

The optical properties of (PVA+PVP) + PANI blends

Jinan M. Hassan Jabir

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

E-mail: alnaji.jinan@yahoo.com

Abstract

Polyaniline polymer has been prepared by chemical oxidation polymerization method in laboratory successfully. The PANI and (PVA+PVP) as a polymer blends in different percentage (30%, 50%, 70%) from Polyaniline was prepared. The sample was studied as optical properties by UV-vis spectrophotometer at (400-700) nm. The result of optical energy gap was 2.23 eV for pure (PVA+ PVP) and with additive was increasing with increasing PANI concentration to become (2.49 for 30% to 2.52 for 70%) PANI. The goal of this project is prepare triple blend polymer and study the effect when add conductive polymer (Polyaniline) on the optical properties and calculate optical constant as energy gap, refractive index, dielectric constant and dielectric losses for (PVA+PVP) blends.

Keywords

Polyaniline polymer blends, Optical properties, Optical constant.

Article info.

Received: Jun. 2015

Accepted: Nov. 2015

Published: Dec. 2015

الخواص البصرية للخلائط البوليميرية (PVA+PVP) + PANI

جنان محمد حسن جابر

قسم الفيزياء، كلية العلوم، جامعة بغداد، العراق

الخلاصة

تم تحضير البولي انيلين مختبرياً بواسطة بلمرة الاكسدة الكيميائية وقد تم استخدام البولي انيلين مع البولي فاينيل الكحول وبولي فاينيل بايرولدون لعمل خلطات بوليميرية ذات تراكيز مختلفة من البولي انيلين وبنسب (30%، 50%، 70%). ثم تم دراسة الخواص البصرية للنماذج المحضرة باستخدام uv-vis spectrophotometer للاطوال الموجية من (400-700) نانومتر من الطول الموجي. ان نتائج فجوة الطاقة كانت (2.23 eV) لل (PVA+PVP) ومع زيادة نسبة الخلط بنسب (30%، 50%، 70%) للبوليمر PANI ازدادت فجوة الطاقة تصاعدياً بالقيم التالية (2.49, 2.5, 2.52). ان الهدف من البحث هو تحضير خلطات بوليميرية ثلاثية ودراسة تأثير اضافة بوليمر موصل على الخواص البصرية وحساب الثوابت البصرية مثل فجوة الطاقة، ومعامل الانكسار، وثابت العزل الحقيقي والخيالي للخليط المحضر من (PVA+PVP).

Introduction

A polymer blend or polymer mixture is a member of a class of materials analogous to metal alloys, in which at least two polymers are blended together to create a new material with different physical properties. Polymer blends can be broadly divided in to three categories, immiscible polymer blends, and Compatible polymer blends, Miscible polymer blends.

A Polyvinyl Alcohol is a synthetic resin prepared by the polymerization of

vinyl acetate, followed by partial hydrolysis of the ester in the presence of an alkaline catalyst. The chemical name of Polyvinyl Alcohol is Ethenolhomo polymer and chemical formula is $(C_2H_3OR)_n$ where $R=H$ or $COCH_3$ (randomly distributed). The physical characteristic of the product depend on the degree of polymerization and the degree of the hydrolysis [1].

A polyvinylpyrrolidone (PVP) is

soluble in water and other solvents. When dry it is a light flaky hygroscopic powder, readily absorbing up to 40% of its weight in atmospheric water. In solution, it has excellent wetting properties and readily forms films. This makes it good as a coating or an additive to coatings.

A polyaniline (PANI) has been known for more than a century in its "aniline black" form, an undesirable black deposit formed on the anode during electrolysis involving aniline. Among the conducting polymers, polyaniline is the most promising polymer due to its low cost, ease of preparation, chemical

stability [2], controllable electrical conductivity as well as excellent environmental stability [3]. PANI is represented by the general following formula and structure, where B denotes a benzoidreduced unit and Q is aquinoid oxidized unit, both Q and B = C₆H₄ [4]. PANI is a typical phenylene-base polymer having a chemically flexible-NH-group in the polymer chain flanked on either side by a phenylene ring, Fig. 1 show the Structure of the polyaniline chain [5, 6].

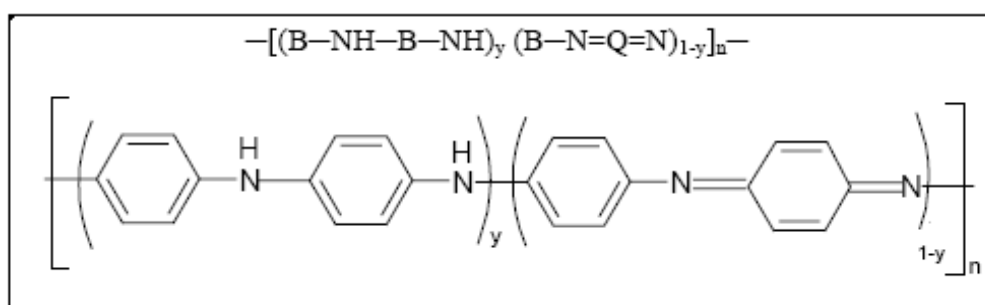


Fig.1: Structure of the polyaniline chain.

Theoretical part

The optical properties of material can be defined as any property that involves the interaction between electromagnetic radiation or light with the matter, including absorption, polarization, reflection, and scattering effects [7].

The optical constants fully describe the optical behavior of materials; they are important and fundamental properties of mater. Knowledge of optical constant of a film from a given material is basic importance in determining the characteristics of light transmission in the film. Such Knowledge of the optical parameters of the material is of importance when designing devices through which electromagnetic radiation absorbed or transmitted.

The absorption coefficient of the material is a very strong function of the photon energy and band gap energy. Absorption coefficient represents the attenuation that occurs in incident photon energy on the material for unit thickness, and the main reason for this attenuation is attributed to the absorption processes. The absorption of light by molecules occurs only if the difference between two energy levels exactly equal to the energy of the incident photon [8].

$$E = hv = E_2 - E_1 \quad (1)$$

where E_2 and E_1 are the energies of single molecules in the final (higher level) and initial (lower level) states, respectively.

Optical constants included refractive index (n), extinction coefficient (k), and real (ϵ_r) and imaginary parts (ϵ_i) of

dielectric constant. The refractive index (n) can be calculated from the following equation [9].

$$n = \left[\left(\frac{4R}{R-1} \right) - K^2 \right]^{\frac{1}{2}} - \frac{(R+1)}{(R-1)} \quad (2)$$

where

R : is the reflectance and given by the equation

$$R = \frac{(n-1)^2 + K^2}{(n+1)^2 + K^2} \quad (3)$$

The extinction coefficient (imaginary part of the refractive index), which is related to the exponential decay of the wave as it passes through the medium and can be determined by using equation

$$K = \frac{\alpha\lambda}{4\pi} \quad (4)$$

Where λ : is the wave length of the incident radiation and the absorption coefficient, α , is given by

$$\alpha = 2.303 \frac{A}{t} \quad (5)$$

where A : is the absorption and t is the sample thickness.

The real and imaginary part of the dielectric constant (ϵ_r and ϵ_i) can be calculated by using equations.

$$\epsilon_r = n^2 - k^2 \quad (6)$$

$$\epsilon_i = 2nk \quad (7)$$

Taucput the empirical equation between the optical energy gap and energy of incident photon which is [10, 11]:

$$\alpha h\nu = D(h\nu - E_g)^r \quad (8)$$

Where D is a constant, $h\nu$ is the energy of incident photon, which can be calculated using the equation $h\nu$ (eV) = $\frac{1240}{\lambda nm}$. And 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 point in k -space, while the transition is called indirect if the transition is 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.

Experimental part

Raw material

We have used the following materials for synthesis the polyaniline. All chemical materials which used in this paper has high purity and which supplied from different companies such as Aniline hydrochloric ($C_6H_5NH_2.HCL$) from Hopkin and Williams, Ammonium persulphate ($(NH_4)_2S_2O_8$) from BDH, (PVA-PVP) from Panreac, Hydrochloric Acid(HCL) from BDH, Acetone from BDH and Dimethyl for Amide (DMF) from (BDH).

Preparation of polyaniline

Pure polyaniline was prepared at room temperature. A three-necked round bottomed flask equipped with a thermometer. Electromagnetic stirrer and condenser were used to polymerize polyaniline. The preparation of (PANI) is based on the oxidation of (0.2M) aniline hydrochloric with (0.25M) ammonium peroxydisulphate in aqueous medium. Both solutions are mixed in a round bottomed flask and gentle stirring to polymerize the mixture. The reaction is found to be exothermic. The mixture was left to rest to the next day. The precipitate (PANI) was collected on filter papers and washed with three 100 ml of (0.2 MHCL) and 150 ml of acetone. After that (PANI) was dried in air for one hour and then in vacuum oven at ($80^\circ C$) for 6 hours. The average yield was (2.3)g.

Preparation of (PVA+PVP) blend

The solutions of (PVA+PVP) were prepared separately. The casting solution was prepared by mixing the appropriate amount of each stock to achieve the desired blend composition, the final concentration of each casting

solution was adjusted to the (30%, 50%, 70%) of PANI, the blend solution was cast onto a glass plate. The 1g of total (PVA+PVP) was dissolved in 10 ml of distal water, the solution was where heated at 60 °C on the magnetic starrier for one hr to allow polymer to dissolve completely to yield clear solution. The PANI solution was prepared by weighted 0.1g of PANI and dissolved in 10 ml of (MDF, die methyelformade) and stirring for 3 hr after allowing them to dissolve completely the three solutions were mixed together.

A glass plate (10 cm) diameter washed with hot water and then cleaned with acetone was used as a substrate. To achieve perfect leveling and uniformly in the thickness of the film the glass plate was kept freely in the air for 24 hr and for another 2 hr in oven and the film was heating at constant temperature (50 °C) to remove the traces of solvent finally, the film was remove from the glass plate and then

was measured by UV-Vis, the absorbance A and transmittance T of the sample were measured in the wave length range (400-700nm) using UV-Vis spectrophotometer model (UV/160) manufactured by Shimadzu Co. (Japan).

Results and discussion

Fig. 2 shows the variation of transmittance of all samples as a function of wave length, when the λ changed from (400-700 nm). We note from the figure, the samples are transmitted in the visible range and value is greater than 70% from the transmittance. The change of transmittance with concentration was not systematic, because the thickness of sample is not the same for all the samples, due to the preparation method (casting method) and we not control on the thickness, but in general the transmitted decreasing with increasing of PANI concentration.

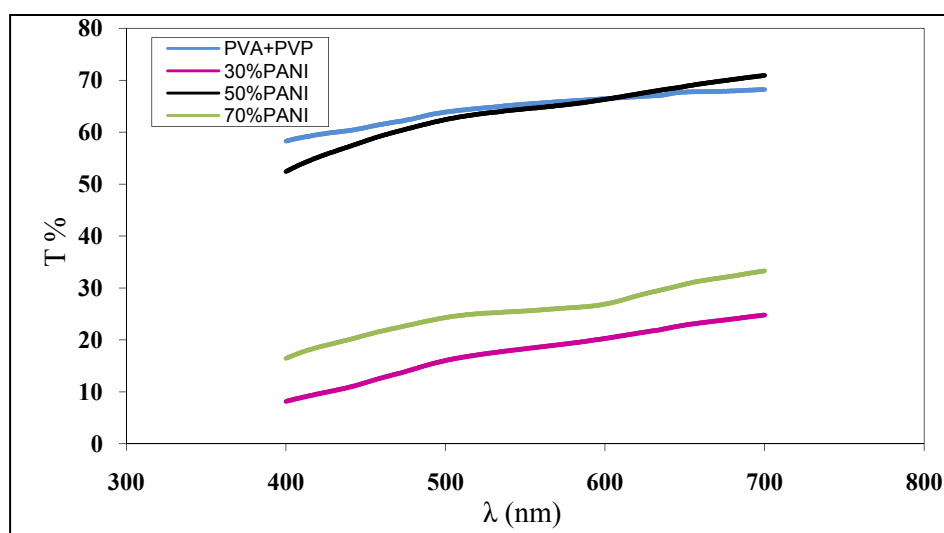


Fig. 2: The transmittance vs. wave length for (PVA-PVP) pure and additive PANI blends polymer.

Fig.3 shows that the variation of absorption of the samples as a function of wave length and show the

absorption beak at (UV) range in the 250 nm. And the absorption decreases in the visible region.

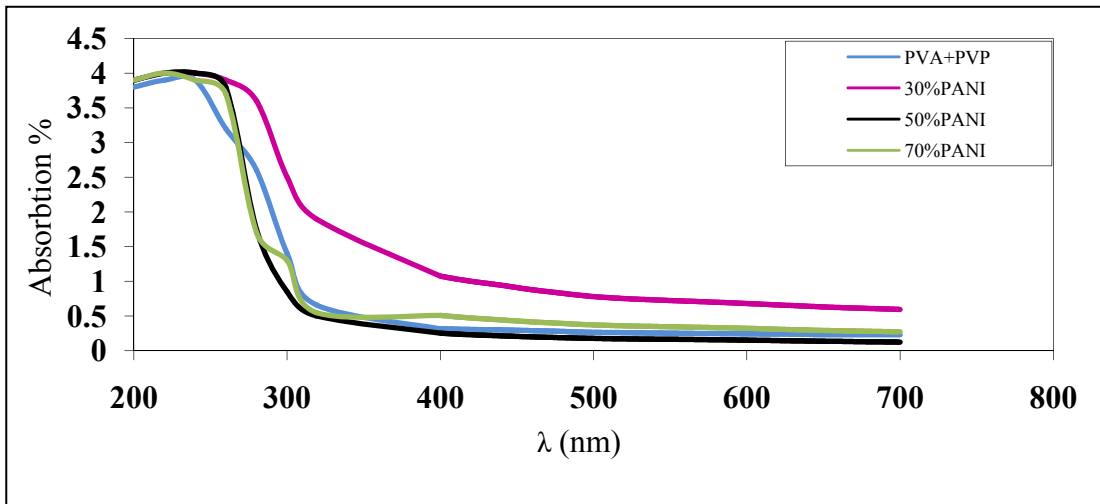


Fig. 3: The absorbance vs. wave length for (PVA-PVP) pure and additive PANI blends polymer.

Fig. 4 shows the variation of $(\alpha h\nu)^3$ with photon energy ($h\nu$) for indirect allowed transition to pure and blends samples and the optical energy gap are determined from this figure as listed in Table 1. From the table the PANI additive increases the optical band gap from (2.3eV to 2.52eV). The

increasing in the optical band gap is probably due to the increasing the legalized state in optical energy gap due to increasing the PANI Concentration, that means the increasing in the optical band gap is probably due to modification of the polymer structure[10, 12].

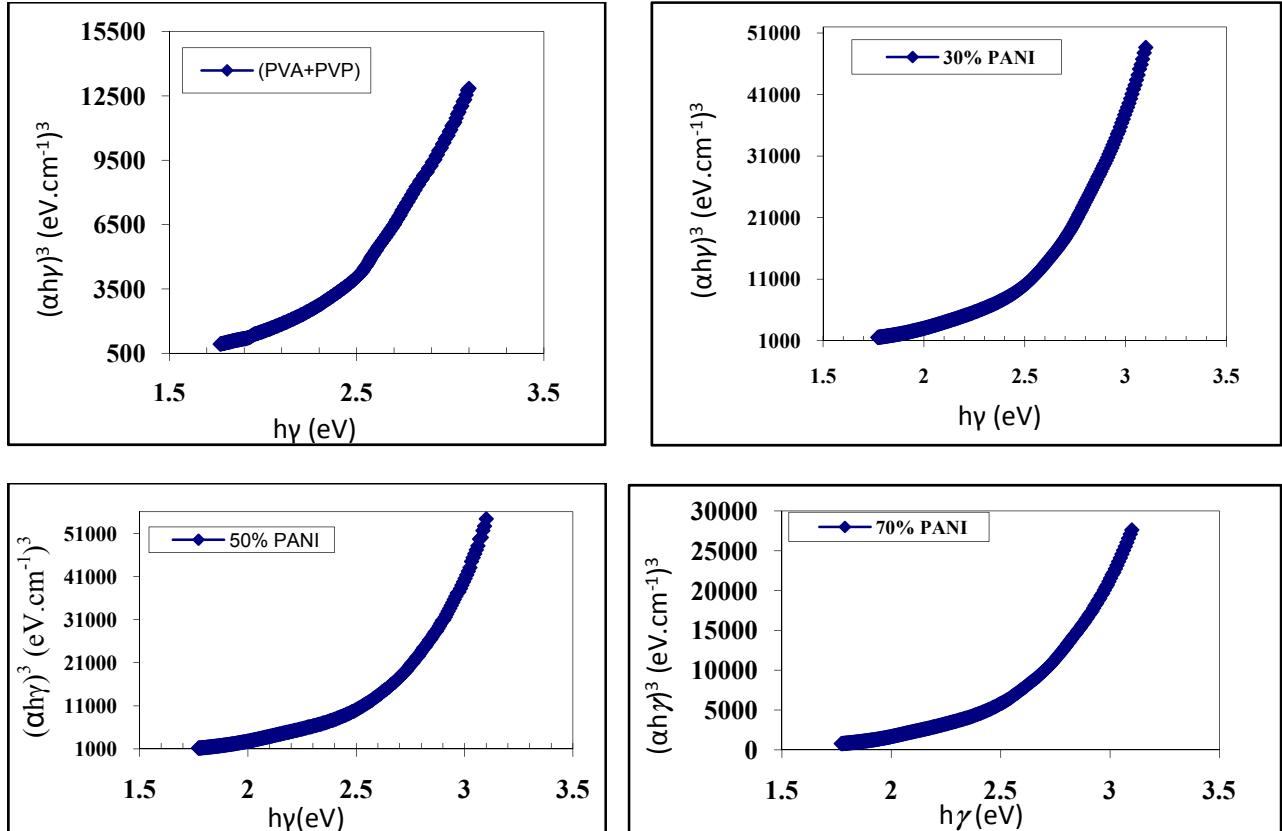


Fig. 4: The $(\alpha h\nu)^3$ vs. ($h\nu$) for (PVA-PVP)+PANI blends polymer prepared with different PANI per-centage as an additive polymer.

Table 1: The optical energy gap of polyaniline and additive level.

PANI content (wt.%)	Optical energy gap(eV)
PVA+PVP	2.23
30% PANI	2.48
50% PANI	2.5
70% PANI	2.52

Fig. 5 shows the dispersion curve of $n(\lambda)$ for pure (PVP+PVA) and blends PANI+(PVA+PVP) samples. The refractive index is as a function of light wavelength. The refractive index increasing in PANI additive has higher

values compared with (PVA+PVP) matrix, in general, the reflective index increases by increasing the C-H bonds, which leads increasing in cross linking in polymer chain[13]. The dependence of the extinction coefficient k on wavelength was carried out using Eq.(4) and depicted in Fig.6. The extinction coefficient for doped sample is increasing for PVP+PVA, The explanation of this behavior of k can be describes to increase of absorption coefficient according to Eq.(4).

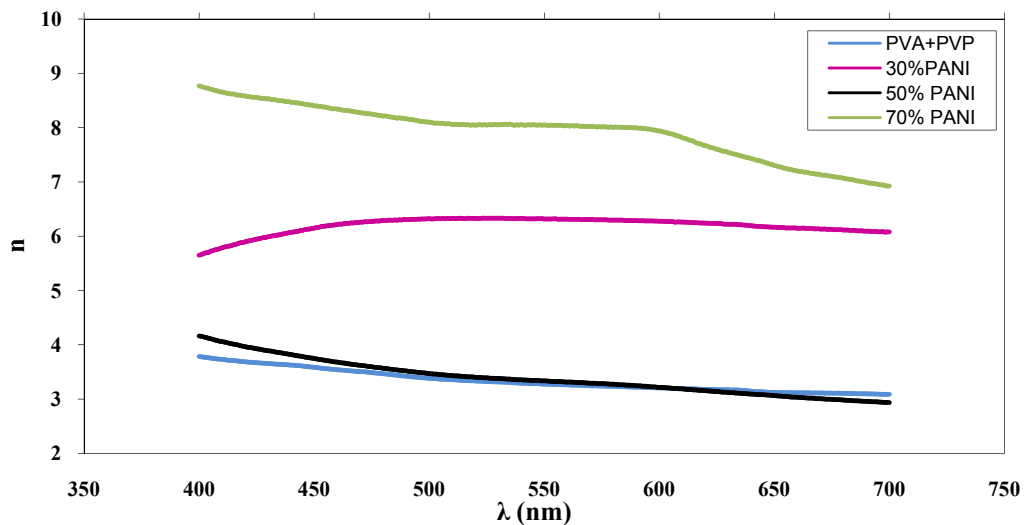


Fig. 5: The refractive index vs. wave length (nm) for (PVA-PVP) +PANI blends polymer.

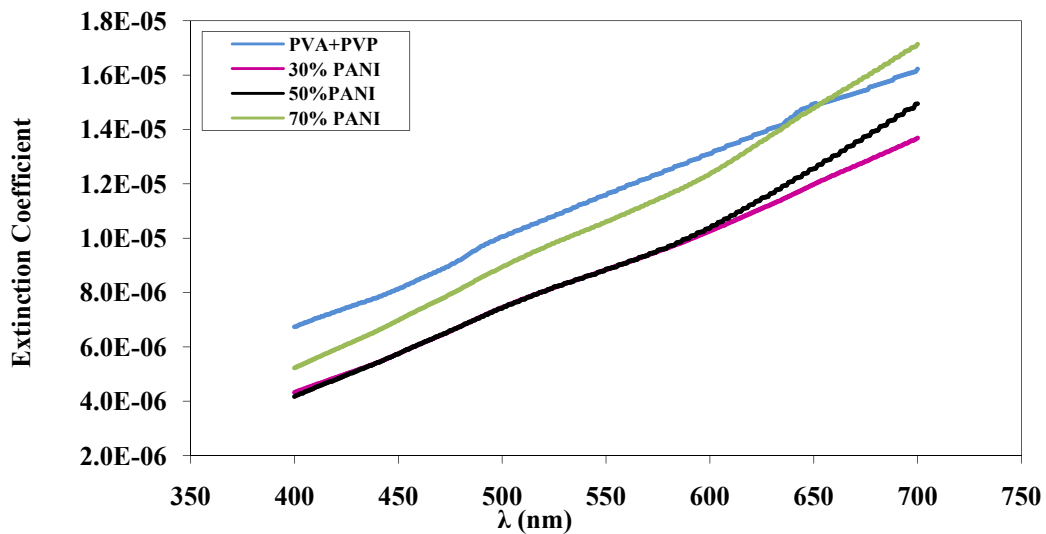


Fig.6: The extinction coefficient (K)vs. wave length (nm) for (PVA-PVP) +PANI blends polymer.

Fig. 7 shows the variation of ϵ_r and ϵ_i as a function of light wavelength in the range (400-700nm) at different PANI percentage in blend samples, at room temperatures. The variation of ϵ_r and ϵ_i , with the increase of wave length of the incident radiation is due to the change of reflectance and absorbance. The increasing of dielectric constant is due to increasing of cross linking polymer chain which leads to increasing the scattering operation which means prevent the dipole alignment with the field (distribution of dipoles) which

leads decreasing the dielectric constant with wave length. The behavior of ϵ_r is similar to that of the refractive index because of the smaller value of k^2 compared with n^2 , while ϵ_i mainly depends on the k value, which is related to the variation of absorption coefficient. In general at higher wave length (interfacial polarization) is caused by the alternating accumulation of charges at interfaces between different phases of the material[14, 15].

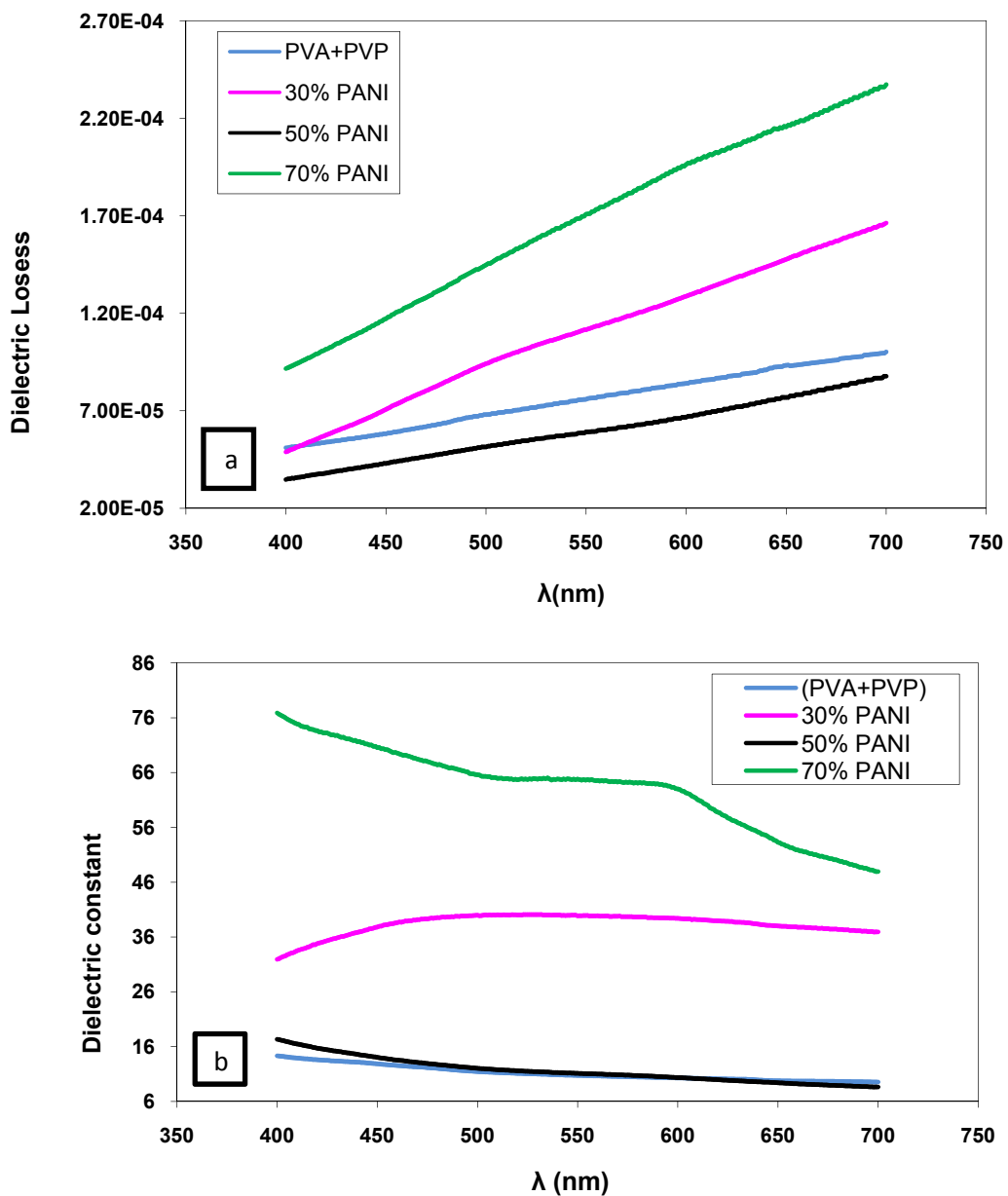


Fig. 7: Dielectric constant, (a) dielectric loss (b) dielectric constant vs. wave length (nm) for (PVA-PVP) + PANI blends polymer.

Conclusions

In this work we have prepared a triple blend (PVA-PVP)+PANI polymers, PVA and PVP was the matrix and we add PANI polymer in different concentrations. Optical properties for (PVA-PVP)+PANI blends have been investigated, the optical energy gap and optical constants such as the reflective index, the extinction coefficient and dielectric constants were determined from the optical transmission and absorption in the wave length range (400-700)nm, the measurements of those parameter are strongly depending on the light wave length. Our results indicate that the samples have allowed indirect transition. Also, it was found that the optical energy gap depends on the percentage of PANI polymer in the blends sample, the refractive index and dielectric constants increased with the increase of the PANI additives.

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