

Synthesis and Modified of Poly(Vinyl chloride) Contains Triazole Moieties and Studying the Optical Properties of New Polymers

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Abstract

New modified poly(vinyl chloride) was prepared by reacting of PVC with heterocyclic compounds that have thiole group (SH) in tetrahydrofuran as solvent. Heterocyclic compounds were characterized by FTIR, ^1H NMR spectroscopy and CHN analysis, while the new polymers have been characterized by FTIR spectrophotometers; the optical properties of synthesized new polymers were studied.

Keywords: PVC, five member ring, optical absorption, modified polymers and heterocyclic compounds.

Introduction

Poly (vinyl chloride) is the greatest synthetic and used material, its use in many applications such as building, Industry and medicine [1,2]. The multiple uses because of its cheap price find us trial polymer, the unmodified polymer is brittle and sensitive to factors and weather conditions which that making it sometimes useless material[3,4]. Modification of polymers has received greater attention as it brings specific properties to the modified material, such as enhanced thermal stability, multiphase physical responses, compatibility, impact response, flexibility, and rigidity [5]. Therefore the use of the variety modifiers in PVC to prevent crack and toughness of polymers. Uses two types of molecules which elastomers and core-shell rubber are the most common modifiers. Chlorinated polyethylene adapt well with PVC where a high degree diffusion in polymer which increases the impact properties [6,7]. Optical properties of polymer films are very important for many technological applications [8], ranging from protective coatings to paintings, microelectronic, semiconductors, and optoelectronic devices depending on the reflectance and transmittance properties of the films during their preparation [9,10].

Experimental

Materials and reagents

All reagents were obtained commercially (Aldrich and Fluka) and used without further purification. Solvents used in the synthesis

were distilled from appropriate drying agent immediately prior to use.

Spectrophotometer analysis

Elemental analysis (CHN) were carried out on a Heraeus instrument (Vario EL). FTIR spectra were recorded as KBr discs using a Shimadzu 8400 S FTIR spectrophotometer from 4000-400 cm^{-1} . ^1H NMR spectra were acquired in DMSO- d_6 solution using a Jeol 400 MHz spectrometer with tetramethylsilane (TMS) as an internal standard for ^1H NMR analysis.

Synthesis

Synthesis of Benzoic acid hydrazide (1) [11]

A mixture of (3 ml.) of hydrazine hydrate (80%) and (5 ml., 0.0399 mol.) of methyl benzoate was refluxed for (4 h.). Then (5 ml.) of ethanol was added and refluxed for (1 h.). After cooling, the product was filtered off. Recrystallized from ethanol, yield (91%).

FTIR: 3298-3199 (NH_2), 3018 (C-H aromatic), 1660 and 1610 ($\text{C}=\text{O}$ amide).

Synthesis of 4-Amino-5-phenyl-4H-1, 2, 4-triazole-3-thiol (2)[11]

Compound (1) (5 g., 0.0367 mol.) was dissolved in absolute ethanol (25 ml.) with (2.05 g., 0.0367 mol.) of potassium hydroxide. The mixture was stirred for (15 min.). Carbon disulphide (2.17 ml., 0.0367 mol.) was added, and continues stirring until the solution become homogenous with evaluation of hydrogen sulfide then added (5 ml.) of ether and stirring the solution for (15 min.), after that reaction

mixture was filtered and dried, washed with ether (2 × 10 ml.), dried to give potassium xanthate.

Hydrazine hydrate (80%), (5 ml.) was added to potassium xanthate product, the suspension mixture was refluxed with stirring, the solution became homogenous with evolution of hydrogen sulfide. The reaction was stopped when hydrogen sulfide ceased (lead acetate paper). The reaction mixture was filtered then diluted with cold water (10 ml.) and acidified with concentrated of hydrochloric acid to give a white precipitate. Recrystallized from (ethanol), yield (76%). FTIR: 3256-3186 (NH₂), 3023 (C-H aromatic), 2534 (S-H), 1619 (C=N). ¹H NMR (ppm): 7.6 (m, 5H, Ar-H), 7.8 (s, 2H, NH₂), 14.4 (s, 1H, S-H). C H N, Calculated (%): C, 49.98; H, 4.19; N, 29.14; S, 16.68; found (%): C, 50.02; H, 4.41, N, 28.99; S, 17.01.

General procedure for synthesis of Schiff bases (3)-(7)[11]

A mixture of compound (2) (1 g., 0.0005 mol.) with appropriate aromatic aldehyde in absolute ethanol (20 ml.) and two drops of glacial acetic acid was refluxed for (7 h.). The mixture was cooled to form the precipitate, recrystallized from ethanol. The physical properties for the synthesized compounds (3)-(7) are shown in Table (1).

¹H NMR, compound (3), δ(ppm): 7.30-7.89 (m, 10H, Ar-H), 10.33 (s, 1H, N=CH), 14.80 (s, 1H, SH). C H N, compound (3), Calculated (%): C, 64.26; H, 4.31; N, 19.98; S, 11.44; found (%): C, 64.30; H, 4.55, N, 20.09.; S, 11.84.

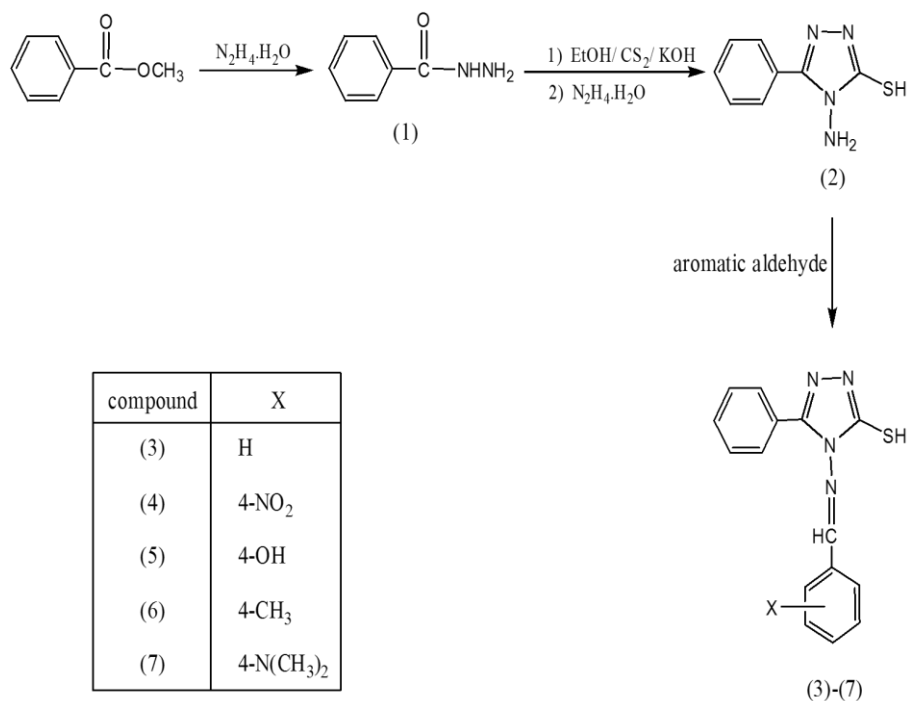
¹H NMR, compound (4), δ(ppm): 7.27-7.96 (m, 9H, Ar-H), 10.33 (s, 1H, N=CH), 13.91 (s, 1H, SH). C H N, compound (4), Calculated (%): C, 55.38; H, 3.41; N, 21.53; O, 9.84; S, 9.86; found (%): C, 55.41; H, 3.51, N, 21.50; O, 9.90; S, 9.81.

Table (1)
Physical data of compounds (3)-(7).

| Comp. No. | X | Molecular Formula | Molecular weight | Yield % |
|-----------|------------------------------------|---|------------------|---------|
| (3) | H | C ₁₅ H ₁₂ N ₄ S | 280.35 | 82 |
| (4) | 4-NO ₂ | C ₁₅ H ₁₁ N ₅ O ₂ S | 325.35 | 87 |
| (5) | 4-OH | C ₁₅ H ₁₂ N ₄ OS | 296.35 | 81 |
| (6) | 4-CH ₃ | C ₁₆ H ₁₄ N ₄ S | 294.37 | 73 |
| (7) | 4-N(CH ₃) ₂ | C ₁₇ H ₁₇ N ₅ S | 323.42 | 76 |

Table (2)
FTIR data of compounds (3)-(7).

| Comp. No. | X | ν C-H Aromatic cm ⁻¹ | ν S-H Very week cm ⁻¹ | ν C=N str. Exocyclic cm ⁻¹ | ν C=N Endocyclic cm ⁻¹ | Others cm ⁻¹ |
|-----------|------------------------------------|---|--|---|---|-------------------------------|
| (3) | H | 3099 | 2621 | 1650 | 1589 | - |
| (4) | 4-NO ₂ | 3054 | 2587 | 1652 | 1560 | NO ₂ 1524, 1348 |
| (5) | 4-OH | 3037 | 2560 | 1655 | 1597 | O-H 3372 |
| (6) | 4-CH ₃ | 3023 | 2586 | 1659 | 1564 | C-H aliphatic 2939 |
| (7) | 4-N(CH ₃) ₂ | 3069 | 2643 | 1624 | 1577 | C-H aliphatic 2924 |



Scheme (1) Synthesis route of compounds (1)-(7).

Synthesis of Modified Polymers PVC + (3)-PVC + (7)

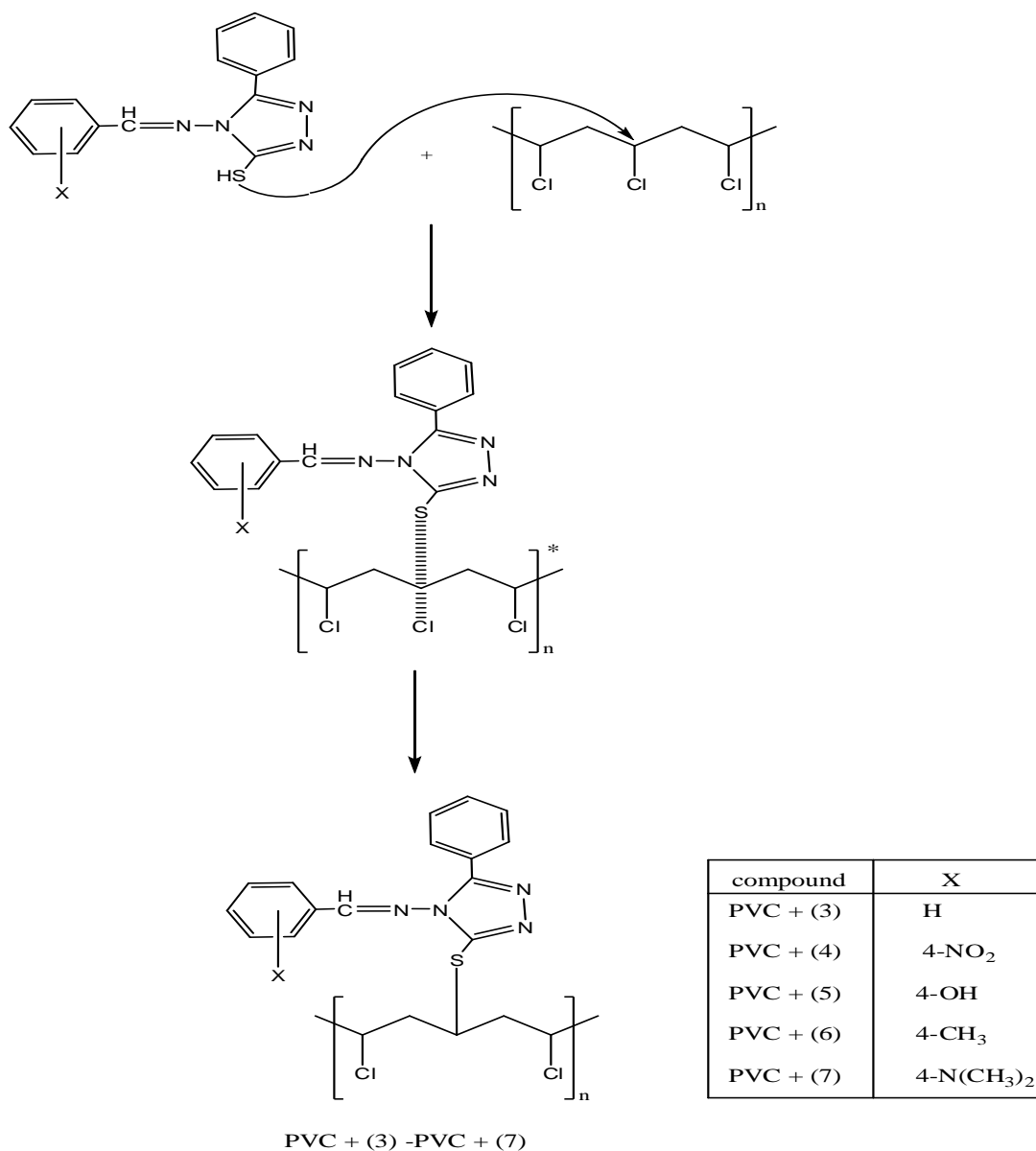
Synthesis of modified poly vinyl chloride by dissolving (0.1 g.) of pure poly(vinyl chloride) in (20 ml.) of tetrahydrofuran with (0.1 mol.) of compounds (3)-(7) respectively. The reaction mixture was heated under reflux, after (5 h.), the hot mixture was transferred to casting molds to preparation of films for modified polymers.

Films Preparation

(0.5%) concentrations of poly vinyl chloride solution in tetrahydrofuran were used to prepare 30 micrometer thickness of polymer films, (measured by a micrometer type 2610 A, Germany). The films were prepared by evaporation technique at room temperature for (24 h.). To remove the possible residual tetrahydrofuran solvent, film samples were further dried at room temperature for three hours under reduced pressure.

Table (3)
FTIR data of modified polymers PVC + (3)-PVC (7).

| Comp. No. | X | $\nu\text{C-H}$ Aromatic cm^{-1} | $\nu\text{C-H}$ Aliphatic cm^{-1} | $\nu\text{C=N str.}$ Exocyclic cm^{-1} | $\nu\text{C=N}$ Endocyclic cm^{-1} | $\nu\text{C-Cl}$ cm^{-1} | Others cm^{-1} |
|-----------|------------------------------------|---|--|---|---|-----------------------------------|-------------------------------|
| PVC + (3) | H | 3078 | 2940 | 1617 | 1556 | 690 | - |
| PVC + (4) | 4-NO ₂ | 3065 | 2901 | 1656 | 1561 | 683 | NO ₂ 1529, 1355 |
| PVC + (5) | 4-OH | 3022 | 2984 | 1632 | 1545 | 691 | O-H 3320 |
| PVC + (6) | 4-CH ₃ | 3101 | 2924 | 1689 | 1554 | 675 | - |
| PVC + (7) | 4-N(CH ₃) ₂ | 3044 | 2955 | 1635 | 1583 | 688 | - |



Scheme (2) Synthesis route of modified polymers PVC + (3)-PVC + (7).

Optical properties measurements

Optical transmittance and absorbance were recorded in the wavelength range (200-800) nm using computerized UV- visible spectrophotometer (Shimadzu UV-1601 PC). Optical transmittance and absorbance were reported in order to study the effect of modified polymers on the parameters under investigation.

Results and Discussion

The reaction was initiated by the attack of the lone pair of sulfur atom on the carbon carrying chlorine atom in the polymeric chain followed by departure of chloride anion as a good leaving group (nucleophilic substitution

reaction). The structure of the modified polymers was established on the basis of its FTIR spectroscopy, each of the present polymers showed other bands characteristic of its structure. The successful modification of PVC with different triazole compounds can be demonstrated by FTIR spectroscopy. absence of absorption bands due to (-SH) stretching frequencies of triazoles, clearly indicated the reaction between PVC and prepared compounds (3)-(7), these compounds clearly revealed the characteristic vibrations of the C-H aromatic, C=N exocyclic and endocyclic ring.

The optical properties of films by means of optical absorption in the UV-Vis region of

(200-800) nm have been investigated; Fig.(1) shows the dependence of absorbance on wavelength. It is observed that in the visible region of all films have very low transparent, then absorbance is rapidly decreased with increasing wavelength. This behavior may be attributed to perfection and stoichiometry of the films. Also it can be observed from the Fig. (1) that the absorbance increased with increasing the doping of compounds PVC + (3)-PVC + (7). It has been observed that the absorption peaks appears at wavelengths 205, 300, 310, 320 and 325 nm as the concentration polymers PVC + (3)-PVC + (7) mol/L in Poly vinyl chloride matrix respectively. The shifting occurred in the spectra may be due to the polarity of solvent used in the synthesis or may be due to the dispersion of rare earth oxide particles in the PVC matrix.

From the transmittance data and according to Tauc relation [12-13], the most satisfactory representation is obtained by plotting the quantity $(\alpha h\nu)^2$ as a function of $(h\nu)$. The plot of $(\alpha h\nu)^2$ versus $h\nu$ for different modified poly vinylchloride percentage in samples are shown in Fig. (2). The observed behavior suggests allowed direct transition for amorphous material [14-18]. The values of optical energy gap E_{opt} obtained from the extrapolation of the linear region are found to be decrease from 5.2 to 3.2 eV with increasing the percentage of PVC + (3)-PVC + (7). The Fig.(2) shows that a linear dependence for pure PVC in one region representing one optical absorption edge as mentioned before in previous work [19]. The value obtained in this work is close to others previously reported for the forbidden direct transition.

The refractive index is an important parameter for optical materials and applications. Thus, it is important to determine optical constants of the films. The refractive index of the films was determined from the following relation [20].

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

Where k is the extinction coefficient ($k = \alpha\lambda/4\pi$). n and k values dependence of wavelength are shown in Figs.(3) and (4) respectively. As seen in these figs., n and k

values increase with increasing the doping concentration of modified polymers PVC + (3)-PVC + (7). Such behavior corresponds to the density of absorbing centers such as impurities absorption, excitation transition, and other defects in the crystal lattice dependent on the conditions of sample preparation.

The dielectric constant is defined as $\epsilon(\omega) = \epsilon_1(\omega) + i\epsilon_2(\omega)$, real and imaginary parts of the dielectric constant are related to the n and k values. The ϵ_1 and ϵ_2 values were calculated using the formulas [21].

$$\epsilon_1 = n^2 - k^2 \quad \dots\dots\dots (2)$$

$$\epsilon_2 = 2nk \quad \dots\dots\dots (3)$$

The ϵ_1 and ϵ_2 values dependence of photon energy are respectively shown in Figs.(5) and (6). The ϵ_1 values are higher than that of ϵ_2 values. It is seen that the ϵ_1 and ϵ_2 values increase with increasing the doping concentration with new polymers PVC + (3)-PVC + (7).

The values of real and imaginary parts of the dielectric constant at 400 nm for pure new polymers PVC + (3), PVC + (4), PVC + (5), PVC + (6) and PVC + (7) content were 1.3, 1.59, 3.52, 4.38, 4.47, and 4.63 and 0.000031, 0.000133, 0.00089, 0.00130, 0.00183 and 0.000239 respectively.

The optical conductivity was calculated using the relation (4).

$$\sigma = \alpha n c / 4\pi \quad \dots\dots\dots (4)$$

Where c is the velocity of light.

It was observed that the optical conductivity increases as the percentage of synthesized polymers PVC + (3)-PVC+ (7) in the sample increase. It can be notice from the Fig. (7) that the optical conductivity for all films increased in the high photon energies region and decreased in the low photon energy region, this decrease is due to the low absorbance of the films in that region.

The skin depth could be calculated using the following relation.

$$\chi = \lambda / 2\pi k \quad \dots\dots\dots (5)$$

Where λ is the wavelength of the incident photon, k is the extinction coefficient [22,23]. Fig.(8) shows the variation of skin depth as a function of wavelength for all films. It is clear from the figure that the skin depth increase as the wavelength increase, this behavior could be seen for all samples, but the skin depth decreases as the doping concentration increases, so the skin depth is a transmittance related.

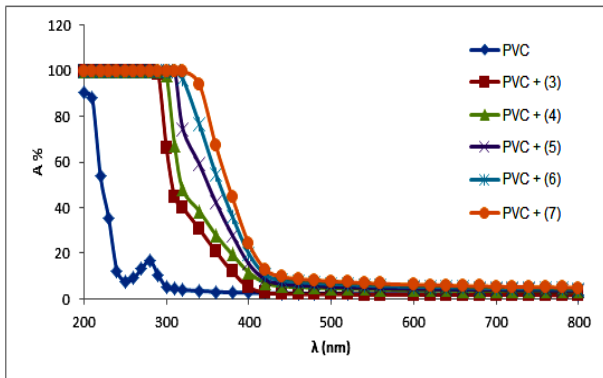


Fig. (1) The variation of absorbance with wavelength for films.

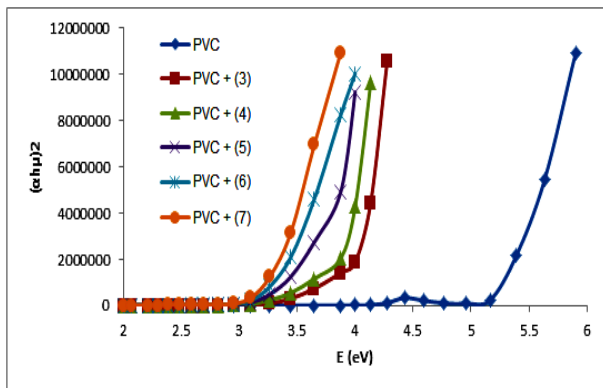


Fig. (2) $(ahv)^2$ for thin films versus photon energy.

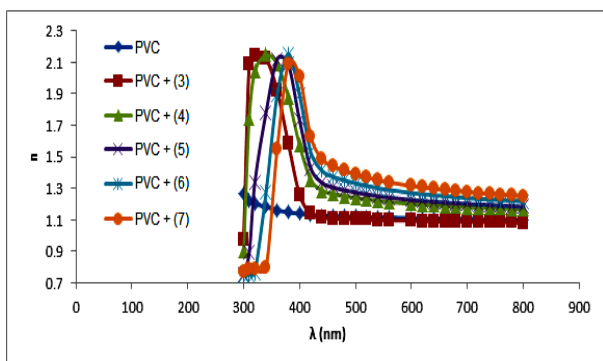


Fig. (3) The variation of refractive index with wavelength for films.

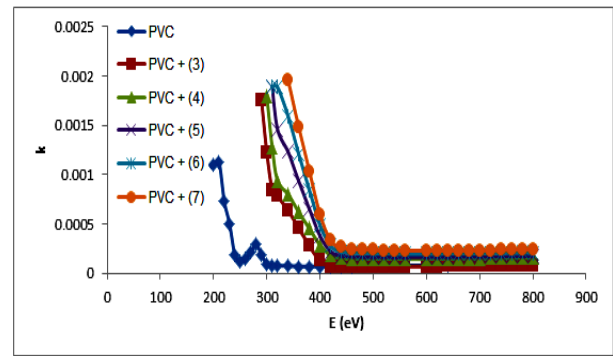


Fig. (4) The variation of extinction coefficient with wavelength for films.

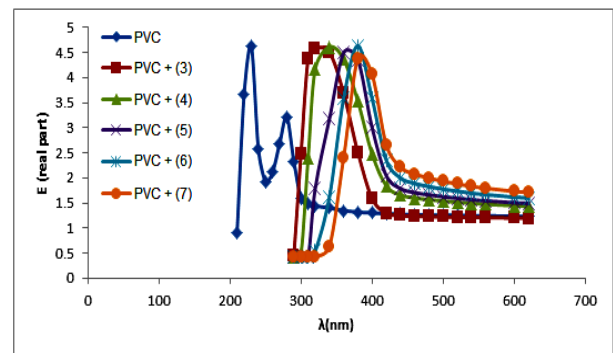


Fig. (5) The variation of real part of dielectric constant with wavelength for films.

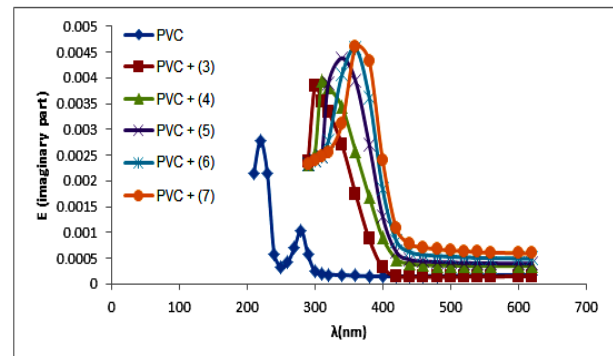


Fig. (6) The variation of imaginary part of dielectric constant with wavelength for films.

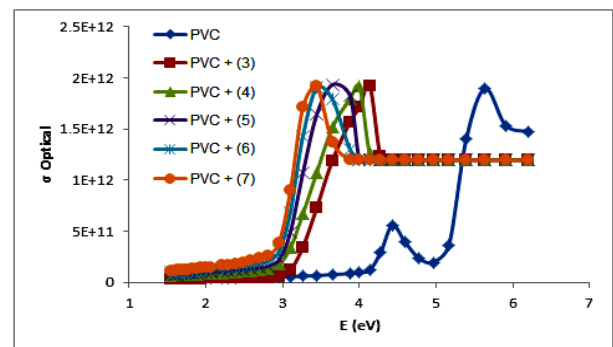


Fig. (7) Optical conductivity versus energy.

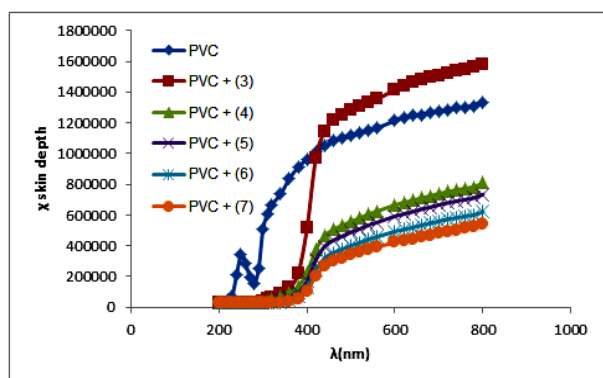


Fig. (8) Skin depth versus wavelength for films.

Conclusion

Poly(vinyl chloride) bonded to compounds (3)-(7) by chlorine displacement reaction. Showed all the new polymers prepared PVC + (3)-PVC (7) good optical properties compared to the original polymer.

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الخلاصة

تم تحضير بوليميرات جديدة محوره لبوليمير كلوريد الفايثيل من مفاعلة بوليمير كلوريد الفايثيل مع مركبات حلقيه غير متجانسة تحتوي على مجموعة الثايول بأستخدام رباعي هيدرو فيوران كمذيب. تم تشخيص المركبات الحلقيه غير المتجانسة بواسطة مطيافية الاشعة تحت الحمراء والرنين النووي المغناطيسي للهيدروجين والتحليل الذري للعناصر بينما تم تشخيص البوليميرات المحورة بواسطة مطيافية الاشعة فوق البنفسجية. وكذلك تم دراسة الخواص البصرية للبوليميرات الجديدة.