Optical Properties of Biodegradable Polylactic Acid/Silver Nanocomposites: A Study

Nadia Abbas Ali*

University of Baghdad, College of Science, Department of Physics, Baghdad, Iraq
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ABSTRACT

In this work nano silver added to the biodegradable polylactic acid can be prepared by casting method at room temperature and thickness (120 μm) at different concentration of nano silver powder. Optical properties have been measured in the range of (300-800) nm. The electronic transition in pure polylactic acid (PLA) and PLA/Ag nanocomposites indicated direct allowed transition. Also, it is found that the energy gap of polylactic acid is 3.3 ev and this value decreased within range of (3.3-2.7) eV when the concentration of nano silver powder increased from (2, 4, and 6%) respectively. The optical constants which include the refractive index (n), real (ε_1) and imagenerary (ε_2) part of dielectric constant calculated at λ=550 nm and find it decreased with increasing of nano silver.

Keywords: Biodegradable; Polylactic acid; Nano silver; Optical properties; Energy gap
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INTRODUCTION

Biodegradable polymers were first introduced in 1980s. Polymers from renewable resources have attracted an increasing amount of attention over the last two decades, predominantly due to two major reasons: firstly environmental concerns, and secondly the realization that our petroleum resources are finite. There are many sources of biodegradable plastics, from synthetic to natural polymers. Natural polymers are available in large quantities from renewable sources, while synthetic polymers are produced from non-renewable petroleum resources. Biodegradation of polymeric biomaterials involves cleavage of hydrolytically or enzymatically sensitive bonds in the polymer leading to polymer erosion [1,2]. Polylactic acid (PLA) is prominent among the polymers that are biodegradable and biocompatible due to versatility of its applications and relatively low cost of production at industrial scale. PLA, is linear aliphatic thermoplastic polyester, produced from renewable resources, has several attractive properties such as biocompatibility, high strength, and thermo plasticity. It has been used in medical applications, such as surgical sutures, implants, tissue culture, and controlled drug delivery, the high stiffness and brittleness at ambient temperatures associated with PLA must be improved to allow for more applications such as packaging food [3-5].
Polylactide (PLA) have been known for several decades but only recently have these polymers gained commercial significance as a leading environmentally benign plastic available from renewable resources. Therefore, it is highly desirable to understand the optical properties of these materials so that they can be manipulated to develop materials of desirable characteristics for a specific objective. Optical properties such as color, clarity, and refractive index are important in dyeing operations for textile and in various packaging applications [6,7]. The absorption and transmission of light by polymers is especially important in the food packaging industry where the packaged goods are light sensitive. Another issue in fresh food packaging is the effect of irradiation in the package since ultraviolet light irradiation is a common method used for lowering microbial population in foods [8,9]. Transparent materials are materials that allow one or more of the frequencies of visible light to be transmitted through them. Several important parameters are currently used to characterize visible light transmission and color of plastics, such as transparency which is defined as the transmission of visible light in the 540–560 nm range. The average

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transparency of food packaging films is around 95% [10,11]. Refractive index is a fundamental physical property of a substance that is often used for its identification, to confirm its purity or to measure its concentration. By definition, the refractive index of a medium is a measure of how much the speed of light is reduced inside the medium. It is a fundamental optical property of polymers that is directly related to other optical, electrical, and magnetic properties. Knowledge about this property is valuable due to its application in the design of new optical polymeric materials. The addition of nanosized inorganic or organic dopants to polymers allows the modification of the polymers' physical properties enabling the realization of functionalized polymers with new application fields, for example, in microoptics [12].

Optical Energy Gap
The experimental results on optical absorption in glassy materials have been reported by Mott and Davis [13,14].
One important difference between amorphous and crystalline solids is that; in the crystalline nonmetallic solids, there is a sharp well defined lattice absorption edge and energy gap (Eg) given by the relation:

$$Eg = hc/\lambda \dots\dots\dots\dots\dots\dots\dots(1)$$

Where: Eg=energy gap, h= Planks constant, c=velocity of light, λ=wavelength.
 The absorption coefficient (α)which is defined as the decrement ratio of incident radiation relative to unit length in the direction of wave propagation inside the medium is relating with the absorbance (A) through the relation:

$$\alpha = \frac{2.303A}{t} \dots\dots\dots\dots\dots\dots(2)$$

Where: (t) is the thickness of sample.
Many researchers put the empirical equation between the optical energy gap(E_g) and energy of the incident photon which is:

$$(\alpha\, h\nu) = B(\, h\nu - E_g)^r \dots\dots\dots\dots\dots(3)$$

Where B is proportion with the inverse of amorphousity, (hν) is the energy of incident photon, which can be calculated using the equation:

$$h\nu = \frac{1240}{\lambda(nm)} \dots\dots\dots\dots\dots(4)$$

r is the order of the optical transition depending on the nature of electronic transition. The transition is called direct if the extremities of V.B and C.B lie at the same K-space, while the transition is called indirect if the transition possible only with phonon assisted ($\Delta k \neq 0$). Thus the value of r may be 1/2,2,3/2, and 3 corresponding to the allowed direct, allowed indirect, forbidden direct and forbidden indirect transition respectively. The extinction coefficient (K) (imaginary part of the refractive index) can be calculated by the relation:

$$k = \lambda\alpha/4K \dots\dots\dots\dots\dots\dots (5)$$

The refractive index (n) can be measured (when the reflectance (R) and (k) are known) by using the equation (6), Where (n) is the refractive index given by:

$$n = \left[\frac{(1+R)^2}{(1-R)^2} - (k^2 - 1)\right]^{1/2} + \frac{1+R}{1-R} \dots\dots\dots\dots (6)$$

R is the reflectance and given by equation:

$$R = (n-1)^2 + k^2 /(n+1)^2 + k^2 \dots\dots(7)$$

The dielectric (ε) is the complex dielectric constant can be introduced by:

$$\varepsilon = \varepsilon_1 - i\,\varepsilon_2 \dots\dots\dots\dots\dots\dots(8)$$

The parameter ε_1 is the real part of dielectric constant, ε_2 is the imaginary part of dielectric constant, from equations (7) and (8) one can obtained:

$$\varepsilon_1 = n^2 - k^2 \dots(9) \quad \varepsilon_2 = 2nk \dots\dots(10)$$

EXPERIMENTAL SECTION

Lactic acid (99.9%), Tin chloride dehydrated ($SnCl_2.2H_2O$) P-toluene sulfonic acid (TSA). Methylene Chloride, Nano silver with particle size (13.69 nm) is shown in Figure 1 measured of nano Ag.

Preparation of Pure PLA and PLA/Sliver Nanocomposites
100 gm of lactic acid acid was mixed with methylene chloride for 5 hrs at reflux temperature without any catalyst. After the removal of water of the condenser, the reaction vessel was cooled at 50°C, the required amount of catalyst $SnCl_2.2H_2O$ (0.5 wt%), TSA (0.4 wt%) were add and this was followed by slow heating of the reaction mixture to

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the refluxing temperature of the solvent under mild stirring with the help of magnetic stirring bar. The temperature gradually increased to 160°C in 3 hrs, and the reaction mixture was stirred continuously. Polymerizations are done at 120-160°C for 5 hrs. At the end of the reaction, the flask was cooled, and the product was dissolved in chloroform and subsequently precipitated in methanol. The resulting solid was filtered and dried Under vacuum at 60°C under vacuum for 24 hrs.
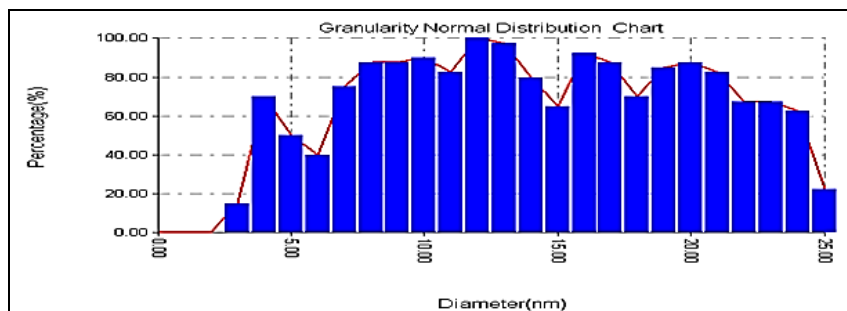

Figure 1: Granularity normal distribution chart for nano Ag

Powder PLA weighted grade (1 wt%) dissolved in chloroform to obtain 20 wt% solution of PLA by slowly in 60°C for 2 hours and cast on glass plates. PLA/ nano silver composite films were prepared by different weight percentages (2, 4 and 6%) nano silver and swollen in chloroform by mixing for 2 hours while polylactic acid dissolved in chloroform then nano solution were mixed by shearing mixer at 800 rpm for one hour to have good distribution and less agglomeration. Then cast on the glass plates and then kept at 60°C in the vacuum oven for 24 hour to ensure complete solvent removal. The thickness of PLA/ silver nanocomposite thickness of 120 μm.

UV-Vis Spectrophotometer
The UV- visible spectra recorded with the help of SHIMADZU UV- in range (300–800) nm. UV spectra gave information about transmission of pure PLA, and PLA/Ag nanocomposites.

RESULTS AND DISCUSSION

Transmission of Pure PLA and PLA/Ag Nanocomposites
Figure 2 shows the variation of transmition as a function of wavelength of pure PLA at UV region is 70% and 87% at visible region. It can be observed from this figures that the transmition increase with increasing of (λ) for all Ag contact this revealed to the smooth reflecting surfaces of the samples and there was not much scattering loss at the surface. In PLA/Ag nanocomposites transparency is an effective index for providing information on the size of dispersed particles in the polymer matrix, typically observing aggregate domains larger than visible wavelength could obstruct light, leading to translucent or opaque films while highly dispersed nanoparticles in a transparent polymer matrix result in optically clear nanocomposites in visible light given that the size of particles is smaller than the wavelength. As shown in Table 1 the transmission at UV and visible spectra (300–800) nm wavelength.
In the visible range (400-700 nm), each wavelength causes a particular sensation of color as the eye is not equally sensitive to light emitted at all wavelength, the transparency of plastic sheeting is defined as the transmission of visible light in the short range of 540-560 nm. The measurement of the transmission percentage at 550 nm reveals that all substrates are transparent with around 87% for the pure PLA that show the highest transmittance, around 80% transmittance for the PLA/Ag at 2% samples and around 70% transmittance for PLA/Ag at 4% and 65% for PLA/Ag at 6% (Table 1).

Optical Energy Gap
Figure 3 represent the optical energy gap for pure PLA and PLA/Ag nanocomposites, for the pure PLA the band was (3.3) eV and decreased from (3.3-2.7) eV this indicated that allowed direct transition is involved which is due to $\Pi - \Pi^*$ transition. The experimental results to calculate the energy gap according to Tauce relation, indicate that the electronic transition for these polymer equal to (r=1/2).

Optical Constant
The optical constants $(n, \varepsilon_1, \varepsilon_2,)$ where determined from both the transmittance (T) and absorbance (A). Figure 4 shows the variation of reactive index (n) for PLA and PLA/Ag nanocomposites calculated from eq.(6) it is found

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that the values of refractive index decreasing slightly with increasing (λ) from (2.65-2.1) this behavior can be explained on the basic of that increasing silver (lowering the packing density) which in turn increase propagation velocity of light through them (Figures 5 and 6).
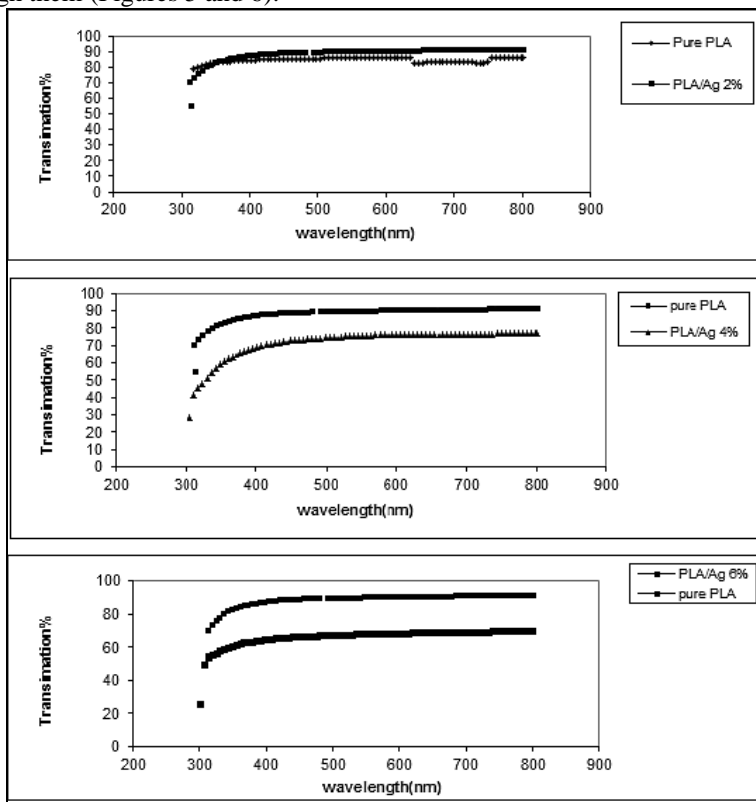

Figure 2: Transmittance as function to wavelength for PLA, PLA/Ag nanocomposites

Table 1: UV-VIS transmission at selected wavelength (300 and 550) nm of pure PLA and PLA/Ag nanocomposites

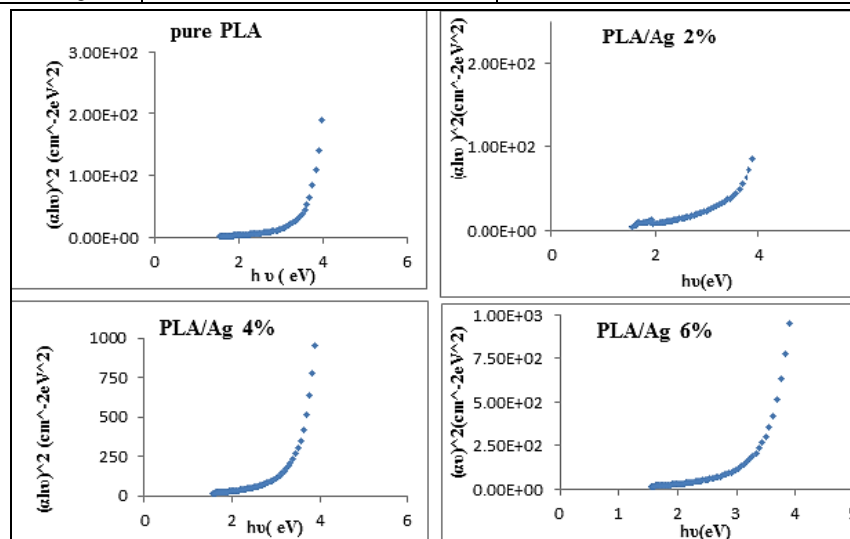| Samples	Transmission in UV at 300 nm %	Transmission in Visible at 550 nm %
Pure PLA	70	87
PLA/Ag2%	68	80
PLA/Ag 4%	40	70
PLA/Ag 6%	50	65

Figure 3: The variation of (α hυ)^2 versus (hυ) for pure PLA and PLA/Ag nanocomposites
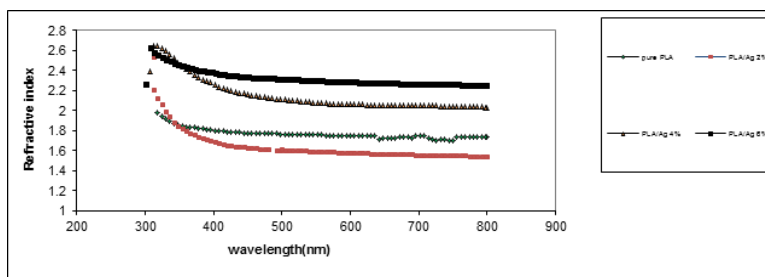
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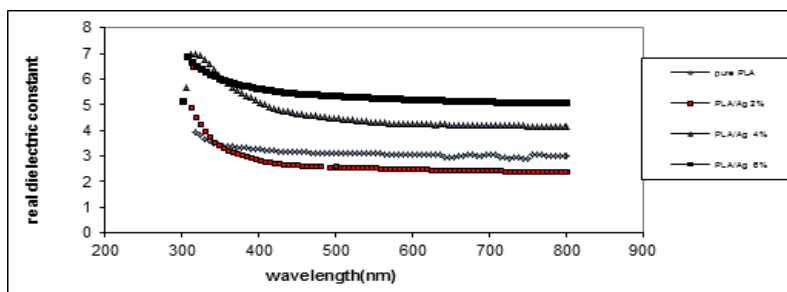**Figure 4: The variation of refractive index (n) versus wavelength for PLA and PLA/Ag nanocomposites**

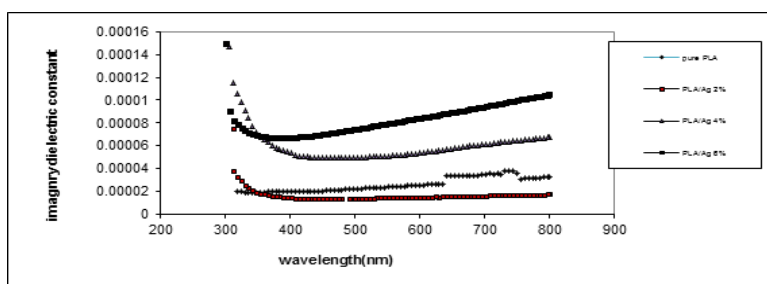**Figure 5: The variation of real part of dielectric constant (ε_1) for PLA and PLA/Ag nanocmposites**

Figure 6: The variation of imaginary part (ε_2) versus wavelength for PLA and PLA/Ag nanocomposites

CONCLUSION

The dielectric constant of real part (ε_1) and imaginary part (ε_2) which depend on the frequency of the electromagnetic waves, the variation of (ε_1) (ε_2) with the wavelength of the incident radiation is due to the change of reflectance and absorbance. It can observe that the variation of ε has similar trend to the variation of (n) because of smaller values of k^2 in comparison with n^2, where $\varepsilon_1 = n^2 - k^2$ while the variation of ε_2 mainly depends on the variation of k values which are related to the variation of α, where $\varepsilon_2 = 2nk$.

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