„AlexandruIoanCuza“University,Iași
Faculty of Physics

PhD Thesis Summary

CONTRIBUTIONS TO THE STUDY OF ELECTRO-OPTICAL PROPERTIES IN ANISOTROPIC MEDIA

Scientific supervisor,
Professor Dana Ortansa Dorohoi, PhD

PhD student,
Ojog Beatrice Carmen
(married **Zelinschi)**

Iași-2012

I want to thank the POSDRU/88/1.5/S/47646 Project,co financed from the European Social Fund, by the Human Resources Development Operational Program 2007-2013.

INTRODUCTION

There are a lot of substances for which their physical properties do not depend on the direction taken into consideration. These substances are called isotropic substances. In nature there are substances called anisotropic substances. Following an optical point of view, a media becomes anisotropic if its optical properties for a transmitted plane electromagnetic wave depend on the propagation direction of the electromagnetic wave. The goal of this thesis is to analyze the electro-optical properties of some anisotropic media, as their potential use in the simulation and in the projection of optical interferential devices that can be applied in both medical and technical fields. The thesis is structured as follows:

The first chapter includes 2 subchapters that touche on the theoretical topics regarding the actual stage of knowledge related to references from the literature inspired by electrical and optical properties of anisotropic media, then describing the basic characteristics of the studied anisotropic media: the quartz and calcite crystals, PPMAECOBA LC and the general properties of PVA. Thenthere is the description of some study methods on the properties of anisotropic media (XRD, FTIR, DSC,TGA,AFM). Chapter II presents the XRD study of natural quartz crystals, the determination of the main refraction indices and of the birefringence using the Rayleigh interferometric method, but also the channeled spectra method. PVA foils obtained by the sedimentation method and which contain chemical dyes were studied, experimentally evaluated andcompared later their optical properties. Chapter III presents the computerized simulation of some devices in order to obtain and describe polarized

radiations; the conditions in which special anisotropic plates are made; the penetration depth of an evanescent wave in anisotropic media; the study of transmission factor for polarized interferential filters containing anisotropic layers. Chapter IV follows the detailed study of donepezil's controlled release included in polymeric PVA matrix. In the last part, we underline the personal contributions, the general conclusions and the scientific papers published during the elaboration process of the thesis.

CHAPTER I Actual stage of knowledge in the field of electro-optical properties of anisotropic media

I.A.1 The Maxwell equation system

The electromagnetic waves can be studied in degree using the Maxwell equation system. These equations together with material relations, describe completely the electromagnetic field in every point in space [1]:

$$\begin{aligned} &\nabla \cdot \vec{e} = \frac{\rho}{\varepsilon_0} \\ &\nabla \times \vec{e} = -\frac{\partial \vec{b}}{\partial t} \\ &\nabla \cdot \vec{b} = 0 \\ &\nabla \times \vec{b} = \mu_0 \cdot \vec{J} + \mu_0 \varepsilon_0 \frac{\partial \vec{e}}{\partial t} \end{aligned} \qquad \text{(I.1.)}$$

I.A.2. The material laws in crystalline media

Based on their microscopic nature, substances can be classified in: amorphous substances and crystalline substances.The crystalline structure gives the anisotropic property. The spatial network is a regular periodical arrangement of an infinite mass of discrete points from space (x,y,z) which, through repeated translations stretches infinitely following 3 non coplanar directions [1]. The vectors $\vec{a}$, $\vec{b}$ and $\vec{c}$ determine a parallelepiped called elementary cell (fig. I.1.).

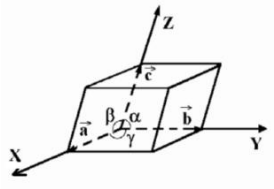


Fig.I.1 The elementary space cell

The macroscopic theory of electromagnetic field establishes the relation between $\vec{D}$ and the state measures $\vec{E}$ and $\vec{P}$, under the form of the law of material in [1]:

$$\vec{D} = \varepsilon_0 \vec{E} + \vec{P} \qquad \text{(I.2.)}$$

I.A.3. Electro-optical properties of anistropic media

The crystalline substances group in substances with crystalline networks of high symetry, medium symetry and low symetry. In general, in anisotropic media, the propagation direction of constant phase surface is different from the incidence of optical radiation– fig.I.2. [2]

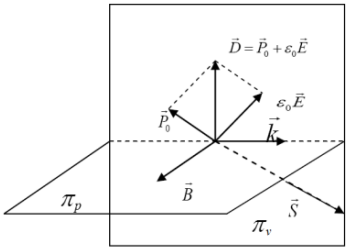


Fig.I.2. The orientation of the vibration surface and of the polarization surface in an anistropic media

I.B.1. Main features of studied anisotropic media

The quartz and the calcite

Quartz is an important material used for devices that combine its electrical and optical properties leading to a special chemical and physical resistance. Its chemical bonds with those of silicate are covalent. The main substance is SiO_4in which there is a silicon atom surrounded by 4 oxygen atoms (fig.I.3). The calcite is a mineral from

the carbonate class, whose structureis presented in fig.I.4.,it crystallizes itself in a rhomboedric shape and it has the chemical formula $Ca[CO_3]$.

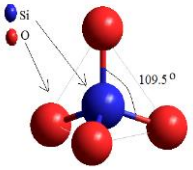


Fig.I.3. The SiO_4 tetrahedron

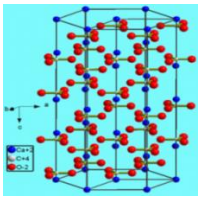


Fig. I.4. The structure of calcite

The PPMAECOBA liquid crystal

The liquid crystals can be defined as an intermediate state between liquids and solid crystals, feature which is specific only to certain organic substances. The liquid crystals can be described by the phenomena of polymorphism. A lyotropic liquid crystal with the structural formula shown in fig. I.5. is PPMAECOBA and it has an inherent anisotropy [1].

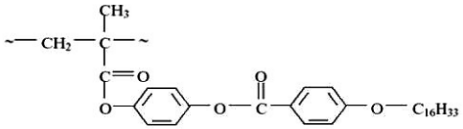


Fig.I.5. PPMAECOBA's structural formula

The poly(vinylic alcohol)

The PVA is a polymer obtained through a polymer-analog transformation of the vinyl polyacetate. The PVA has a relatively simple structure with pendant hydroxyl group –fig.I.6.

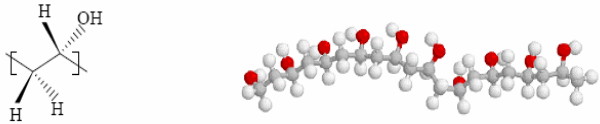


Fig.I.6. The structure of the PVA monomer and polymer

The PVA is not toxic to the human body, it is biodegradable and it has good physical-mechanical properties, being used in the drug controlled release systems.

CHAPTER II Description of anisotropic samples

II.1. XRD study of anisotropic samples

The studied anisotropic media have been represented by anisotropic media such as quartz, apatite and calcite, but also polymeric foils, chemically colored and extended, for which we have studied the birefringence, the dichroism [3] and their variation based on their extension degree. We have analyzed natural quartz samples from Ceahlau area (C1,C2) and from Maramureș area (C1'- C5'). These samples were compared to the reference sample–S1.We have recorded the diffractograms of the reference sample S1 and of the C1 and C2 samples. The C1 and C2 crystals' diffractograms after the milling process have been compared to those of the reference sample, S1 (fig.II.1-II.2.). We can observe that only a limited number of known reference maxima were present in the maxima of the 2 crystals.

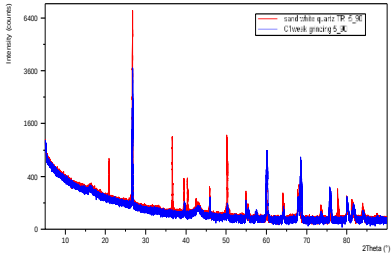


Fig.II.1.Superposition of the C1 and S1 diffractograms samples

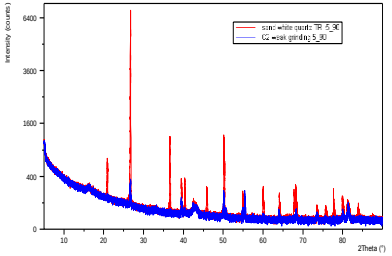


Fig.II.2.Superposition of the C2 and S1 diffractograms samples

The XRD analysis shows that the C1 and C2 quartz crystals are not pure; they have a low crystalline composition because of the temperature variations to which they have been exposed during the crystallization process over time. For the natural quartz samples from Maramureș area we have performed the XRD analysis and we have gained thediffractograms. In fig.II.3., we can see the comparison between the C1' sample's diffractogram and the diffractogram of the quartz from the data base realized with X'Pert High Score. We can observe that there is a perfect correspondence between the diffraction maxima of this crystal and those of the data base quartz.

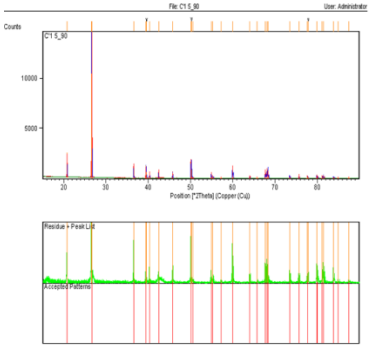


Fig.II.3. The comparison of the C1 crystal diffractogram with the quartz's diffractogram from the data base

II.2. Determination of the refractive indices and the birefringence of using the Rayleigh interferometer method

Determining the refractive indices and the birefringence was made for uniax anisotropic media such as the quartz from Maramureș area, the apatite and the calcite. The refractive indices of refraction have been calculated with the equation [4]:

$$n_i = n + \frac{k\lambda}{L},\ i = o, e \qquad \text{(II.1.)}$$

The fig.II.4 and II.5 contain the values of the refraction indices and the electrical permittivities for the quartz, apatite and calcite(λ=589,3nm)[5-6]:

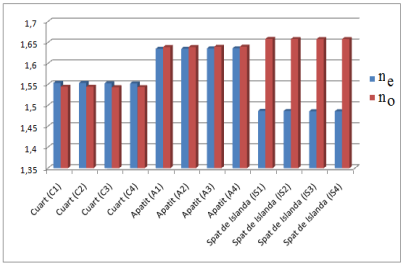


Fig.II.4.The values of the refraction indices for quartz, apatite, calcite

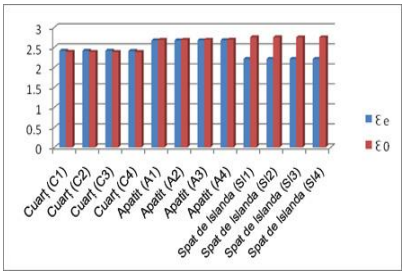


Fig.II.5.The values of the permittivities for quartz, apatite, calcite

II.3. Determination of birefringence for anisotropic quartz crystals using the channeled spectra

The channeled spectra for an uniax anisotropic media – the natural quartz crystal from Maramureş area – is presented in fig.II.6.

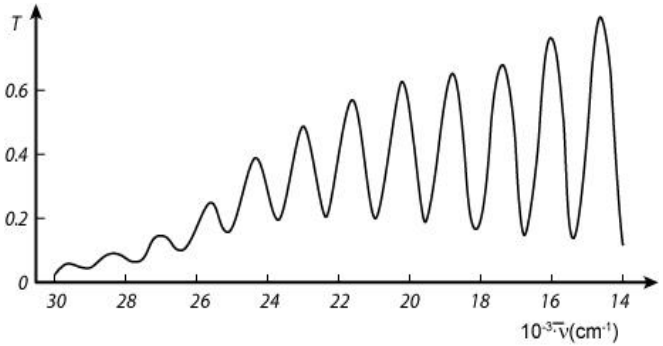


Fig.II.6. Channeled spectra of a natural quartz crystal

The variation of the anisotropic quartz's birefringence with the wave's number can be observed in fig.II.7: the quartz crystal's birefringence decreases at the same time with the wave's number.

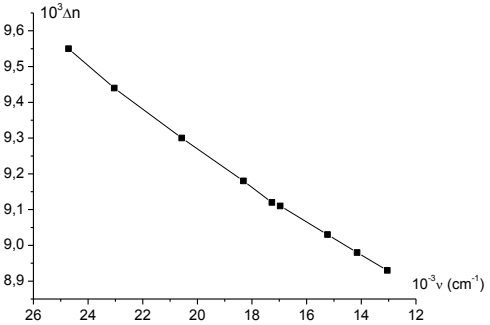


Fig.II.4.The variation of quartz's birefringence with the wave's number

II.4.The study of some optical properties of PVA films containing Congo red by a spectral method

As a polymer, we have used PVA totally hydrolized polymer and as a chemical dye – Congo red [7]. The polymeric foils from pure

PVA have been obtained with the sedimentation method. The chemical dye concentrations of the resulted samples are presented in table II.1.

Table II.1. The concentration of CR in PVA samples

Samples	Concetration of Congo red (%)
PVA+CR1	2
PVA+CR2	2,5
PVA+CR3	3
PVA+CR4	6
PVA+CR5	7

II.5. The evaluation of the properties of the PVA foils colored with CR

The CR dopped PVA foils, by known concentrations were submitted to XRD analysis. In fig.II.8. we have represented the crossed diffractograms of the pure PVA samples, of the pure CR and PVA+RC with various concentrations.

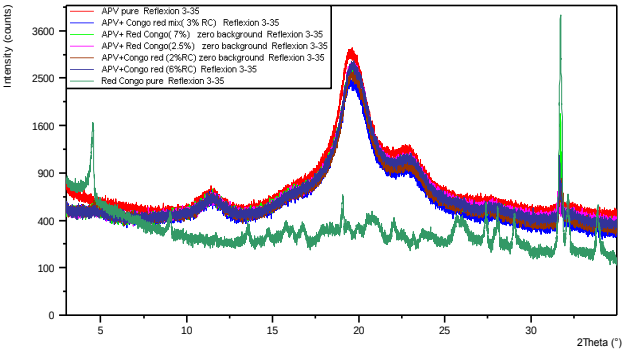


Fig.II.8. Crossed diffractograms of pure PVA samples, of the pure CR and PVA+RC with various concentrations.

The diffractogram of the pure PVA foil presents a maximum of diffraction at a 2θ angle of $19,5^0$and 2 maxima for 2θ angles of $11,2^0$ and $22,8^0$ and for the pure CR at $32,2^0$. The degree of crystallinity is calculated using the (II.2.) equation and is presented in the table II.2.:

$$\% \text{ crystallinity} = \frac{100A}{(A+B-C)} \qquad \text{(II.2.)}$$

Table II.2. Values of the degrees of crystallinity for the PVA foils colored with CR in various concentrations

Samples	Concetration of Congo red (%)	Degrees of crystallinity (%)
PVA+CR1	2	88,948
PVA+CR2	2,5	89,371
PVA+CR3	3	90,210
PVA+CR4	6	93,511
PVA+CR5	7	98,693

As the CR's concentration in the PVA polymeric foils increases, we can observe an increase of the samples' degree of crystallinity.We have determined the characteristics of the polymeric foils [8-9] with a different CR component for the highest degree of extension-3, leading us to the conclusion that the dichroic ratio is maximal in the sample that has the highest RC concentration and that it's range parameter does not overcome 35% from the total number of spectral active molecules.

Table II.3. Characteristics of the PVA foils with CR

Samples	Dichroic ratio	The order parameter	Birefringence
PVA+CR1	2.210	0.276	0.022
PVA+CR2	2.149	0.286	0.032
PVA+CR3	2.216	0.287	0.045
PVA+CR4	2.307	0.304	0.061
PVA+CR5	2.501	0.332	0.083

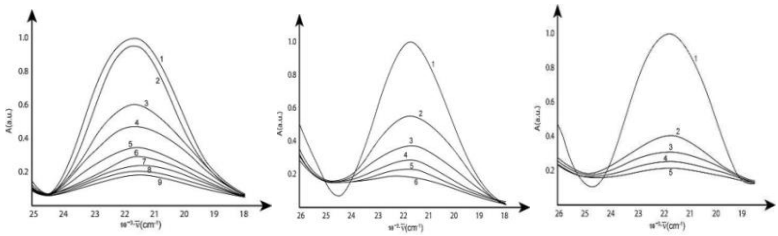
II.6. The study of optical properties for PVA foils containing cycloimmonium ylides

The cycloimmonium ylides (CY) are zwitterionic molecules, with different electrical charges, separated on a nitrogen heteroatom, belonging to the heterocycle, and on a carbon atom that contributes to the ylidic bond, called carbanion [10-11] (table II.4.).

Table II.4. The chemical structure of the carbanion substitutes from the CY

Ylides	R_1	R_2
CY1	–H	$–CO–C_6H_4–OCH_3$
CY2	–H	$–CO–C_6H_4– C_6H_5$
CY3	–H	$–CO–C_6H_4– (NO_2)_p$
CY4	$–COC_6H_5$	$–COC_6H_5$
CY5	$–COC_6H_5$	$–COC_6H_5$
CY6	–CN	$–CO_2 C_2H_5$

The electronic absorption spectra of pure PVA films and PVA withCY are presented in fig.II.9.



a) b) c)

Fig.II.9. The electronic absorption spectra of the ylides: a)CY1; b)CY2; b)CY3.

The dependence of the dichroism and the order degree by the stretching degree of the PVA foils with piridazinium ylidesCY1 CY2 CY3 is exponential:

$$D(CY1) = 0,69341 - 1,4982e^{-\gamma/1,27242}$$

$$g(CY1) = 0,61520 - 1,16583e^{-\gamma/1,54899} \quad \text{(II.3.)}$$

$$D(CY2) = 0,67965 - 2,30447e^{-\gamma/0,79871}$$

$$g(CY2) = 0,61619 - 1,52614e^{-\gamma/1,15434} \quad \text{(II.4.)}$$

$$D(CY3) = 0,68259 - 3,75784e^{-\gamma/0,547898}$$

$$g(CY3) = 0,59384 - 2,51444e^{-\gamma/0,68490} \quad \text{(II.5.)}$$

Colored foils were obtained with ftalazinium ylides (CY4-CY6) in the solution of PVA. For the same stretching degree-1, were represented

in the fig. II.10-II.11. the values of the dicrhoism and the order degree of the PVA foils colored with ylides: CY4, CY5, CY6.

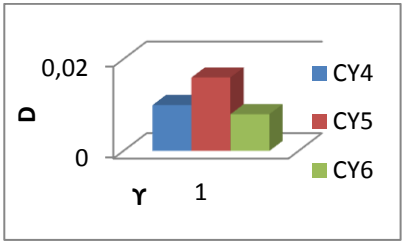


Fig.II.10.The dichroism for PVA foils colored with CY4, CY5, CY6 for γ=1

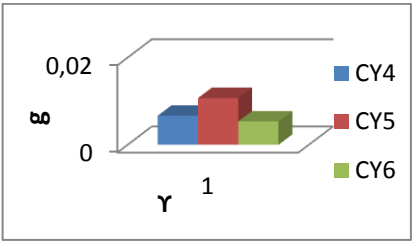


Fig.II.11.The order degree of PVA foils colored with CY4, CY5, CY6 for γ=1

II.7. AFM analysis of PVA films containing donepezil submitted to the extension process

The structure of the surface in pure PVA films and in those containing 2% donepezil has been studied using AFM. The surface's roughness was determined for each foil before and after their extension. The AFM typical image of the pure PVA foil's structure and of PVA with 2% donepezil at various stretching degrees is presented in fig.II.12. a), b), c),d). In the case of the PVA +D % films, we can observe that the roughness increases when we add donepezil in the PVA foils, but also it decreases during the extension process.

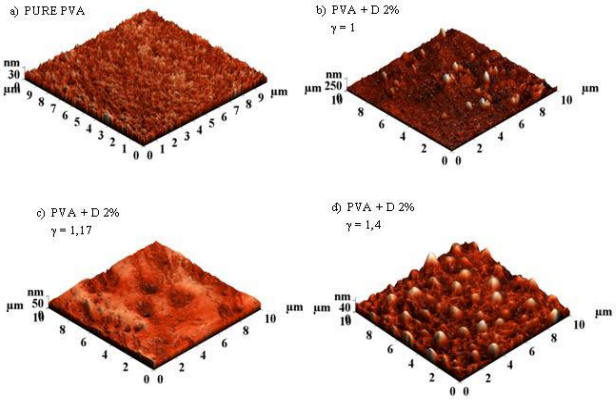
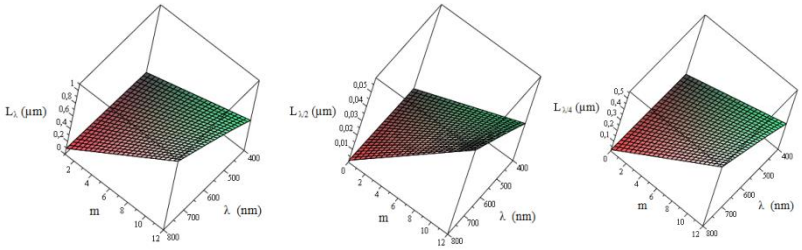


Fig.II.12. AFM images for a) pure PVA; b) PVA+D2% for extended foils ($\gamma = 1$); c) PVA+D2% (γ=1,17); d) PVA+D2% (γ=1,4)

CHAPTER III Computerized simulation of some devices in order to obtain and describe polarized radiations

III.1. Anisotropic special plates of quartz,calcite and PPMAECOBA LC

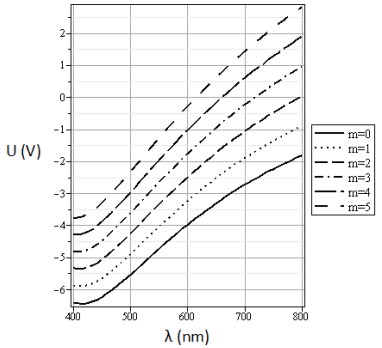
In order to simulate the thickness of the special plates [12] based on the interference order and the wavelength, we have used the values of the main refraction indices of the quartz and calcite crystals, determined before using the interferometric method. We performed a 3D simulation of the thickness for the quartz and calcite special plates based on λ and m with the help of the Maple programme, having as support the experimental data gained previously-.fig III.1.



a) b) c)

Fig.III.1. The thickness of the quartz layer (a), calcite(b+c) as a plate: a)λ; b) λ/2 and c)λ/4 based on λ and on the interference order m

The PPMAECOBA system in TCM is a lyotropic liquid crystal [13]. The experimental data show that the CL PPMAECOBA‘s birefringence increases when applying an external electrostatic field, the maximal tension allowed for adjustment is $U_{max}=E_{max}L=1,96V$. We have performed the simulation of the dependency U in relation to λ (fig.III.2.-III.3.) for PPMAECOBA LC special plates containing one layer and 2 layers with the same thickness. The special plates made of PPMAECOBA LC to which an external electrostatic field was applied, can be electrically controlled on certain sub-intervals of the visible field.



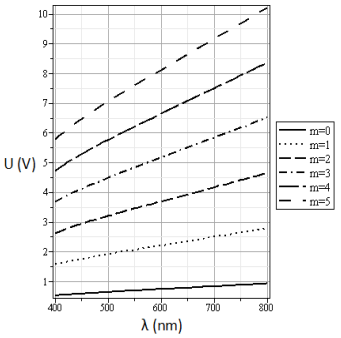
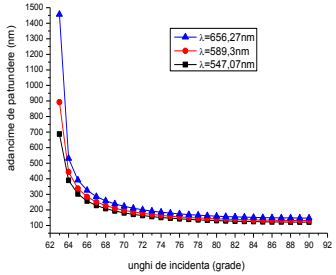


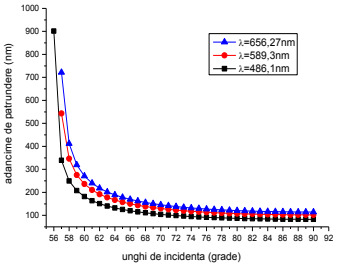
Fig.III.2.The U(V) dependence on λ for λ/4 a single layer of PPMAECOBA (L=14μm)

Fig. III.3.The U(V) dependence on λ forλ/2 a double layer of PPMAECOBA (L=14μm)

III.2. Penetration depth of an evanescent wave

Given the values of the refraction indices determined previously using the interferometric method, we have presented the penetration depth of an evanescent wave in a living cell (n_2=1,38) on a quartz and calcite support for various λ based on the incidence angle for the extra ordinary component but also for the ordinary one in fig.III.3.a) and b). The penetration depth of an evanescent wave is higher when approching to the limit incidence angle, being superior in the case of the extraordinary component than in the ordinary one.





a) b)

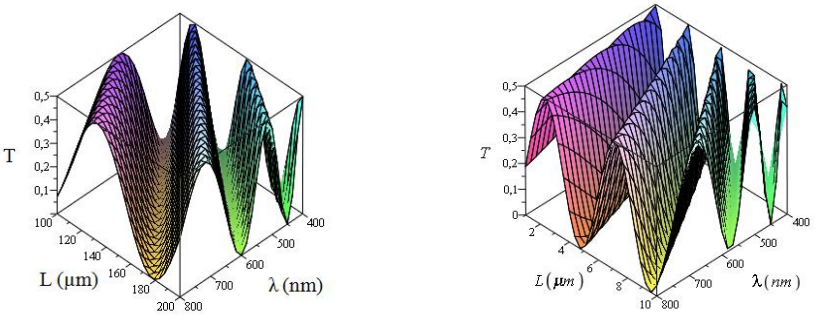
Fig.III.3.The variation of an evanescent wave with the incidence angle for different wavelength at the crossed surface a) quartz-living cell; b) calcite-living cell

III.3. Simulation of the transmission factor for the polarization interferential filter made of anisotropic layers

The transmission factor of a Wood filter depends on the wavelength, the thickness of the anisotropic layer and it's birefringence [14]:

$$T(\lambda_0) = \frac{1}{2}\sin^2 \frac{\pi \cdot \Delta n \cdot L}{\lambda_0} \qquad \text{(III.1.)}$$

The variation of the Wood 's filter transmission factor based on L of the quartz and calcite layer and on λ is presented in fig.III.4. a) and b). From the 3D chart–fig.III.4. we can identify the maximal T of the quartz and calcite plates for a certain λ. For λ=800nm, T is maximal when L= 130μm for quartz and when L=2μm and 7μm for calcite.



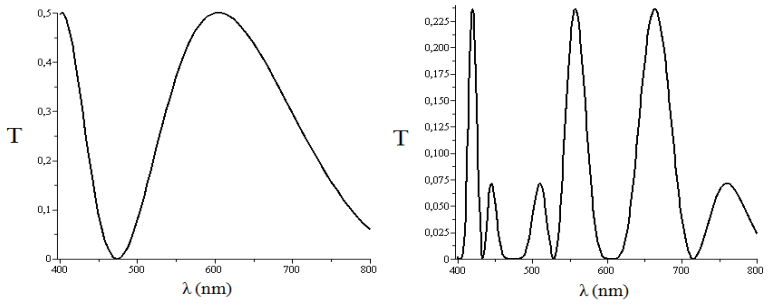
a) b)

Fig.III.4. Transmission factor vs L vsλ for a)quartz b)calcite

The transmission factor of a one layer Lyot filter is given by (III.2.):

$$T = \frac{1}{2} sin^2\left(\frac{\Delta\varphi}{2}\right) = \frac{1}{2} sin^2\left(\frac{\pi \cdot L \cdot \Delta n}{\lambda}\right) \qquad \text{(III.2.)}$$

For a single or 3 layer Lyot filters [15-16] (L=100μm), the simulation of the transmission factor based on λ for the quartz, using the Maple programme, highlights the existence of the main transmission band in the channeled spectra (T=23%) which is separated by 2 secondary transmission bands (T=7%), like in fig.III.5 a) and b).



a) b)

Fig.III.5. The transmission factor of a Lyot filter with a)one layer; b) 3 layers with anisotropic quartz plates(L=100μm)

CHAPTER IV Applications for PVA foils used in *in-vitro* drug release studies

IV.1.Characteristics of PVA and donepezil foils used for *in-vitro* drug release studies

Although it has a simple structure, the PVA is biodegradable, biocompatible and water-soluble[17], its structure is represented in fig.IV.1. Donepezil is a drug used in treating Alzheimer disease, its molecular structure is presented in fig.IV.2.

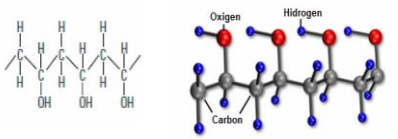


Fig.IV.1. The PVA's zig-zag planar structure

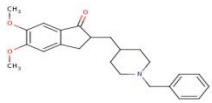


Fig.IV.2.The donepezil's structure

IV.2. Materials and methods

In order to obtain polymeric foils, we have used PVA purchased from the Merck Company. For the PVA foils containing 2 polymorphs of donepezil included in the polymeric matrix, we used completely hydrolyzed PVA solution .We have obtained gel, pure PVA foils and PVA foils with donepezil by dissolving the polymer into distilled water at a 75-80^0 C temperature. The active substance was dissolved in ethanol/ acetonitrile and added in the PVA solution. In vitro release studies have been realized at pH=5,5.The release tests were performed

by diving some PVA with donepezil (100mg) into 50 ml of buffer solution. At certain time frames (0-24 hours) we have extracted a sample of 5ml buffer solution with the drug, sample that was analyzed with UV-VIS spectroscopy using the absorption band at 232nm.

IV.3. Results and their interpretation

a)The XRD analysis of PVA and donepezil

The semi-crystalline feature of PVA can be emphasized using the XRD. In fig.IV.3., we have presented the diffractogram of a PVA film. For the donepezil added later in the PVA's polymer matrix, the diffractogram of the A polymorph is presented in fig.IV.4., according with the EP patent nr. 166349 [18].

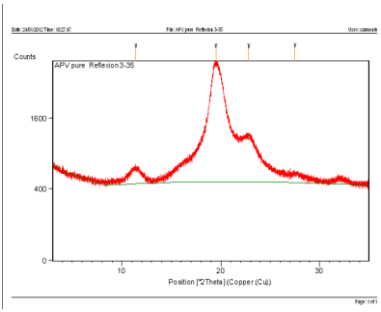


Fig.IV.3. The diffractogram of a PVA foil

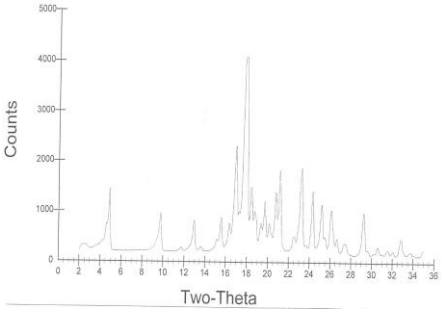


Fig.IV.4. The diffractogram of donepezil's A polymorph[18]

b)The DSC and TGA analysis of PVA polymer

The DSC thermogram realized on a 10°C/min heating/ cooling rate for the pure PVA foil is presented in fig.IV.5. In the DSC chart of the PVA, we can observe a large maximum at 100°C-120°C, this maximum being associated with the release of water molecules from matrixof the completely hydrolyzedpolymer,the other 2 maximum being related to other two thermal events: the melting of the polymer and its crystallization. The TGA thermogram is presented in fig.IV.6. at a heating rate of 10°C/min; we can observe a change in the total mass that starts at temperatures like 71°C, up to 200°C.

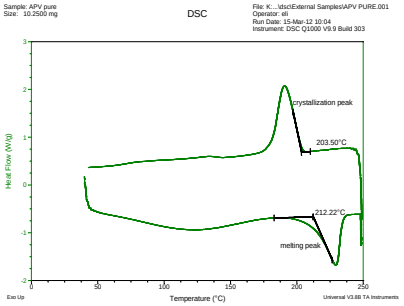


Fig.IV.5.The PVA thermogram

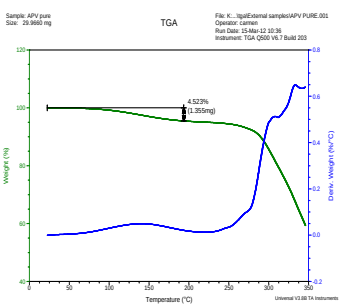


Fig. IV.6. The thermogravimetric analysis for PVA

c)Controlled drug release of the 2 donepezil 's polymorphs

The controlled release is determined by the polymer's structure and its properties [19-20]. In order to estimate the released donepezil's concentration, we realize the calibration curve. The donepezil' s calibration chart is shown in IV.7. and it is correlated with an absorption band of 232nm.

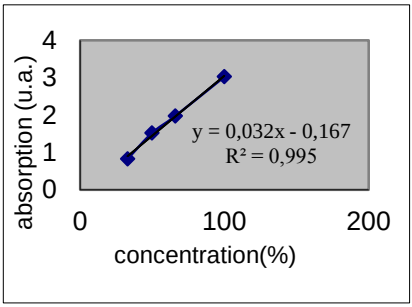


Fig.IV.7.The donepezil's calibration curve

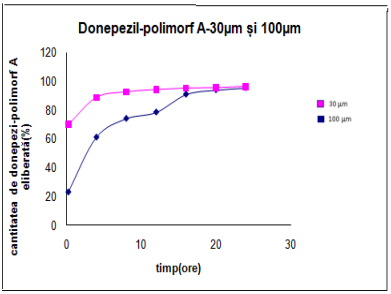


Fig.IV.8. The release profiles of donepezil's A polymorph

The profiles of donepezil–A polymorph have been obtained by controlled release for 2 different sizes of particles: 30µm and 100µm (fig.IV.8.). For a 30µm size of donepezil's particles, we can observe a rapid increase in quantity for the active substance that is released in the first 15 minutes (70 %) , followed by an increase in concentration nearly up to the saturation point, in the 1-8 hours time frame. For a 100µm size of donepezil's particles, the release in the first 15 minutes

reaches only 23%, followed by a rapid release of the active substance in the 4-12 hours time frame. The experimental data that we have got were processed by applying all mathematical patterns of the controlled realease kinetics. We have presented in fig.IV.9.-IV.10. the optimal realease kinetics for the 2 dimensions, 30µm and 100µm.

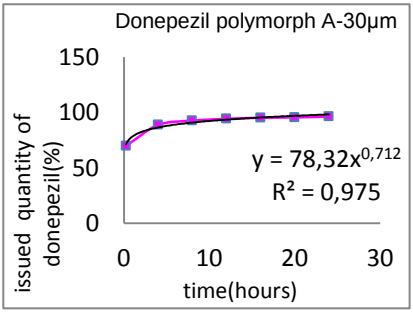


Fig.IV.9.The Korsmeyer- Peppas -PVA+donepezil A polymorph (30µm) kinetics

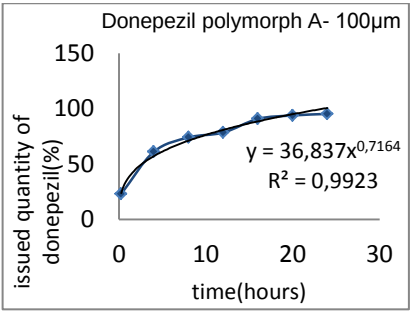


Fig.IV.10.The Korsmeyer- Peppas -PVA+donepezil A polymorph (100µm) kinetics

The controlled release profiles for donepezil in the PVA foils at different extension degrees are presented in fig.IV.11. from which it is obvious that the release of the donepezil's particles from the PVA films is rapid in the first 60 minutes of dive. For the non-extended PVA foil containing donepezil, the release process is slower than in the case of extended PVA foils with donepezil (at $\gamma>1$). The donepezil's maximum concentration released after 60 minutes is 51.52% (for the non-extended foils) ($\gamma=1$) and increases with the extension degree. The patterns of the controlled release kinetics are available in the case of PVA+ D2% foils at different extension degrees, the results being presented in table IV.3.

IV.11. The controlled release profiles of donepezil in the PVA foils at various extension degrees

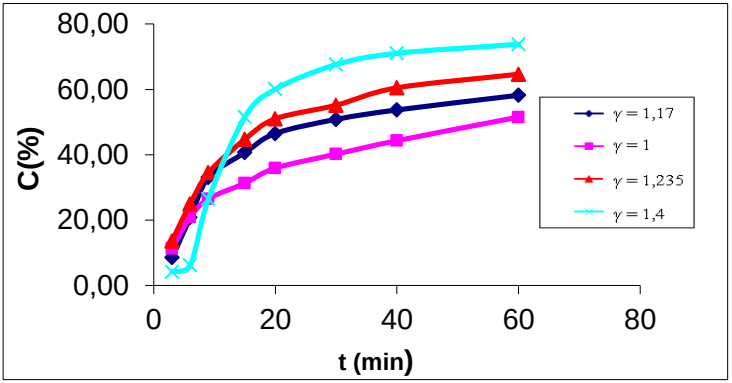


Table IV.3. The correlation quotient's values for the dissolution constants of PVA+D2% samples

Sample	Stretching degree	Kinetics of zero order		Kinetics of order I		Korsmeyer-Peppas kinetics	
		K_0	R^2	K_1	R^2	R^2	n
PVA+D 2%	1	0,0031	0,788	-0,0042	0,9029	**0,988**	0,4690
PVA+D 2%	1,17	0,0029	0,9801	-0,0007	0,9835	**0,989**	0,5329
PVA+D 2%	1,235	0,0018	0,9515	-0,0048	0,9631	**0,984**	0,5629
PVA+D 2%	1,4	0,0154	0,8272	-0,0042	0,8486	**0,877**	0,6326

V. GENERAL CONCLUSIONS

The XRD studies on natural quartz anisotropic crystals have demonstrated the crystallinity of the samples and have allowed us to measure the ordinary and the extra ordinary refraction indices using the interferometric and the channeled spectra method. This way, our experimental data gained a good correspondence.

For the CR dopped PVA foils, the optical properties increase with the extension degree of colored polymeric films. The optical birefringence of CR dopped PVA foils is directly proportional to the extension degree, but also with the dye's concentration level. The birefringence, the dichroism and the orientation degree of molecules in PVA foils colored with CY increase with the extension degree. The morphological structure of foils' surfaces through the atomic force microscopy reveals the increase in roughness of PVA +D 2% films, unlike the pure PVA foils, but also a decrease in roughness following the extension process. The special plates of PPMAECOBA LC, of L=14μm thickness, with simple or double layer, to which we have applied an external electrostatic field, can be electrically controlled on certain sub-intervals of the visible field. The penetration depth of the evanescent wave at the crossed surface between an anisotropic media and the livig cell increases with theλ, being much bigger in the case of the extraordinary component than in the ordinary one at studied anisotropic samples. The transmission factor simulation for interferential Wood or Lyot filters made of anisotropic media has allowed us to estimate the maximal transmission factor from the channeled spectra, which depends on the thickness of the anisotropic layer and of the anisotropic media's birefringence. According to the experimental findings, the release rate of donepezil from the PVA foils depends on the time factor, on the primary drug concentration and on the properties of the polymeric matrix in which it is included. The released concentration of the active substance increases with the extension degree of the PVA+D2% and that have been submitted to the extension process.