

Enhancement of the solubility of polyaniline and studying the optical properties of (PANI+PVA) polymers blends.

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Abstract

The optical transmission and UV-VIS absorption spectra have been recorded in the wavelength range (200-1100nm) for different composition of polyaniline and polyvinyl Alcohol (PVA) blends thin films. Polyaniline was prepared in acidic medium to enhancement the solubility and processibility, The optical energy gap (E_{opt}) refractive index and optical dielectric constant real and imaginary part have been evaluated. The effects of doping percentage of prepared polyaniline on these parameters was discussed and the non-linear behavior for all these parameters was investigated.

Key words

Optical properties,
PANI-PVA blends,
prepared polyaniline,
Enhancement solubility.

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تحسين الذوبانية للبولي انيلين ودراسة الخواص البصرية لخليط البوليمرات (البولي انيلين + بولي فاينيل الكحول)

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الخلاصة

لقد تم تحضير خلائط من البولي انيلين المحضر بنسب وزنية مختلفة مع بولي فاينيل الكحول. وتم تعيين قيم فجوة الطاقة البصرية و الثوابت البصرية مثل معامل الانكسار و عامل الخمود و غيرها بواسطة النفوذ البصري ضمن مدى الاطوال الموجية (200-1100 نانومتر). لقد تم تحضير البولي انيلين النقي في وسط حامضي من حامض الكبريتيك و بتركيز 2 مولاري لغرض تحسين الذوبانية اشارت النتائج الى ان البولي انيلين ولمختلف النماذج تمتلك الانتقال المباشر المسموح. وكذلك وجد بأن فجوة الطاقة البصرية تعتمد على شروط التحضير و النسبة المئوية الوزنية من البولي انيلين.

Introduction

Conducting polymers have become very popular in the field of material science due to their promising and novel electrical and optical properties. Preparation of blends of polyaniline (PANI) has been considered to improve the processability of PANI. These blends have the ability to enhance their material properties with desirable mechanical and physical characteristics (Raghavendra et al. 2003)[1]. PANI is a unique and one of the technologically promising

conducting polymers because of its ease of preparation, low cost, high environmental stability, and relatively stable electrical conductivity and especially for its very simple acid doping and base de-doping chemistry [2]. Since the conductivity of PANi depends on both the oxidation state of the main polymer chain as well as the degree of protonation of the imine sites (MacDiarmid 2001)[3], polyaniline can be prepared in three major forms that differ in the degree of oxidation (Y) (the ratio of amine nitrogen over

the total number of nitrogen atoms). For the fully reduced Leucoemeraldine base (LEB) that, Y is one, the half oxidized emeraldin base (EB), Y is 0.5 and for fully oxidized Pernigraniline base (PNB), Y is 0 as in Fig. 1 [4,5]. Polyaniline is an insulator in each of these forms with a band gap around

3.6eV. These polymers can also exist in the corresponding protonated (salt) forms but only emeraldin salt (ES) has shown high electrical conductivity [6]. The structure of the Polyaniline (PANI) chain can be expressed by the general formula [7].

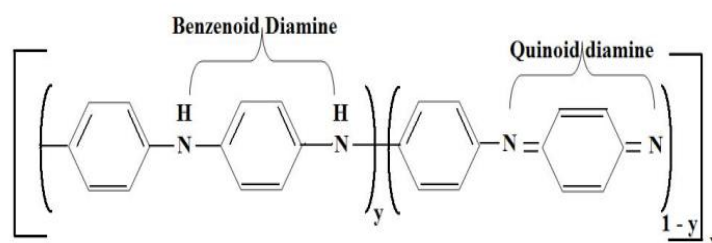
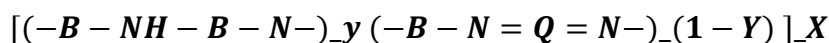


Fig. 1: The structure of the polyaniline chain [7].

where B and Q denote the C₆H₄ ring in benzenoid and quinoid form. y denotes the oxidation state varying from zero to 1. Polyaniline is a P-type material, which indicates that the carriers charge transfer (holes) take place in the valence band and the charge carriers are holes [5]. Polyaniline can be obtained by chemical and electrochemical synthesis [8]. PANi has a great variety of potential applications including anticorrosion coatings, batteries, sensors, separation membranes and antistatic coating (Chandrasekhar 1999). Organic light emitting diodes [9-10].

Experimental

This part presents raw materials and preparation method used to prepare PVA/PANI blends in different weight present.

Raw materials

The raw material used to prepare the samples were: aniline hydrochloride (C₆H₅ NH₂.HCl) as a monomer, supplied by Hopkin and Williams company and purity 99.999%, Ammonium persulfate

(NH₄)₂S₂O₄ supplied by BDH company and purity 99.95%, Polyvinyl alcohol (PVA) water-soluble powder of molecular weight (MW 14000) and purity 99.9%, supplied by Merck Schuchardt OHG. Hohenbrunn, Germany.

Preparation of polyaniline

The preparation of (PANI) is based on the oxidation of (0.2M) aniline hydrochloride with (0.25M) ammonium peroxy disulfate in aqueous medium. The monomer was dissolving in (1M) H₂SO₄ solution in a volumetric flask to 50 ml, ammonium peroxy disulfate is similarly dissolved in (1M) H₂SO₄ also to 50ml of solution both solution are mixed at (0 °C) in a rounder, and gentle stirring to polymerize the mixture is left to rest to the next day. The (PANI) precipitate is collected on a filter and washed with 300ml of (0.2M) HCl, and 150ml of acetone. Polyaniline (emeraldin) hydrochloride powder is dried in air about one hour and then in vacuum oven about (80 ° C) for 6 hours the average yield is (1.95) g. The solution of PANI and PVA were prepared

separately. The casting solution was prepared by mixing the appropriate amount of each stock solution to achieve the desired blend composition. The final concentration of each casting solution was adjusted to the (30%, 50%, 60%) of PANI, the blend solution was cast onto a glass plate.

Preparation of PVA PANI blends

The 1.00g of PVA was dissolved in 10ml of distilled water, the solution was where heated at 70°C on the magnetic stirrer for one hr to allow polymer to dissolve completely to yield clear solution.

The PANI solution was prepared by weighting 0.1 g of PANI and dissolving it in 10ml of distilled water and stirring for 3 hr. the solution was mixed with PVA solution to get the blend samples in different percentage.

A glass plate (10cm) diameter washed with hot water and then cleaned with acetone was used as a substrate. To achieve perfect leveling and uniformity in the thickness of the film the glass plate was kept freely in the air for 24 hr and for another 2hr in oven. Then the film was heated at constant temperature (50 C°) to remove the traces of water. Finally, the film was removed from the glass plate and then was examined by UV-Vis, spectroscopy. The optical absorption spectra and transmittance were recorded at room temperature in the wavelength region (200-1100nm). UV-Vis spectrophotometer model UV/160 manufactured by Shimadzu Co. (Japan). From these spectra, optical constant such as optical energy band gap (E_g) and reflective index, optical dielectric constant have been determined.

Basic relations

The complex refractive index N is given by

$$N = n - ik \quad (1)$$

where, (n) is the real refractive index, and extinction coefficient (k) which is the imaginary part of N and can be obtained from the relation

$$k = \frac{\alpha\lambda}{4\pi} \quad (2)$$

where, α is the absorption coefficient which is the decrement ratio of incident radiation relative to unit length in the direction of wave propagation inside the medium. λ is the wavelength. The reflectance part (R) of incident electromagnetic plane wave can be obtained when the transmittance (T) and the absorbance (A) part are known since

$$R = 1 - (A + T) \quad (3)$$

For normal incident of plane electromagnetic wave the reflectance is given by the equation (4)

$$R = \frac{(n + 1)^2 + k^2}{(n - 1)^2 + k^2} \quad (4)$$

which leads to

$$n = \sqrt{\frac{4R}{(R - 1)^2} - k^2} - \frac{R + 1}{R - 1} \quad (5)$$

thus n can be calculated when the reflectance R and k values are known.

The transmittance part of incident light is depending on α through the following equation [11]

$$I = I_0 \exp(-\alpha d) \quad (6)$$

where d is the thickness of the sample. Thus the absorption coefficient α that is corresponding to any wavelength λ , can be calculated by applying the relation:

$$\alpha = \frac{1}{d} \ln \left(\frac{I_0}{I} \right) \quad (7)$$

The dielectric constant ϵ which represents the responsiveness of electron in matter to be the incident electromagnetic field, depends on frequency [11]. Its real part is ϵ_1 which represents the polarization term and its

imaginary part ε_2 can be calculated from equation.

$$\varepsilon_1 = n^2 - k^2 \text{ and } \varepsilon_2 = 2nk \quad (8)$$

Tauc [12] put the empirical equation between the optical energy gap and energy of incident photon which is

$$\alpha h\nu = A(h\nu - E_g)^r \quad (9)$$

where A is a constant, $h\nu$ is the energy of incident photon, which can be calculated using the equation $h\nu = 1240/\lambda(\text{nm})$. 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 ($\Delta k \neq 0$) [13]. 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.

Result and discussion

Fig.2 presents the absorption spectra of samples as a function of wave length. It can be stated that the samples have absorbing beak at 220nm and another at 280nm. The intensity of these beak increased with increased of PANI concentration .also Fig.2 shows the spectra have low absorbance in the visible and near infrared region.

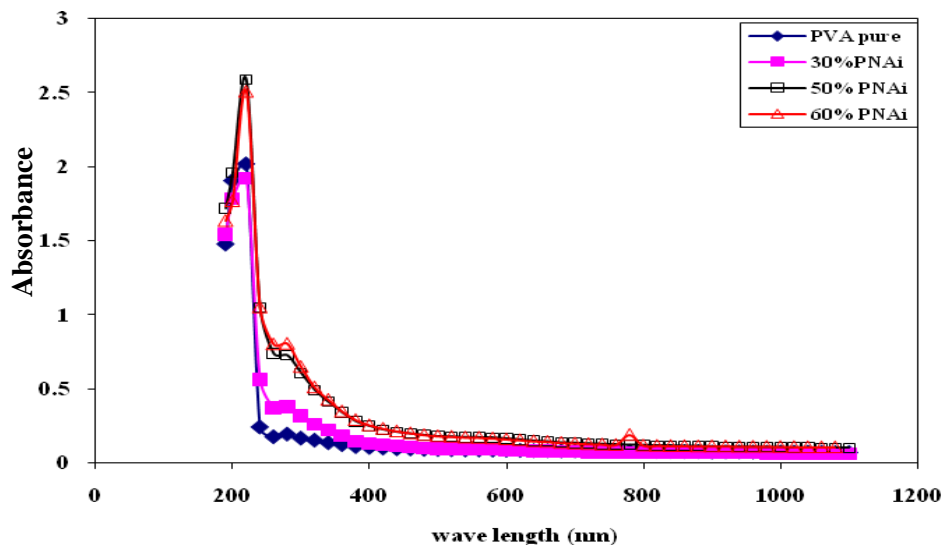


Fig. 2: Absorption spectra of the samples.

Fig. 3 shows the variation of transmittance of the samples as a function of wave length. From the figure, the samples show good transmittance in the visible and near infrared region. The PVA pure was show higher transmittance than blend

sample, when increased PANI concentration in polymer blends the transmittance decreasing because , the polymer blends will be opaque due to the increasing in cross linking between polymers chine.

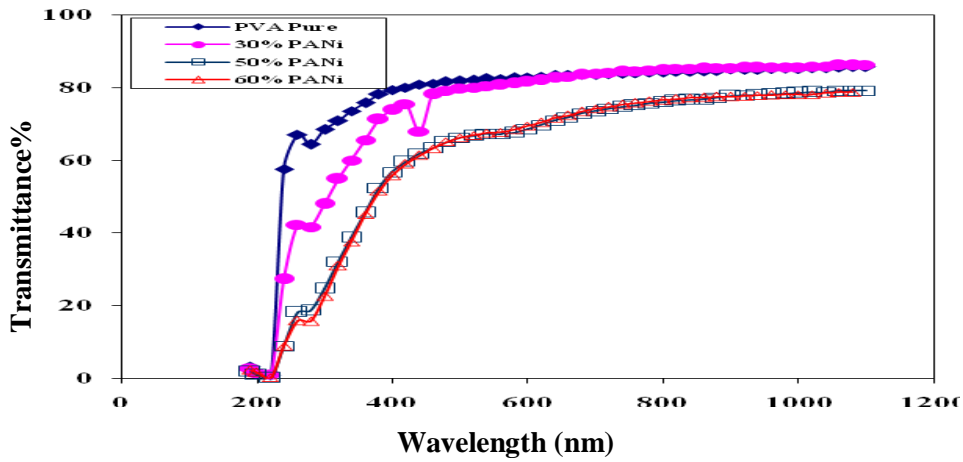


Fig. 3: Transmittance of the blend samples.

Optical energy gap

Fig. 4 shows the variation of $(\alpha h\nu)^2$ with photon energy ($h\nu$) for direct allowed transition to pure and blends samples. The optical energy gap determined from this figure. Extrapolation of the line to the $h\nu$ axis

gives the band gap. are listed in Table1. From the table the PANi blending decreases the optical band gap from (4.2 eV to 2.9 eV). This is due to the increase of the density of localized states in the E_g [14].

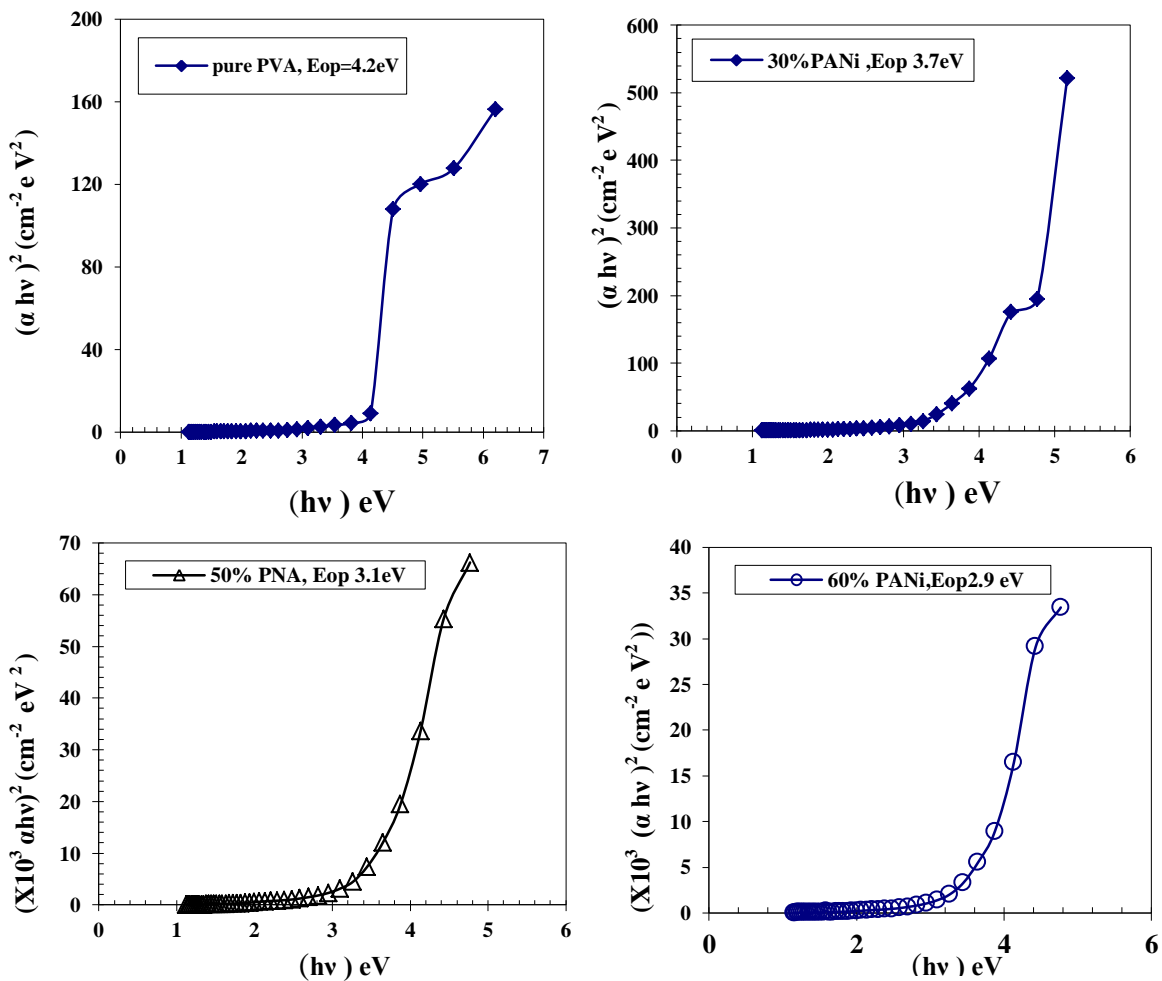


Fig. 4: $(\alpha h\nu)^2$ vs. $(h\nu)$ for (PVA +PNAI) blends polymer prepared with different PNAI percent.

Table 1: The optical energy gap of polyaniline and blending.

PNAI content (wt.%)	Optical energy gap (eV)
Pure PANI	2.70
Pure PVA	4.20
30% PANI	3.70
50% PANI	3.1
60% PANI	2.90

Table1 shows the relation between the energy gap and the concentration percentage of PANI. It can be seen that all samples show one direct optical energy gap. We have found that the energy gap decreases with the concentration percentage of PANI, this decreasing in the optical energy gap can be explained. The addition of PANI, increases the degree of disorder and increasing the cross linking, then. Increasing the degree of disorder causes the band tail to decrease which, according to the electronic structure of amorphous materials, will

lead to an decreasing of the estimated optical energy gap [15].

Refractive index

The dispersion curve of $n(\lambda)$ is presented in Fig. 5 for pure and blends of (PANI+ PVA) samples. The refractive index is a function of light wavelength. The refractive index increases with increasing the percentage of polyaniline in blend samples. The refractive index increases by increasing the C – H bonds[16], and increasing the cross-linking that prevent the propagation of the light wave, i.e decreasing the speed of light in the sample.

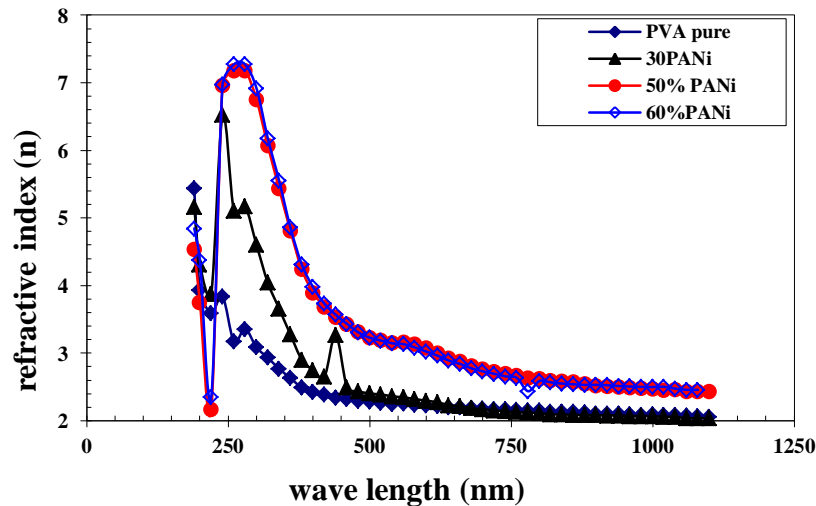


Fig. 5: Refractive index vs. wave length (nm) for (PVA +PNAI) blends polymer prepared with different PNAI percentage as a blending.

Dielectric constants

The dielectric constant (ϵ) consists of a real part (ϵ_r) and a imaginary part (ϵ_i) which depends on the frequency of the

electromagnetic wave. The variation of ϵ_r and ϵ_i versus wavelength in the range 200-1100nm at different PNAI percentage in blend samples, at room

temperatures, is shown in Fig.6. The variation of ϵ_r and ϵ_i with the increase of the wavelength of the incident radiation is due to the change of reflectance and absorbance [17]. 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.

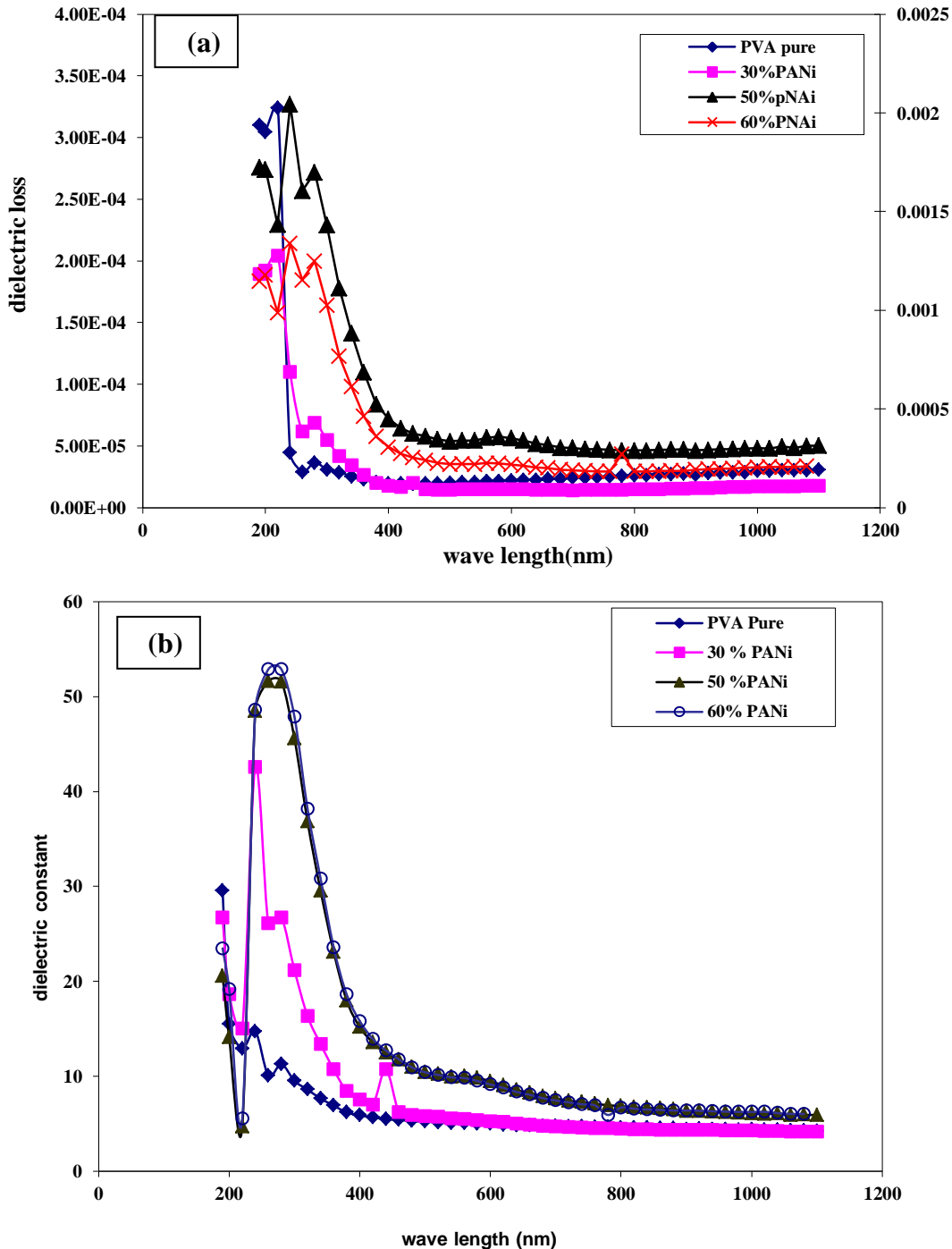


Fig. 6: Dielectric constant, (a) dielectric loss, (b) dielectric constant b vs. wave length (nm) for (PVA +PNAI) blends polymer.

Conclusions

In this work, blends samples have prepared from PANI, PVA polymers by using the casting method. These result showed optical absorption edge and direct optical energy gap have decreased which attributed to the increased blending concentration wt%. The minimum optical energy gap values (2.7 eV for PANI pure and for PVA was 4.2 eV, this value decreasing when adding PANI to PVA to become 2.9 eV at 60%. Refractive index, real and imaginary part of dielectric constant are increasing with increase in the PANI content.

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