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Fast neutrons effect on the frequency-dependent dielectric properties of PVA/HPC blend

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ABSTRACT

The frequency-dependent dielectric dispersion of a thin film of poly(vinyl alcohol)/ hydroxypropyl cellulose (80/20 wt/wt%) blend prepared by the solution-cast technique is investigated in the frequency range 1-100 kHz. The effect of different fast neutron fluencies in the range 10^5-10^8 n/cm^2 on the prepared film is also studied. Dielectric relaxation has been analyzed based on the examination of the wide range of molecular mobility of the amorphous phase of the blend system. The obtained results noticed that, measureable changes in the behavior and values of the dielectric properties are detected. These changes may be attributed to degradation and/or cross-linking process by the presence of HPC with PVA or by the irradiation with fast neutron which may be suggested that the observed dispersion depends on composition and irradiation of the blend matrix.

KEYWORDS

Poly(vinyl alcohol);
Hydroxypropyl cellulose;
PVA/HPC blend;
Fast neutrons irradiation;
Dielectric properties.

INTRODUCTION

In the recent years, studies on the electrical properties of polymers have attracted much attention in view of their applications in electronic devices[1]. The electrical conduction in polymers has been studied aiming to understand the nature of the charge transport prevalent in these materials. Moreover, conducting polymers have shown great potential for many applications such as rechargeable batteries, light-emitting diodes, molecular sensors, and gas separation membranes[2]. To be useful in these applications, the polymers must be highly processable and chemically stable for long periods of time. Poly(vinyl alcohol) has high mechanical strength and water-soluble and desirable physicochemical properties and its biocompatibility[3]. These advantages have played as main role for this selection as compared to other polymer matrices[4]. Also, PVA has been used as a host polymer because PVA is semi-crystalline polymer and has very important applications due to the role of OH group and hydrogen bonds[1].

Polyvinyl alcohol is a potential material having a very high dielectric strength (> 10000 kV/mm), good charge storage capacity and dopant-dependent electrical and optical properties. So the wide range of applications of PVA can be even more extended by incorporation of dopant into PVA matrix[5]. In addition, poly(vinyl alcohol) can be blended with hydroxypropyl cellulose and hydroxypropyl methyl cellulose[3,6-9]. Here, hydrogen bonding interaction is an important aspect of miscibility since intermolecular interactions regulate the compatibility among the component polymer molecules[10].

Hydroxypropyl cellulose (HPC) has been used already for a year by paper of conservators as glue and sizing material[11]. Also, HPC can be used for production of time controlled delivery systems and is also used as a topical ophthalmic protectant and lubricant[12]. In pharmaceuticals applications, HPC is used as a disintegrants and a binder for the wet granulation method of making tablets[13].

On other side, chemical or physical cross-linking can be achieved using functional cross-linking agents or by using ionizing radiation[14]. Ionizing radiation such as gamma or electron-beam produces two types of free radicals on PVA chains[15]. In addition, chemically cross-linked PVA hydrogel has been gaining increasing attention in the field of biomedics[16].

The dielectric behavior of poly(vinyl alcohol) composite films is studied in this work. The present study will help in understanding the effect of 20 wt% of HPC on the dielectric property and ac conductivity of PVA. The influence of fast neutrons with different fluencies on the dielectric properties of the composite polymer is also investigated.

EXPERIMENTAL WORK

In the present study, poly(vinyl alcohol) (PVA) granules with molecular weight of 125 kg/mole (El-Nasr Company, Cairo, Egypt) and hydroxypropyl cellulose (HPC; Pharmacoat 606) with molecular weight of 95 kg/mole (Shin Etsu Chemical Co., Tokyo, Japan) are used.

Thin film of pure PVA and HPC and their PVA/HPC blend (80/20 wt/wt%) is prepared by using solution-cast technique[3,7,17]. This technique depends on the dissolution, separately, the weighted amounts of the PVA granules and HPC powder in double distilled water. Complete dissolution is obtained using a magnetic stirrer in a 50 °C water bath. To prepare thin film of the PVA and HPC and their blend PVA/HPC (80/20 wt/wt%), the solutions are mixed together at 50 °C with a magnetic stirrer. Thin films of appropriate thickness (about 0.01 cm) are cast onto stainless steel Petri dishes (10 cm diameter). The prepared films are kept at room temperature (about 25 °C) for 7 days until the solvent completely evaporated and then kept in desiccators containing fused calcium chloride to avoid moisture.

The prepare thin film (80/20 wt/wt%) of the blend of PVA/HPC is irradiated with fission neutrons with mean energy of approximately 4.2 MeV from Americium-Beryllium (^{241}Am-Be) neutron source of activity 5 Ci (185 GBq) and with emission rate 0.87×10^7 n/s at room temperature. During irradiation the samples are fixed in positions that neutrons were incident approximately normal. The films are exposed to different fast neutron fluencies covers the range 1×10^5 - 1×10^8 n/cm^2 [9]. The fast neutron fluence is measured using a calibrated TLD-700 Thermoluminescence detector at the location of the sample.

The electrical measurement (dielectric permittivity, dielectric loss factor and ac conductivity on the prepared thin films of PVA, HPC and their PVA/HPC blend are measured in the frequency range from 1 to 100 kHz at room temperature using a Hioki 3531Z Hiester Programmable Automatic RLC Meter (Japan)[4]. The accuracy of the dielectric measurements was within ±1%.

RESULTS AND DISCUSSIONS

Dielectric permittivity (ε’) study

One of the most methods of unravelling the origin of dielectric dispersion is the study of the real part of dielectric (dielectric permittivity) of the polymeric materials[18,19]. Figure 1 illustrates the frequency-dependence of the dielectric permittivity (ε’) for pure PVA, HPC and their PVA/HPC blended sample. From the figure it is clear that, the value of ε’ decreases monotonically with the increase of the frequency of the applied electric field. The values of ε’ for 80/20 wt/wt% blend are in the intermediate value between the values of the homopolymers (PVA and HPC) which may be indicated that there is a compatibility and miscibility between the blend system. The variation of ε’ must be mainly due to the space-charge polarization up to 10^4 Hz and at higher frequencies it must be due to the contributions from ionic, dipolar and electronic polarization[18,19]. Moreover, the values of ε’ decreased as the applied frequency increased and they showed anomalous dispersion[20,21]. The addition of HPC may cause an increase in the number of ionisable charge carriers which affects the inherent ability of the dipoles to orient themselves[22] and also may cause the distribution of HPC molecules in the inter-aggregates space which decrease the polymer chain elongation and consequently may result in a decrease in the dielectric permittivity.

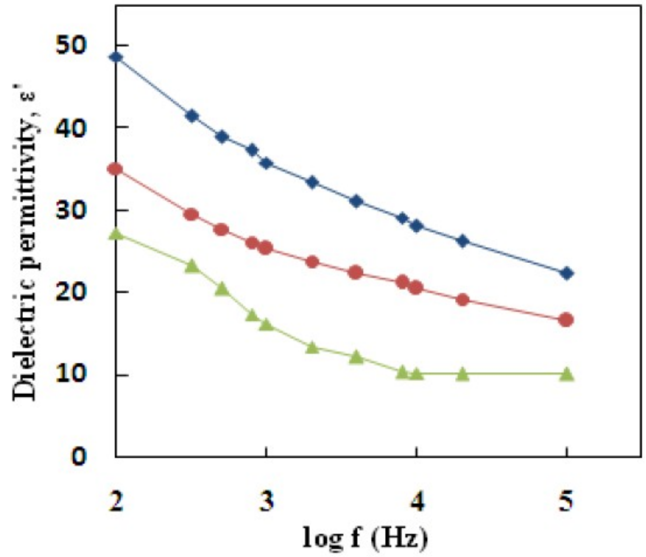

Figure 1 : Frequency-dependence of the dielectric permittivity (ε2) for PVA/HPC blends : (◆) 100/0, (●) 80/20 and (▲) 0/100 wt/wt%.

Figure 2 shows the variation of ε' with frequency for 80/20 wt/wt% PVA/HPC blended sample before and after irradiation with different fast neutron fluencies. It is clear from the figure that the values of ε' decrease with increasing frequency approaching a nearly constant value at higher frequencies. It is clear from the figure that, all curves shown are not adhered with Deybe model. The dielectric permittivity as depicted in the figure decreases with the increasing of frequency. This may be attributed to the tendency of dipoles in polymeric samples to orient themselves in the direction of the applied field. It could be explained by dipoles orientation, which difficult to rotate at high frequency range[23].

Dielectric loss factor (ε") study

Figure 3 represents the dependence of dielectric loss factor (ε") on frequency for pure PVA, HPC and their PVA/HPC blended sample. From the figure, it is noticed that, the values of ε" for the blended sample (80/20 wt/wt%) are lower than that of the pure PVA and pure HPC values over the whole frequency range. The dielectric loss factor decreases with frequency and the larger value of dielectric loss factor at low frequency could be due to the mobile charges within the polymer backbone[4].

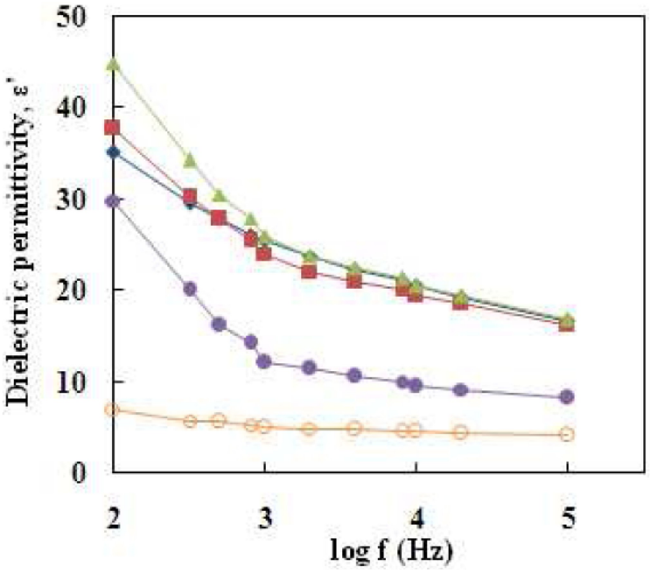

Figure 2 : Frequency-dependence of the dielectric permittivity (ε2) for unirradiated and irradiated 80/20 wt/wt% blended sample with different fast neutron fluencies. (◆) unirradiated, (■) 1 x 10^5, (▲) 1 x 10^6, (●) 1 x 10^7 and (○) 1 x 10^8 n/cm^2.

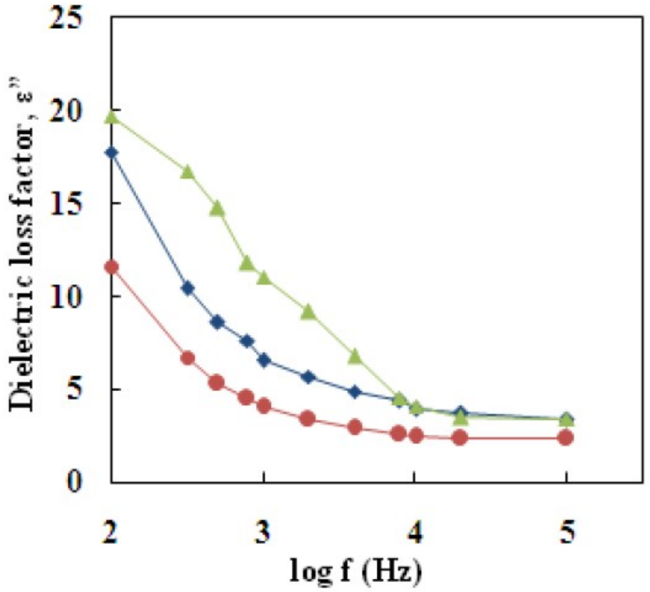

Figure 3 : Frequency-dependence of the dielectric loss factor (ε") for PVA/HPC blends : (◆) 100/0, (●) 80/20 and (▲) 0/100 wt/wt%.

Figure 4 shows the dependence of the dielectric loss factor (ε") on frequency for 80/20 wt/wt% PVA/HPC blended sample before and after irradiation with different fast neutron fluencies. The plots show a steep decrease in ε" at low frequencies. This is a general sequence attributed to decrease in the stir effect hinder-

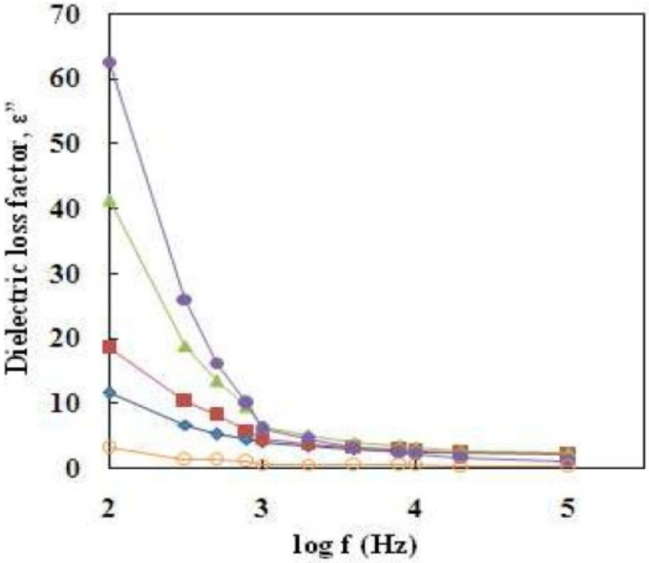

Figure 4 : Frequency-dependence of the dielectric loss factor (ε'') for unirradiated and irradiated 80/20 wt/wt% blended sample with different fast neutron fluencies. (◆) unirradiated, (■) 1 x 10^5, (▲) 1 x 10^6, (●) 1 x 10^7 and (○) 1 x 10^8 n/cm^2.

ing the micro-Brownian motion. At high frequencies the variation of ε'' with frequency is marginal and tends to be a constant value.

It is recognized from the figure that neutron irradiation plays a predominant role in both morphological and microstructure change occurring in the polymer matrix[24]. Such blended sample behaves as a system in which one phase relaxes like the amorphous one while the existence of crystalline phase restrict the general long-range segmental motions in the amorphous phase[25]. Therefore, the variation of magnitude of the dielectric loss factor may be due to the change in the microstructure induced by fast neutrons.

All dielectric materials have two types of losses: the conduction loss representing the flow of actual charges through the dielectric material, and the dielectric loss due to movement or rotation of the atoms in an alternating field. Treatment of polymers by blending with appropriate additives modifies the perturbation of phonons during application of electric field. Moreover, the dielectric relaxation of polymers is influenced by water in various ways[24] which enhances the local relaxation process by dipole-dipole coupling and it can act as an effective plasticizer in polar polymers. If water can form a hydrogen bonded super-structure, it produces a very specific dielectric response, "anomalous low frequency dispersion"[26]. The essence of this kind of response is that both ε' and ε'' decrease with increasing frequencies as noticed from the obtained results.

A.C. conductivity (σ_{ac}) study

The conductivity of the amorphous materials where the charge carriers experience on approximately random potential energy on diffusing is found to obey the equation[27]: $\sigma_{ac}(\omega) = A\,\omega^S$, where A is a complex constant and the index S is the exponent of the angular frequency (ω). The value of the exponent S has been determined from the linear slope of –!log $\sigma_{ac}(\omega)$ versus –!log ω. Figure 5 represents the frequency dependence (–!log ω) of a.c. conductivity (–!log σ_{ac}) for pure PVA, HPC and their PVA/HPC blended sample. It is clear from the figure that due to the addition of HPC, σ_{ac} values decrease in the whole frequency range. This decrease may be due to the decrease in the mobility of charge carriers due to scattering of ionized molecular aggregates which may be formed due to inhomogeneous distribution as well as the non-bonding parts of the blend. Also, from the figure, σ_{ac} is monotonically increases with increasing frequency. This behavior is well defined as the conduction of which occurs by hopping mechanism[27].

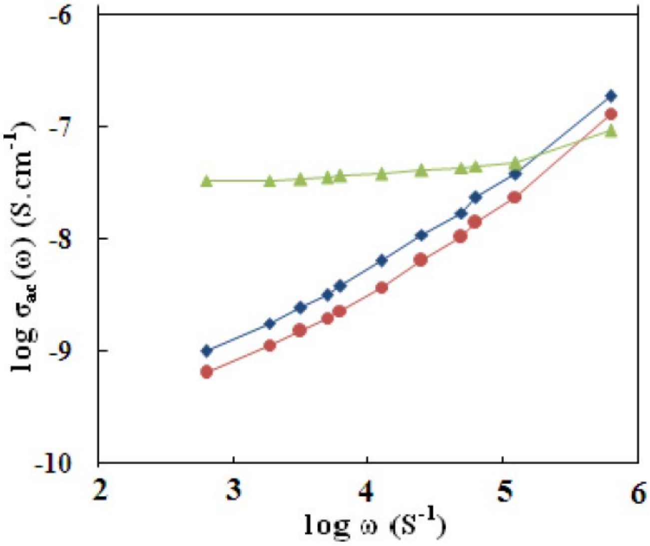

Figure 5 : Frequency-dependence (log ω) of a.c. conductivity (log σ_{ac}) for PVA/HPC blends : (◆) 100/0, (●) 80/20 and (▲) 0/100 wt/wt%.

Figure 6 shows the relation between log ω and log σ_{ac} for unirradiated and irradiated 80/20 wt/wt% PVA/

HPC blended sample. As can be seen from the figure for the unirradiated and irradiated samples, the plots has yielded nearly straight lines up to 10 kHz. This type of behavior reveals that the exponent S is approximately independent of frequency; hence, the mechanism responsible for a.c. conduction mechanism could be a hopping one[27,28].

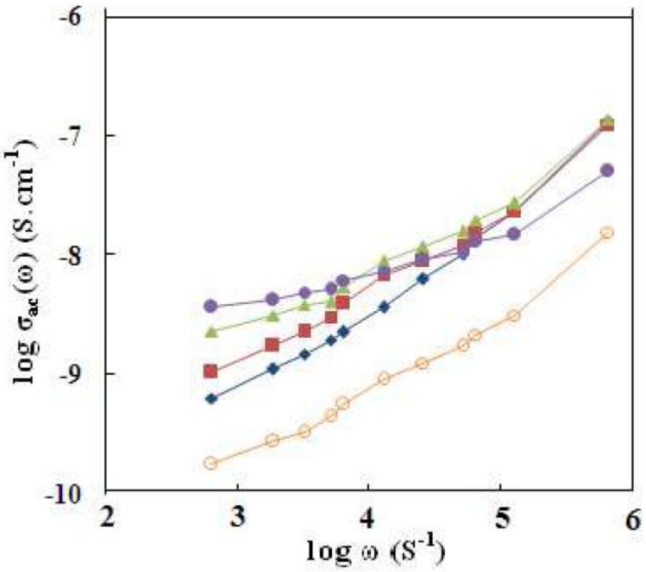

Figure 6 : Frequency dependence (–!og ω) of a.c. conductivity (–!og σ_{ac}) for unirradiated and irradiated 80/20 wt/wt% blended sample with different fast neutron fluencies. (◆) unirradiated, (■) 1 x 10^5, (▲) 1 x 10^6, (●) 1 x 10^7 and (○) 1 x 10^8 n/cm^2.

Two distinct mechanisms have been proposed for the relaxation phenomena[29]: quantum mechanical tunneling (QMT) of electrons or polarons through the barrier separating localized states, and correlated barrier hopping (CBH) model over the same barrier. The values of S were derived by calculating the slopes of the graphs in Figures 5 and 6 which use a single exponent S and represent the hopping conduction near the Fermi level and are recorded in TABLES 1 and 2. From the data obtained it is observed that the exponent S decreases with increasing neutron fluencies up to 1 x 10^7 n/cm^2 and then increases with increasing the fluence towards the unirradiated value. Also, the exponent S stills less than unity, i.e. S < 1. The obtained results of frequency and fast neutron irradiation dependence of a.c. conductivity were found to support the CBH model, where the frequency dependence of a.c. conductivity is nearly linear, and the exponent S is irradiation dependent decreasing with increasing fast neutron fluence and frequency range employed. This suggests that the CBH mechanism depends on the irradiated blend matrix.

TABLE 1 : Values of the exponent S for PVA/HPC blended samples.

Blend sample PVA/HPC (wt/wt%)	100/0	80/20	0/100
Exponent S	0.739	0.712	0.087

TABLE 2 : Values of the exponent S for 80/20 wt/wt% PVA/HPC blended sample with different fast neutron fluencies.

Blend sample PVA/HPC (80/20 wt/wt%)	**Unirradiated**	**1 x 10^5**	**1 x 10^6**	**1 x 10^7**	**1 x 10^8**
Exponent S	0.712	0.616	0.561	0.308	0.602

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REFERENCES

[1] H.M.Ahmad, S.H.Sabeeh, S.A.Hussen; Electrical and optical properties of PVA/LiI polymer electrolyte films, Asian Transactions on Science & Technology, ATST ISSN: 2221-4283, **1**, 6, 16 **(2012).**

[2] S.H.Hosseini, A.A.Entezami; Studies of thermal and electrical conductivity behaviours of polyaniline and polypyrrole blends with polyvinyl acetate, polystyrene and polyvinyl chloride, Iranian Polymer Journal, **14,** 3, 201 **(2005)**.

[3] Osiris W.Guirguis, M.T.H.Moselhey; Optical study of poly(vinyl alcohol)/hydroxypropyl methylcellulose blends, Journal of Materials Science, **46**, 5775 **(2011)**.

[4] M.H.Harun, E.Saion, A.Kassim, E.Mahmud, M.Y.Hussain, I.S.Mustafa; Dielectric properties of poly(vinyl alcohol)/polypyrrole composite polymer films, Journal for the Advancement of science & Arts, **1(1)**, 9 **(2009)**.

[5] O.G.Abdullah, S.A.Hussen; Variation of optical band gap width of PVA films doped with aluminum iodide, International Conference on Manufacturing Science and Technology (ICMST 2010), 55 **(2010)**.

[6] P.Sakellariou, A.Hassan, R.C.Rowe; Phase separation and polymer interactions in aqueous poly(vinyl alcohol)/hydroxypropyl methylcellulose blends, Polymer, **34**, 1240 **(1993)**.

[7] Osiris W.Guirguis, M.T.H.Moselhey; Thermal and structural studies of poly(vinyl alcohol) and hydroxypropyl cellulose blends, Natural Science, **4**, 57 **(2012)**.

[8] Osiris W.Guirguis, M.T.H.Moselhey; Optical properties of poly (vinyl alcohol)/hydroxypropyl cellulose blends, Materials Science:An Indian Journal, **9**, 8 **(2013)**.

[9] M.M.Abutalib, Osiris W.Guirguis, N.A.El-Zaher; Optical studies of fast neutron irradiated poly(vinyl alcohol)/hydroxypropyl cellulose blends, Materials Science: An Indian Journal, **9**, 433 **(2013)**.

[10] M.J.Folkes, P.S.Hope; Polymer blends and alloys, Chapman and Hall, London, **(1993)**.

[11] J.Hofenk-deGraaff; Central research laboratory for objects of art and science, Gabriel Metsustroat and 1071 EA, Amsterdam, **(1981)**.

[12] C.M.Eaga, J.M.Kandukuri, V.Allenki, M.R.Yamsani; In-situ gels -a novel approach for ocular drug delivery, Der Pharmacia Lettre, **1**, 21 **(2009)**.

[13] T.Ishikawa, B.Mukai, S.Shiraishi, N.Utoguchi, M.Fujii, M.A.Matsumoto, U.Watanabe; Studies of rapidly disintegrating tablet prepared by direct compression method, Chemical and Pharmaceutical Bulletin, **49**, 134 **(2001)**.

[14] H.Bodugoz-Senturka, J.Choi, E.Oral, J.H.Kung, C.E.Macias, G.Braithwaite, O.K.Muratoglu; The effect of polyethylene glycol on the stability of pores in polyvinyl alcohol hydrogels during annealing, Biomaterials, **29**, 141 **(2008)**.

[15] N.V.Bhat, M.M.Nate, M.B.Kurup, V.A.Bambole, S.Sabharwal; Effect of ã-radiation on the structure and morphology of polyvinyl alcohol films, Nuclear Instruments and Methods in Physics Research Section B, **237**, 585 **(2005)**.

[16] S.J.Kim, C.K.Lee, Y.M.Lee, I.Y.Kim, S.I.Kim; Electrical/pH-sensitive swelling behavior of polyelectrolyte hydrogels prepared with hyaluronic acidpoly(vinyl alcohol) interpenetrating polymer networks, Reactive and Functional Polymers, **55**, 291 **(2003)**.

[17] N.A.El-Zaher, W.G.Osiris; Thermal and structural properties of poly(vinyl alcohol) doped with hydroxypropyl cellulose, Journal of Applied Polymer Science, **96**, 1914 **(2005)**.

[18] P.Frübing; Dielectric spectroscopy, University of Potsdam, Institute for Physics Germany, **(2001)**.

[19] G.E.El-Falaky, Osiris W.Guirguis, N.S.Abd-El-Aal; A.C. conductivity and relaxation dynamics in zinc–borate glasses, Progress in Natural Science: Materials International, **22**, 86 **(2012)**.

[20] T.H.Abou-Aiad, M.Z.El-Sabee, K.N.Abd-El-Nour, G.R.Saad, E.A.El-Sayed, E.A.Gaafar; Miscibility and the specific interaction of polyhydroxybutyrate blended with polyvinylacetate and poly(vinyl acetate-co-vinyl alcohol) with some biological applications, Journal of Applied Polymer Science, **86**, 2363 **(2002)**.

[21] L.G.Parada, L.C.Casteros, E.Meauria, I.Katime; Miscibility in blends of poly(vinyl acetate-co-vinyl alcohol) with poly(N,N-dimethylacrylamide), Polymer, **39**, 1019 **(1998)**.

[22] A.A.Tager; Physical chemistry of polymers, Mir Publishers, Moscow, **(1972)**.

[23] P.Dutta, S.Biswas, S.K.De; Dielectric relaxation in polyaniline-polyvinyl alcohol composites, Materials Research Bulletin, **37**, 193 **(2002)**.

[24] T.Suzuki, K.Adachi, T.Kotaka; Dielectric relaxations of water molecules occluded in polymeric media: Some hydrophobic polymer systems, Polymer Journal, **13**, 385 **(1981)**.

[25] M.S.Abo-Ellil, S.A.Gaafar, F.H.Abd El-Kader, N.A.Kamel; Effect of fast neutrons on dielectric properties of pure and gelatin doped-poly(vinyl alcohol) films, Journal of Polymer Research, **7**, 149 **(2000)**.

[26] L.A.Dissado, R.M.Hill; A cluster approach to the structure of imperfect materials and their relaxation spectroscopy, Proceedings of the Royal Society A, **390**, 131 **(1983)**.

[27] A.K.Sharma, V.Adinarayana, D.Santhi-Sagar; DC-conduction mechanism in Fe-doped polystyrene films, Materials Letters, **12**, 247 **(1991)**.

[28] A.M.Saleh, R.D.Gould, A.K.Hassan; Dependence of AC electrical parameters on frequency and temperature in zinc phthalocyanine thin films, Physica Status Solidi (a), **139**, 379 **(1993)**.

[29] P.Dutta, S.Biswas, M.Ghosh, S.K.De, S.Chatterjee; The DC and AC conductivity of polyaniline-polyvinyl alcohol blends, Journal of Synthetic Materials, **122**, 455 **(2000)**.