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Investigations on Fe³⁺ doped polyvinyl alcohol films with and without gamma (γ)-irradiation

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ABSTRACT

This paper deals with the preparation of pure and ferric chloride (FeCl₃) doped polyvinyl alcohol (PVA) films by solution casting method. Optical and electrical properties were systematically investigated. We have found the decrease in optical band gap energy of PVA films on doping FeCl₃. The optical band gap energy values in the present work are found to be 3.10 eV for pure PVA, 2 eV for PVA:Fe³⁺ (5 mol%), 1.91 eV for PVA:Fe³⁺ (15 mol%) and 1.8 eV for PVA:Fe³⁺ (25 mol%). Direct current electrical conductivity (σ) of pure, FeCl₃ doped PVA films in the temperature range 70–127 °C has been studied. At 387 K dc electrical conductivity of pure PVA film is 5.5795 μΩ⁻¹ cm⁻¹, PVA:Fe³⁺ (5 mol%) film is 10.0936 μΩ⁻¹ cm⁻¹ and γ-Irradiated PVA:Fe³⁺ (5 mol%) film for 900 CGY/min is 22.1950 μΩ⁻¹ cm⁻¹. –1. The result reveals the enhancement of the electrical conductivity with γ-irradiation. FT-IR study signifies the intermolecular hydrogen bonding between Fe³⁺ ions of FeCl₃ with OH group of PVA.

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1. Introduction

Recently the organometallic polymers have attracted the interest of technological, industrial and academic researchers in domains ranging from chemistry to solid state-physics to electrochemistry [1–5], due to their low specific weight and good mechanical strength. Also the ability to tailor the electrical properties of these materials is one of the most attractive features and coupled with improved stability and processability relative to the original conducting polymer systems.

In many technological applications, the observation of change in polymer structure is very essential to tailor its physical properties required to a particular application. The change in polymer structure and even new performance properties can be obtained by introducing suitable metals into a polymer chain and by γ-irradiation [6–9]. So authors have made an attempt to study the change in polymer structure by introducing transition metal ion Fe³⁺ in various mol% to polymer.

Polyvinyl alcohol (PVA) is semicrystalline, water soluble, with low electrical conductivity polymer [10]. PVA has certain physical properties resulting from crystal–amorphous interfacial effects [11,12]. Its electrical properties can be tailored to a specific requirement by the addition of suitable dopant material. Depend-

ing on the chemical nature of the doping substances and the way in which they interact with the host matrix, the dopant alters the physical properties to different degrees [13–17]. Applications of organometallic polymers include, high-temperature coatings, biosensors, storage electrodes for batteries, fuel cells and capacitors, electrochromics, chemical and biochemical sensors, display materials, lasers etc.

2. Experimental

Polyvinyl alcohol and ferric chloride used in this work have been taken from Sigma–Aldrich Company. PVA and PVA:Fe³⁺ films were prepared at room temperature by solution casting method. A known quantity of PVA was dissolved in double distilled water and then heated gently, using a water bath to prevent thermal decomposition of polymer. The hot solution was stirred until the polymer is completely dissolved and forming a clear viscous solution. This is called PVA stock solution. Also different quantities of FeCl₃ was dissolved in doubly distilled water to get the desired concentrations (5, 15 and 25 mol%) and mixed with PVA stock solution, stirred thoroughly with a magnetic stirrer. PVA and ferric chloride doped PVA solution filtered to remove air bubbles trapped in the solution while stirring and kept aside for required duration to get proper viscosity. Known quantity of obtained solution was poured on to a leveled clean glass plate and left to dry at room temperature. After 48 h, the films were peeled off from the glass

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plate and kept in vacuum desiccator [18]. The peeled film was cut into pieces suitable for measurements.

The samples were irradiated for different dosages of γ -rays using ^{60}Co ($T_{1/2} = 5.26$ years) at room temperature.

A JASCO FT/IR-410 spectrophotometer was used for recording the IR spectra of pure PVA and PVA:Fe $^{3+}$ (20 mol%) films at room temperature in the region 500–4000 cm^{-1} . The spectra exhibit bands, characteristic of stretching and bending vibrations of O–H, C–H, C–C and C–O groups.

The optical studies of the pure PVA and PVA:Fe $^{3+}$ films have been analyzed using Ocean optics Spectrophotometer, Model No. USB 2000, USA. The transmittance spectra in the region 300–800 nm has been collected and optical parameters α , and E_g have been evaluated.

The dc electrical conductivity (σ) of pure PVA, and Fe $^{3+}$ doped PVA films with and without γ -irradiation has been studied in the 70–127 $^\circ\text{C}$ using four point probe technique [19]. The conductivity of the films has been measured by taking current values as a function of temperature using a constant voltage source.

3. Results and discussion

3.1. FT-IR spectra

Fig. 1a shows the FT-IR spectrum of pure PVA film. It exhibits several bands characteristic of stretching and bending vibrations of O–H, C–H, C=C and C–O groups. Using FT-IR spectra a strong broad band at 3628 cm^{-1} is assigned to O–H stretching frequency, indicates the presence of hydroxyl groups [20,21]. The band observed at 1744 cm^{-1} corresponding to C=C stretching vibration [22] and 1468 cm^{-1} corresponds to an acetyl group and can be

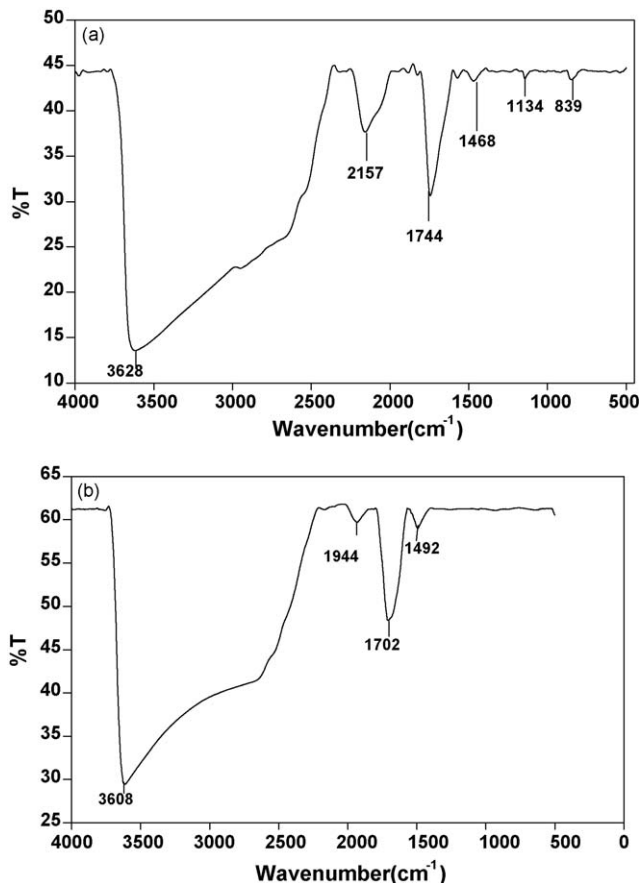


Fig. 1. FT-IR spectra (a) pure PVA and (b) PVA:Fe $^{3+}$ (20 mol%) films.

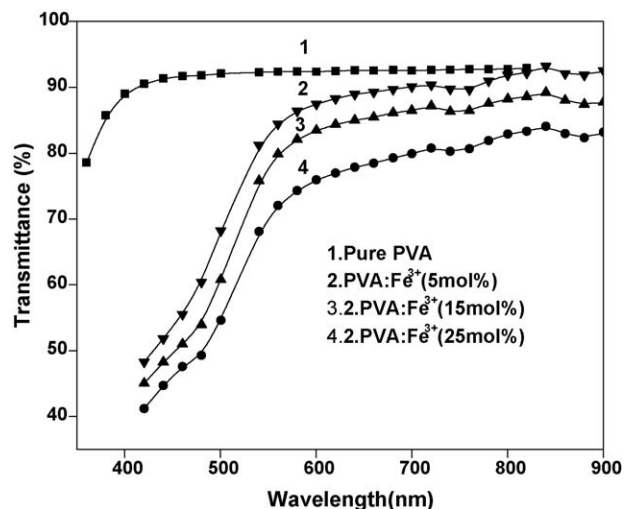


Fig. 2. Transmittance spectra of pure PVA and PVA:Fe $^{3+}$ (5, 15 and 25 mol%) films.

explained on the basis of intermolecular hydrogen bonding with the adjacent OH group. The sharp band at 1134 cm^{-1} corresponds to C–O stretching of acetyl group present on the PVA backbone. Fig. 1b shows the FT-IR spectrum of PVA:Fe $^{3+}$ (20 mol%) film exhibits bands, whose vibrational frequencies and band assignments are found to be similar to several bands observed for undoped PVA. However O–H stretching frequency observed at 3628 cm^{-1} for pure PVA shows the appreciable shift towards low frequency region on doping of Fe $^{3+}$ ions and positioned at 3608 cm^{-1} . This shift indicates the considerable interaction between O–H group of PVA and Fe $^{3+}$ ion of FeCl $_3$.

3.2. Optical studies

Transmittance versus wavelength for PVA and PVA:Fe $^{3+}$ (5, 15, and 25 mol%) recorded at room temperature is shown in Fig. 2. It is evident from Fig. 2 that pure PVA has highest transmission and decreases with increase in Fe $^{3+}$ concentration. This is due to the formation of intermolecular hydrogen bonding between Fe $^{3+}$ ions with the adjacent OH groups justified by FT-IR spectra (Fig. 2). Increase in FeCl $_3$ concentration, increases the intermolecular hydrogen bonding resulting in increase of absorption and decrease of transmission. This is in accordance with the Beer's law, i.e. the absorption is proportional to the number of absorbing molecules. The decrease in transmission of doped PVA reflects the variation in the energy band gap, which arises due to the change in polymer structure. From the transmittance spectra, the absorption coefficient α has been determined using the formula [23] $\alpha = d^{-1} \ln(1/T)$ where 'd' is the thickness of the film and T is the percentage of transmittance. The optical band gap energy for an indirect transition has been determined using the relation [24] $E_{\text{opt}} = h\nu - (\alpha h\nu/\beta)^{1/2}$ where β is a constant. The plot of $(\alpha h\nu)^{1/2}$ versus the photon energy $h\nu$ at room temperature for pure PVA and for PVA:Fe $^{3+}$ (5, 15 and 25 mol%) is as shown in Fig. 3a and b respectively. These figures show linear behavior, which can be considered as evidence for indirect allowed transition. The optical band gap energies (E_{opt}) have been evaluated by extrapolating the linear region of the curve to a point $(\alpha h\nu)^{1/2} = 0$. Here the transitions between the valence and conduction bands are assumed to be allowed indirect transitions. The variation of optical band gap energy (E_{opt}) with dopant concentration is shown in Fig. 4. From Fig. 4, it is evident that the optical band gap energy goes on decreasing with the increase in dopant concentration. This indicates that increase in Fe $^{3+}$ concentration makes PVA film more semiconducting. From the above result the variation of optical

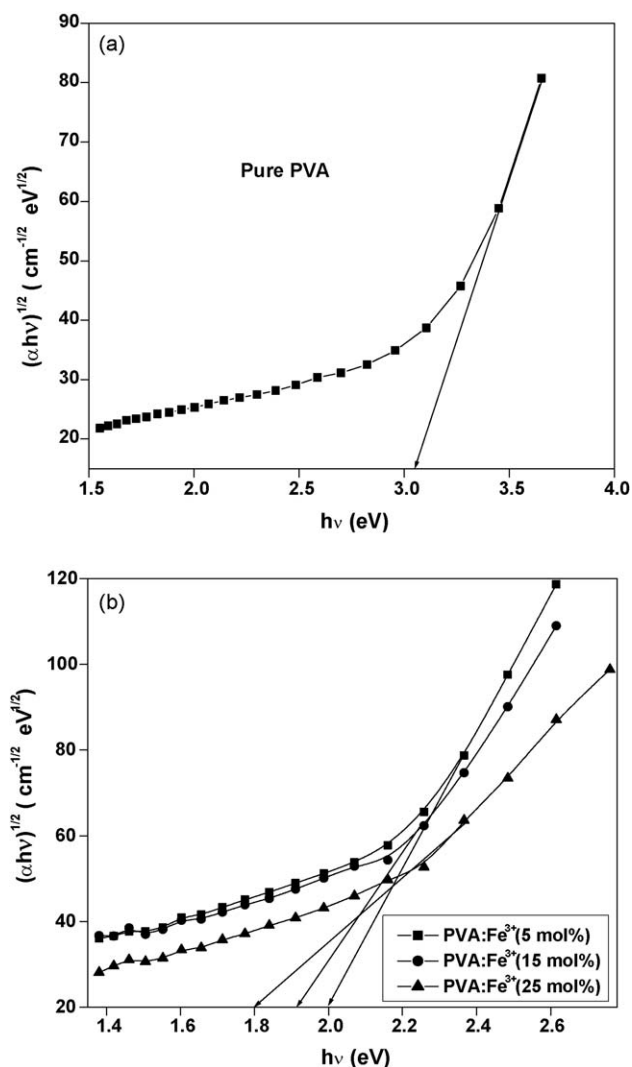


Fig. 3. A plot between $(\alpha h\nu)^{1/2}$ and $h\nu$ for (a) pure PVA films (b) PVA: Fe^{3+} (5, 15 and 25 mol%) films.

band gap energy (E_{opt}) may be explained by invoking the occurrence of local crosslinking within the amorphous phase of the polymer, results in the degree of ordering in these parts [25]. Interaction of Fe^{3+} with $-\text{OH}$ group of PVA and forming metal-polymer complex in the form of intermolecular hydrogen bonding is confirmed by FT-IR study. These interactions and hence the complex formation causes change of polymer structure. The change of polymer structure increase with dopant concentration, which is reflected in the form of decrease in the optical band gap energy (E_{opt}) is shown in Fig. 4.

3.3. Electrical conductivity

The doping, temperature and γ -irradiation dependence of dc electrical conductivity (σ) have been studied for the pure PVA, Fe^{3+} doped PVA and γ -irradiated for the dosages 300, 600 and 900 CGY/min films. The variations of $\log \sigma$ versus $1/T$ for all the films were studied. It has been observed that dc conductivity increases with increase in dopant concentration, temperature and γ -irradiation. Fig. 5 represents the plot of $\log \sigma$ versus $1/T$ for pure PVA, Fe^{3+} (5 mol%) doped PVA and subjected to 300, 600 and 900 CGY/min γ -irradiation.

The electrical conductivity (σ) for pure PVA films is less than that of the Fe^{3+} ion doped PVA films. The electrical conductivity (σ)

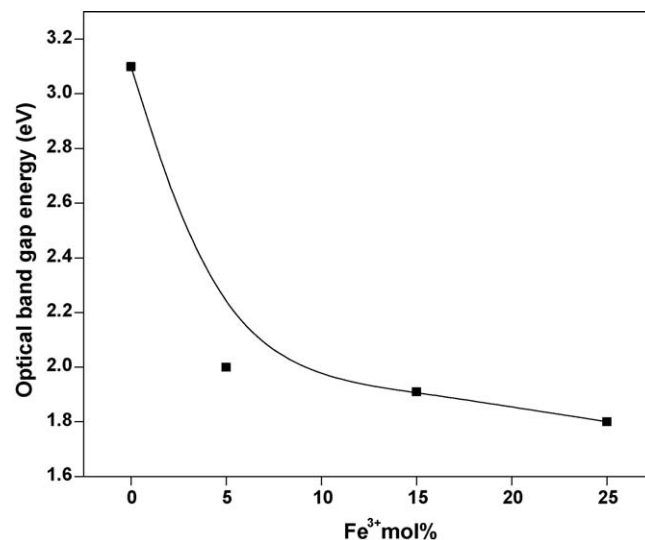


Fig. 4. Variation of the optical band gap energy of pure and FeCl_3 doped PVA films.

increases with dopant concentration. The induced conductivity in Fe^{3+} doped PVA is shown to be dose dependent and can be attributed to the creation of induced charge carriers in the PVA matrix as shown in Fig. 5. This is because of the Fe^{3+} ions coordinated through ionic bonds with hydroxyl group belonging to the different chains in PVA [26]. Addition of dopant results in the reduction of the intermolecular interaction between the PVA molecules or the addition of Fe^{3+} increases the volume required for ionic carriers to drift in the polymer matrix. This enhances the ionic mobility and hence increases the conductivity. Ionic clusters will be formed if the dopants are not distributed homogeneously. Appreciable ionic conductivity is observed only when a critical volume fraction of the ionic conducting clusters is reached, and material actually undergoes an insulator to conducting transition. As the volume fraction of the dopant increases, there is initially very little change in the polymer resistance. At this point the highly conductive clusters are well separated and do not form continuous path through the polymer. At this stage the resistance of the doped polymer is controlled by the poorer conducting phase. At a critical volume fraction of the dopant, the highly conductive phase forms a continuous path across the polymer, and gradual decrease in resistance occurs.

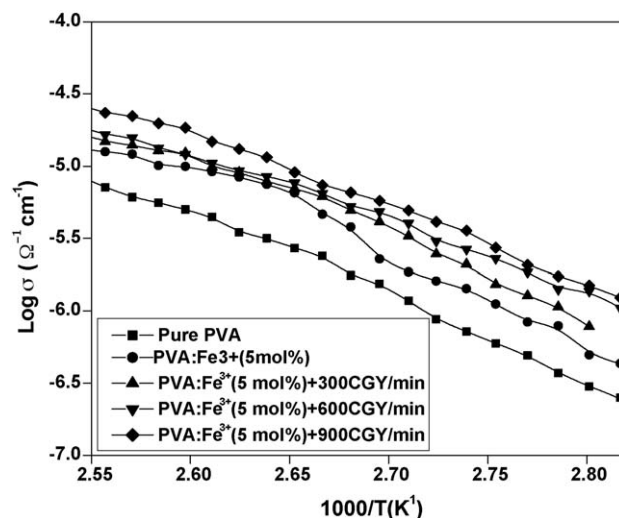


Fig. 5. Variation of electrical conductivity of pure PVA, unirradiated and γ -irradiated PVA: Fe^{3+} (5 mol%) films.

Doped PVA films showed higher conductivity than undoped films and increases with film temperature. This can be observed in Fig. 5. Conductivity (σ) has increased with raise in temperature this may be considered as due to the liberation of electrons or ions through the amorphous region of PVA and also probably the internal stress in the doped PVA. The temperature dependence of electrical conductivity (σ) of pure and Fe³⁺ doped PVA films are shown in Fig. 5. The result obtained in the present work is of the same order reported in the literature [27].

The electrical conductivity for pure PVA films, doped PVA films is less than that of the γ -irradiated films. This can be observed in Fig. 5. The dependence of dc conductivity on the γ -dose might be explained as follows: at the beginning, the conductivity is due to the presence of dopants, the γ -dose would result in an increase in the number of charge carriers created. This can be explained on the basis that, irradiation of polymer is to rupture the ionic bonds and release of ions, electrons and free radicals which are able to migrate through the network resulting in change in electrical conductivity. This process will continue to take place as γ -dose increases until we approach a situation at which most of the possible charge carriers are already created.

In fact at high temperature, reaching this saturation limit is very difficult because of the existence of more complicated conduction mechanism. At high temperature the conductivity is due to the liberation of electrons or ions through the amorphous region of PVA and also probably the internal stress in the doped PVA [28,29]. In addition to this, since irradiation was carried out in air and, the obtained gaseous ions around the films might have been produced on the surface of the film [30]. From the graph it is evident that, the increase in conductivity due to the dopant, temperature and γ -irradiation depicts semiconducting nature of PVA.

4. Conclusions

1. The FT-IR study shows the interaction of Fe³⁺ ions of FeCl₃ with O–H groups of PVA and forms metal–polymer complex via intermolecular hydrogen bonding.
2. Pure PVA has answered for optical band gap energy (E_{opt}) = 3.10 eV. The optical band gap energy (E_{opt}) for the doped PVA films decreases with increase in Fe³⁺ content.
3. Dopant generally increases the electrical conductivity. This is due to the Fe³⁺ ions coordinated through ionic bonds with hydroxyl group belonging to different chains in PVA. This reduces the intermolecular interaction between PVA molecules or the addition of Fe³⁺ increases the volume required for ionic carriers to drift in the polymer matrix
4. Irradiation of polymers also increases the electrical conductivity. This is due to rupture of ionic bonds by irradiation, resulting in release of ions, electrons and free radicals which are able to

migrate through the network resulting in an increase in the electrical conductivity.

5. The change of polymer structure increases with dopant concentration, which is reflected in the form of decrease in the optical band gap energy and increase in electrical conductivity. γ -Irradiation enhances the electrical conductivity (σ) further.

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References

- [1] J.E. Sheats, C.U. Pitman, C.E. Carraher, *Chem. Brit.* 1 (1984) 709.
- [2] C.E. Carraher, *J. Chem. Educ.* 58 (1981) 921.
- [3] D. Wohrle, *Adv. Polym. Sci.* 50 (1983) 45.
- [4] J.S. Miller (Ed.), *Extended Linear Chain Compounds*, Plenum, New York, 1982, p. 1.
- [5] C.U. Pitman Jr., C.E. Carraher Jr., J.R. Reynolds, in: H.F. Mark, N.M. Bikales, C.G. Overberger, G. Menges (Eds.), *Encyclopedia of Polymer Science and Engineering*, vol. 10, Wiley, New York, 1987, pp. 541–594.
- [6] Y. Tanaka, Y. Mita, Y. Ohki, H. Yoshioka, M. Ikeda, F. Yazaki, *J. Phys. D: Appl. Phys.* 23 (1990) 1491.
- [7] F.H. Abd El-Kader, S.S. Hamza, G. Attia, *J. Mater. Sci.* 28 (1993) 6719.
- [8] F.H. Abd El-Kader, G. Attia, S.S. Ibrahim, *J. Polym. Degrad. Stabil.* 43 (1994) 253.
- [9] X. Lu, N. Brown, M. Shaker, I.L. Kamel, *J. Polym. Sci. Part B: Polym. Phys.* 33 (1995) 153.
- [10] A. Tawansi, M.D. Migahed, M.I.A. El-Hamid, *J. Polym. Sci. Part B: Polym. Phys.* 24 (1986) 2631–2642.
- [11] I. Su, Z.Y. Ma, J.I. Scheinbeim, B.A. Newman, *J. Polym. Sci. Part B: Polym. Phys.* 33 (1995) 85.
- [12] A. Tawansi, H.M. Zidan, *J. Phys. D: Appl. Phys.* 23 (1990) 1320.
- [13] R. Bahri, *J. Phys. D* 15 (1992) 1036.
- [14] A.F. Basha, H.A. Abdel Samad, M. Amin, *Egypt J. Phys.* 16 (1985) 299.
- [15] A.K. Sharma, B. Rukmini, D. Santhisagar, *Mater. Lett.* 12 (1991) 59.
- [16] N. Venugopal Reddy, V.V.R. Narasimha Rao, *J. Mater. Sci. Lett.* 11 (1992) 1036.
- [17] H.S. Nalwa, *J. Mater. Sci.* 27 (1992) 210.
- [18] G.N. Hemanth Kumar, J. Lakshmana Rao, N.O. Gopal, K.V. Narasimhulu, R.P.S. Chakradhar, A. Varada Rajulu, *Polymer* 45 (2004) 5407–5415.
- [19] W.E. Beadle, J.C.C. Tsai, R.D. Plummer, *Quick Reference Manual for Silicon Integrated Circuit Technology*, Wiley, New York, 1985.
- [20] S.N. Ege, *Organic Chemistry*, vol. 1, The University of Michigan, Ann Arbor, 1989 p. 361.
- [21] O.J. Sweeting, *The Science and Technology of Polymer Films*, Interscience Publishers, New York, 1968.
- [22] Z. Sun, Y. Sun, Q. Yang, X. Wang, Z. Zheng, *Surf. Coat. Technol.* 79 (1996) 108.
- [23] D. Mardare, M. Tasca, M. Delibas, G.I. Rusa, *Appl. Surf. Sci.* 156 (2000) 200.
- [24] E.A. Davis, N.F. Mott, *Philos. Mag.* 22 (1970) 903.
- [25] M.A. El-Shahawy, *Polym. Int.* 52 (2003) 1919.
- [26] F.H. Abd El-Kadar, G. Attia, S.S. Ibrahim, *J. Appl. Polym. Sci.* 50 (1993) 1281.
- [27] A.F. Basha, M. Amin, H.A. Abdel Samed, K.A. Darwish, *Indian J. Polym. Mater.* 5 (1998) 161.
- [28] C.A. Hograth, M.J. Bosha, *J. Phys. D: Appl. Phys.* 16 (1983) 869.
- [29] C. Muralidhar, P.K.C. Pillai, *J. Mater. Sci. Lett.* 6 (1987) 439.
- [30] C. Bowit, *J. Phys. D: Appl. Phys.* 16 (1983) L101.