fragment indicates a good proliferation of the fibroblasts derived from the dermis of laboratory mice, being a good support for cellular growth.

Chapter 4 deals with the structuring of a photosensitive polyimide film by laser microprocessing with two fluences (89 and 244 mJ/cm^2) and different numbers of pulses, monitoring the impact of morphological changes on the hemocompatibility. As a result, it was found that:

- the polymer is prepared by polycondensation reaction in the solution of the photosensitive BTDA dianhydride with aromatic diamine DDM;
- the obtained structure is analyzed by FTIR spectroscopy, which confirms fully transformation of the polyamideimide acid into the corresponding polyimide structure;
- the morphology data shows the appearance of certain cone type structural configurations with different sizes depending on the laser exposure conditions. For 89 mJ/cm^2 there is a tendency for arranging the cones, with a period of 200, 150, 260 nm for 5, 10 and 30 laser pulses. By increasing the laser fluence to 244 mJ/cm^2, the cones from the polyimide surface becomes more evenly distributed and there it cannot be observed a tendency for ordering or packing;
- the polymer surface umectability changes depending on the laser processing conditions. During ablation of the film of poly (BTDA-DDM), it occur a condensation process of the

carbon, a process which is more or less pronounced depending on irradiation conditions.

- it was noticed that the structuring of the oriented surface at 89 mJ/cm^2, 5 and 30 pulses, is useful for making flexible layer for cellular growth;
- from the processing conditions there is a large difference in cones sizes for 10 laser pulses for both fluently. As a result, there have been selected for testing the hemocompatibility samples with the same number of pulses;
- the film non irradiated and the one exposed to 89 mJ/cm^2 does not modify the morphology of the blood cells and does not favors the thrombosis processes, aspect which shows a good hemocompatibility of the photosensitive polyimide film, both before treatment and after laser exposure.

In **Chapter 5** it is aimed to determine the balance between the flexibility and the chains intertwining on the deformation response by textile friction of some co-polyimide films containing oxadiazole and used as transparent alignment layers for liquid crystals. The investigations showed that:

- all the samples show a complex flow behavior, form from a shear thinning region and a Newtonian one, and their order depends on the chemical structure of the polymer;
- the viscosity dependence on the polymer concentration at constant shear speed can be described by a power law whose coefficients indicate the presence of interpenetration between polymer chains according to the polymeric solutions theory in semi-dilute – concentrated domain;
- the flexibility and molecular weight of the investigated polyimides are reflected by the consistency index. In to the dependence of the shear modulus by the frequency a smaller plateau is observed, indicating that the chains interlocking enhances the elastic component of the material;
- the good transparency of the films in the visible domain recommends them to be useful for alignment layers of the nematic liquid crystals. For this reason, the samples are processed by rubbing with textile materials in order to induce the surface orientation;
- the microgrooves created on the polymeric films surface are deeper when the chains interpenetration degree is smaller and the friction is made with diacetate velvet of cellulose, V_{CD}, compared with the cotton one, V_C;
- the effect of the textile fiber on the alignment properties of the co-polyimides was tested with 5CB by microscopy observing the highest contrast in the order in witch is varying the chains intertwining degree: PI1> PI2> PI4> PI3;
- the orientation is more uniform, especially when friction is done with V_{CD}. Therefore,

these polymers with imide structure are good candidates for applications such as the alignment layer for LCD devices.

Chapter 6 presents the optical properties of some polymeric structures with siloxane sequences. There have been synthesized two statistical co-polyimides with new structures from low polarizability dianhydrides and diamines with siloxane sequences and ethereal bridges. The study conducted shows that:

- the introduction of fluorinated, alicyclic and siloxane groups into the polymer base chain has a significant impact on the optical properties: it decreases the chain conjugation and the refractive index;
- the samples transparency is 90% in the 650-1100 nm domain. The fluorinated co-polyimides has a higher energy of the forbidden band (3 eV) resulting a lower probability of optical transitions and therefore better transparency;
- the smoother microstructure leads to lower values of the entropy parameter and determines the increasing of the refractive index;
- between the two co-polyimides it was selected for antimicrobial testing the fluoride sample because it possesses greater transparency. It is planned to investigate the functionalizing efficacy with a biocidal agent on the antibacterial activity by treating in plasma the transparent co-polyimide film. For this, the plasma treated film has been functionalized with a biocidal agent: the silver nitrate;
- to increase the chemical reactivity of the original surface oxygen plasma treatments were carried for two different power of the electric field (40 and 60 W). The EDX and XPS data confirm the binding of the silver on the co-polyimide film surface of for both types of treatment, but especially at 60W;
- it has been evaluated the antimicrobial activity against *Escherichia Coli* indicating that for higher electric field strength are obtained the best results on this bacteria inactivation.

In **Chapter 7** was analyzed the structuring ability of some polyimide precursors by inducing a liquid crystal texture in order to obtain mixed alignment layers for nematic liquid crystals. The main results are:

- there have made newer mixtures of polyimide precursors and HPC in lyotropic phase that interacts through hydrogen bonding, favoring the maintaining of texture induced by HPC;
- the infrared dichroism analysis reflects the orientation of certain chemical bonds on the films surface;
- the AFM images show that the size of the bands depends on the mixture composition and

on the structure of the polyimide precursor. For the system poly (DOCDA-6FADE) / HPC the main bands are thinner and more uniform, and the side of the secondary ones are more pronounced compared to the films of poly (BOCA-6FADE) / HPC;

- the alignment tests show that for the samples set based on DOCDA is obtain a higher contrast of bright and dark states, so a more homogeneous orientation of the 5CB, especially in large percentages of HPC;
- taking into consideration the ability of the HPC polymer to generate orientation and its biocompatibility, and also of its imide precursors, it may be considered that the mixtures of poly (DOCDA-6FADE) / HPC are recommended as guided cellular growth media.

Chapter 8 presents the results on the effect of the UV irradiation and the importance of the optical activity in the release of active substances from polymer matrices. The studies have shown that:

- the glucose release profile from polymer, recorded for different periods of exposure (15 minutes up to 6 hours), is depending on the concentration of glucose – the systems being denoted as S1 and S2 (higher glucose concentration);
- depending on the irradiation time and the amount of glucose, the surface umectability is changing. The surface polarity and the free hydration energy are greater with longer exposure to UV, in particular for lower glucose content – the sample S1;
- the S2 film present denser surface than S1, probably due to the formation of hydrogen bonds between the mixture components;
- The surface morphological and energetically studies shows that photo-oxidative and photo-degradation processes are occurring during the irradiation, causing chemical modifications into the polymeric surface. For longer periods of UV exposure the macromolecular chains of HPC can break favoring faster release of glucose;
- the diffusion coefficient values show that the mechanism involved into the release process of the active substance from the HPC matrix is not damaged by exposure to UV, but by the system glucose proportion. Data from the release profiles recommended the sample S1 as good for UV resistant bandages;
- the proposed method for determining the circular birefringence of the HPC polymer solutions in water show that the circular birefringence of the sample has low values, no matter of the HPC concentration and the rotation dispersion decreases with the increase of the wavelength;
- Specific rotation of the HPC solutions in water does not depend significantly on the polymer concentration. If it is desired to determine the rotation direction of the

polarization plane into the polymer solution studied with grooved spectrum, it is necessary to be conducted further experiments.