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OPTICAL PROPERTIES OF POLYSACCHARIDE/POLYLACTIDE BLENDS

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The present paper aims to investigate a series of polymer blends, prepared from polylactide and a natural polymer, namely a polysaccharide. The latter is a cellulose derivative that exhibits a transmittance of about 80% in the range of 300-600 nm, while the studied polylactide presents an extended transmittance upto 250 nm. The refractive index of each blend was determined at room temperature and at a fixed wavelength, reflecting the contribution of the two polymers. The absorption coefficient was evaluated using the Tauc approach, which allows the determination of the absorption edge and the optical bandgap energy. The obtained results were discussed as a function of the sample composition.

Keywords: polymers, transparency, refractive index, optical bandgap.

1. Introduction

Optical properties of polymers have been widely investigated since they are essential for many practical purposes, including packaging, electronics and pharmacology [1-3]. The study of the optical absorption and transmission characteristics is very important because it gives information about the electronic properties of analyzed materials. Thus, the determination of the parameters describing the electronic transitions, such as: bandgap, valence band tails and lifetime of excited states is useful for a deeper understanding of the polymer structural peculiarities that are related to disorder in the material network, like bond strength and defects. However, the optical absorption is influenced on a convolution of the density of states of conduction and valence bands.

In the literature [4] are reported many models elaborated for evaluation of the optical properties of amorphous semiconductors and dielectrics in the energy range of interband transitions. One of the most applied theoretical approaches is that developed by Tauc [5]. According to this model the shape of the bands near the edge is considered to be parabolic. The bandgap energy, E_g, can be derived from $E(\varepsilon_2)^{0.5}$ as a function of the incident energy, E, where ε_2 is the imaginary part of the relative dielectric function. Subsequently, E_g is obtained by extrapolating $E(\varepsilon_2)^{0.5}$ to zero, according to equation (1):

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$$E\sqrt{\varepsilon_2} = B_T\left(E - E_g\right) \qquad (1)$$

where B_T is a constant and the square of the average matrix element of the dipolar momentum.

In other words, the optical energy gap is usually determined from the absorption spectrum of the polymer at the absorption edge; where more or less a rapid rise in the absorption coefficient with increasing photon energy takes place in a narrow range of photon energies.

The performance of optical characteristics of current macromolecular compounds can be optimized by modification of the chemical structure, through the introduction of specific end/side groups, copolymerization, grafting, or crosslinking reactions [6,7]. Another method, which is more easily applied, consists in blending polymers with different optical properties. This technique is well-known in polymer engineering for creating new materials with improved properties than individual components [8].

Hydroxypropylcellulose (HPC) is one of the most studied ethers of native cellulose, whose diluted solutions display good transparency, while its concentrated solutions present optical properties typical to cholesteric liquid crystals [9]. The good optical properties, combined with its biocompatibility and biodegradability make this polymer suitable in many applications.

Polylactides (PLAs) have gained commercial significance as a leading environmentally plastic available from renewable resources [10]. Therefore, it is highly desirable to understand the optical properties of these macromolecular compounds so that they can be manipulated to develop materials of desirable characteristics for a specific practical purpose. Optical features, such as color, clarity, and refractive index are important in dyeing operations for textile and in various packaging applications. In the latter case, sensitive components of foods (lipids, flavors, vitamins, and pigments) may undergo degradation processes during light exposure. The spectrum and the intensity of the incident radiation, and the degree of light transmittance of the packaging material are factors that can dramatically affect the food quality. Thus, packaging materials must meet some minimal optical requirements for prevention of photodegradation of food components during storage.

Having all these in consideration, the present paper aims to obtain a series of blends based on HPC and PLA and to analyze their optical properties in order to check their suitability as packaging materials. The Urbach rule [11] and the method proposed by Tauc [5] for amorphous materials were applied to obtain the energies describing the absorption edges and the energy gap, respectively. On the basis of these values, the probable electronic transitions have been evaluated and discussed in correlation with the polymer structure.

2. Theoretical background

Optical processes occur by transition of electrons and holes between electronic states (bands, tail states, gap states). The model developed by Tauc [5] for optical absorption at the absorption edge in the high energy region is concisely presented starting from its theoretical foundations, assumptions, results mathematical derivations.

Optical absorption in the proximity of band edges in amorphous materials is widely investigated. It was proved that absorption is a process that is influenced by the presence of defects and whatever the amorphous material the absorption curve has the same shape. The dependence of the absorption coefficient (α) on the incident photon energy (E=$h\nu$) can be divided in four zones (Figure 1) [5].

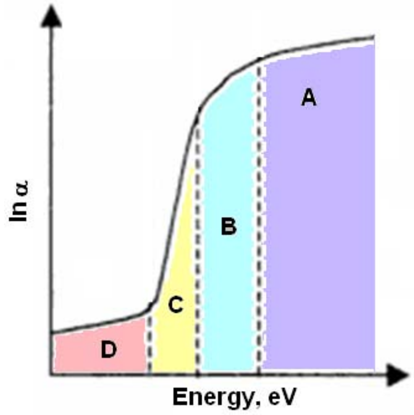

Fig. 1. The dependence of the absorption coefficient on the incident photon energy

The region A can be ascribed to interband transitions between delocalized valence and conduction states separated by energies greater than the mobility bandgap.

The B domain is related to absorption caused by transitions between valence and conduction band states positioned near the respective mobility edges. This region is useful for determining the optical bandgap (E_g).

$$\alpha = C_0(h\nu - E_g)^r \tag{2}$$

where C_0 is a constant and r is an index describing the type of optical transition, it is equal to 1/2 for direct allowed transitions and 2 for indirect allowed transitions.

The absorption in the region C (also named the Urbach region) depends exponentially on the photon energy and the transitions are caused by the defect states in the tails of the density states. Thus, at energies below the bandgap the parameter α tails off in an exponential manner:

$$\alpha(E) = C' \exp(E / A) \tag{3}$$

where *C'* is a constant determined by fits of the experiment, and A becomes either Urbach energy E_U in the exponential region C or E_T describing the low-energy exponential part of the absorption coefficient defined by the D domain.

In region D the absorption is less influenced by energy comparatively to the previous zone, being involved different processes.

3. Experimental details

The studied polysaccharide, namely hydroxypropyl cellulose (HPC) (LF, Klucel) was purchased from the Aqualon Company. According to product specifications, HPC presents the moles of substitution" of 3.4. Polylactide (PLA) and tetrahydrofuran (THF) solvent were achieved from Sigma Aldrich and used as received.

The procedure for preparing the PLA/HPC blends is the following: the polymer powder (PLA and HPC) was weighed and put into jars (also weighed). The aqueous solutions of HPC (5%) were mixed with those of PLA in THF (5%) in different ratios: 30/70, 50/50 and 70/30 wt/wt. The resulting systems were deposited onto glass substrates and then dried in vacuum for 24 h. After solvent complete removal the resulted polymer films were easily stripped from glass support and used in spectral measurements. The thickness of the studied films is not the same for all samples as presented in Table 1, but it is uniform as verified with an electronic calliper. The uniformity of film thickness results also from the preparation procedure since the solutions were deposited with a Gardner casting knife at a controlled speed of 5 mm s^{-1} and fixed gap of 40 μm.

The refractive indices of solution samples were measured experimentally on Abbe refractometer at room temperature using the yellow band from the atomic sodium D-line emission as light source (589.3 nm).

Optical transparency of the samples was recorded on a SPECORD 200 Analitik-Jena spectrophotometer.

4. Results and discussions

The refractive index, n, of the polymers depends on the backbone polarizability, chain geometry and orientation. This parameter is important in evaluation of optical transparency because it contains information on the manner in which is reduced the speed of radiations that are propagating through the polymer medium. Knowledge about this property is valuable due to its application in the design of new optical polymeric materials.

The refractive indices of the polymer solutions are considered as additive functions of the solvent ($w_{solvent}$) and polymer ($w_{polymer}$) compositions, as shown in equation (4) [12, 13]:

$$n_{solution} = n_{solvent,i} \cdot w_{solvent,i} + n_{polymer,i} \cdot w_{polymer,i} \tag{4}$$

where the index i=solvent, HPC, PLA and/or PLA/HPC.

The refractive indices of the studied samples were determined from the refractive indices of the polymer solutions, using Abbe refractometer, with an experimental error of about 3%. According to the provider THF has a refractive index of 1.40 at the wavelength used in experiments. Also, it is well known that water presents a value of 1.33 for n. By introducing these values in equation (4) together with the weight fractions of the counterparts the refractive index of HPC and PLA are obtained. These results are compared with those theoretically estimated for the initial components, as shown in Table 1.

Theoretically, the refractive index of each polymer at room temperature is calculated with the relation proposed by Bicerano [12]:

$$n = 1.885312 + 0.024558 \cdot (17 \cdot {}^{0}\chi^{v} - 20 \cdot {}^{0}\chi - 12 \cdot {}^{1}\chi^{v} - 9N_{rot} + N_{ref}) / N \tag{5}$$

where N_{rot} is the number of rotational degree of freedom and N_{ref} is the correction index, and N is a structural parameter defined by Bicerano [12].

$$\begin{gathered} N_{ref} = -11N_{F} - 3N_{(Cl\ bonded\ to\ aromatic\ rings)} + 18N_{S} + 9N_{fused} + 12N_{HB} + \\ + 32N_{(Si-Si)} \end{gathered} \tag{6}$$

For the initial polymers it can be noticed that there are some small differences between the experimental and theoretical values. This might be explained by considering that the theoretical approach does not comprise information on the polymer-polymer and polymer-solvent interactions. The results regarding n are reflecting the contribution of both polymers showing that the refractive index of the blend increases with increasing the amount of HPC.

Table 1

The thickness of the samples and the refractive index

System HPC/PLA	d, µm	n^a	n^b
0/100	38	1.44	1.46
30/70	36	1.45	-
50/50	36	1.47	-
70/30	39	1.49	-
100/0	37	1.52	1.51

[a] *determined from equation (4)*
[b] *determined from equation (5)*

The transparency of the studied polymers and blends is very important in applications. The roughness of the surface is important in judging the polymer film transparency. When roughness increases, the probability of light scattering increases and thus reduces the transparency. Since visible light wavelength is ca.

400-750 nm, the surface roughness for transparent films should be less than 100 nm [14]. The studied samples present a surface roughness smaller than 60 nm as identified from AFM measurements. However these data cannot be included in this paper because they represent the subject of another work. The transparency of studied samples was spectrally tested. Figure 2 shows the transparency spectra of HPC, PLA and 50/50 PLA/HPC films recorded in the range of 200–600 nm. The polysaccharide presents a reduced transmittance in 200-300 range comparatively with PLA. This difference is also observed in the prepared blends.

In order to determine the optical bandgap, the dependence of absorption coefficient on photon energy was evaluated. The absorption coefficient is obtained from the transmission data, according to the equation (7) [5]:

$$\alpha = (1/d)\cdot\ln(1/T) \qquad (7)$$

where d is the sample thickness and T is the transmittance.

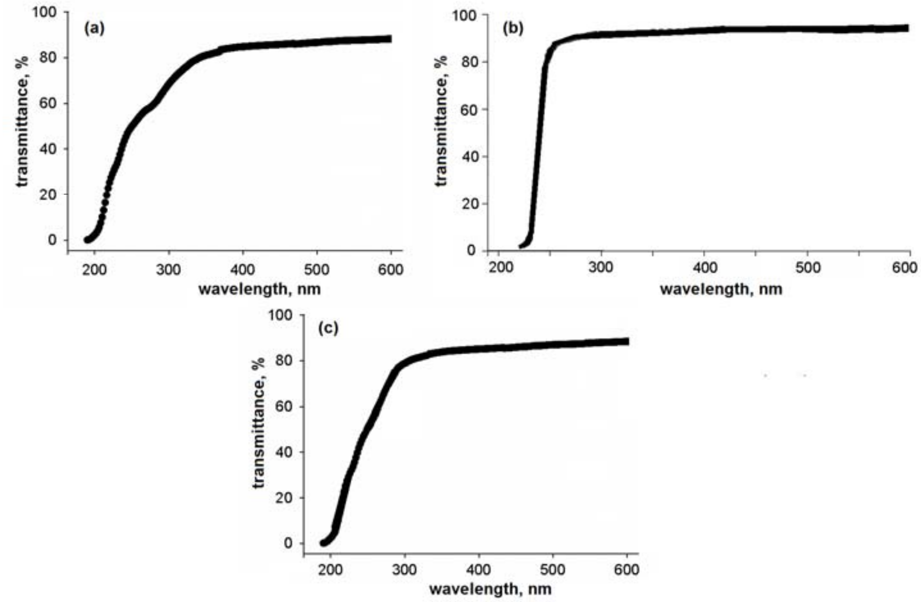

Fig. 2. The transmission spectra of (a) HPC, (b) PLA and (c) 50/50 PLA/HPC

Sharp drops in the transmittance values were noticed in the UV region (200–400 nm). The spectrum of pure PLA exhibits a shoulder like band at 250 nm, while that for the pristine HPC is placed at 330 nm. The corresponding blends exhibit an intermediary behavior. The variation in the transmittance values of the blend samples with increasing the concentration of HPC may be attributed to the fact that enhancing its concentration decreases the transparency of the films in UV region. This may be due to that there is a change in the molecular configuration of the counterparts [15].

The total absorption spectral response for PLA, HPC and their blends were calculated in the (UV/VIS) wavelength range from 200 to 600 nm and in the photon energy domain 2.0–6.2 eV. Figure 3 displays the relation between the absorption coefficient as a function of wavelength in the UV range (200–400 nm) and in the visible range (400–600 nm) for PLA, HPC and the blended samples. It is clear from Figure 3 that the absorption coefficient of the PLA/HPC increases gradually with increasing HPC content.

The increase of absorption coefficient with decreasing PLA amount may be attributed to the change of the molecular configuration, which indicates to the formation of new color centers as previously reported for similar polymer systems [16].

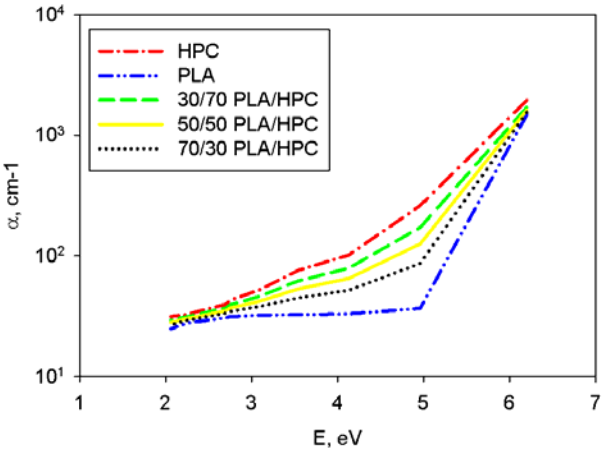

Fig. 3. Dependence of absorption coefficient on photon energy for the PLA/HPC blends

The fundamental absorption edge is one of the most important characteristics of the absorption spectra of crystalline and amorphous materials. The enhanced absorption near the edge is determined by the transition of electrons from the valence band to the conduction band. The absorption coefficient values increases with increasing photon energy and exhibits a steep rise near the absorption edge and a straight line relationship is noticed in the high α-region. The intercept of extrapolation to zero absorption with photon energy axis was taken as the value of absorption edge. Therefore, in equation (2) the transition index was taken as being 0.5 and the dependence $(\alpha E)^{0.5}$ *versus* photon energy is plotted (Fig. 4).

The obtained values were represented as a function of the HPC content in the blend, as shown in Fig. 5. It can be observed that the HPC sample presents higher optical bandgap (E_g) than that of PLA, probably because of its higher polarity given by the ether bridges from the glycosidic units and the side hydroxyl groups. The same trend is noticed for Urbach energy (Eu) values, which are obtained from the reverse slope of the absorption coefficient dependence on photon energy at energies below the bandgap.

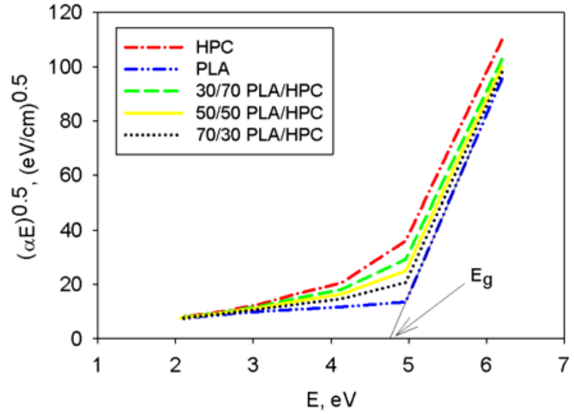

Fig. 4. Tauc plots for the pure HPC and PLA and their corresponding PLA/HPC blends

The resulted values for Eu reveal that the addition of HPC in the system determines a reduction of the structural disorder in the system. This may reflect the induced changes in the number of available final states according to the blend composition.

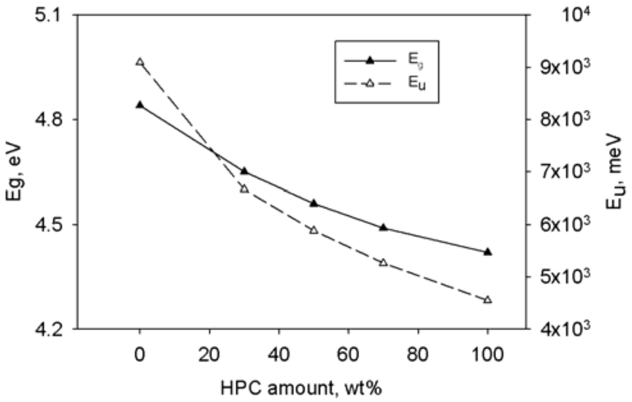

Fig. 5. The variation of E_g and E_u energies with the PLA/HPC blend composition

The Urbach energy is related to the localized states induced by the polymer atomic structure. Such possible structure defects, including the break, the abbreviation or the torsion of polymer chains seem to be responsible for low-energy absorption, described by the Eu parameter.

5. Conclusions

New polymer systems, prepared by blending HPC and PLA were studied from the point of view of their optical properties. Each counterpart presents different refractive index and optical bandgap. These parameters can be tuned depending on the mixing ratio of the polymers.

The refractive indices of the samples range between 1.44-1.52, reflecting the contribution of each blend component.

The absorption edges of all investigated films were found to be similar to the typical edge for amorphous compounds, allowing us to obtain the optical parameters. Increasing the PLA amount in the blend caused an increase of the energy gap. Slightly higher structural disorder may cause an increase of the Urbach energy that describes the low-energy part of the absorption edge.

The obtained results are important in food packaging were transparent and biodegradable coatings are required.

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