Available online at www.sciencedirect.com
ScienceDirect
Dyes and Pigments 75 (2007) 526–532
DYES and PIGMENTS
www.elsevier.com/locate/dyepig

Electric and dielectric properties of some luminescent solar collectors based on phthalocyanines and hematoporphyrin doped PMMA

S.M. Reda

Chemistry Department, Faculty of Science, Benha University, Benha, Egypt

Received 2 December 2005; received in revised form 12 April 2006; accepted 28 June 2006

Abstract

The electrical properties: DC-electrical conductivity (σ_{DC}), AC-electrical conductivity (σ_{AC}), dielectric permittivity (ε') and dielectric loss (ε'') for pure polymethylmethacrylate (PMMA) and mixed with phthalocyanine, Ni-phthalocyanine and hematoporphyrin IX chloride laser dyes have been investigated. The conductivity values for all polymer–dye samples are higher than that of the pure PMMA. For all investigated samples, at the constant temperature, the frequency dependence of (σ_{AC}) was found to obey the relation (σ_{AC}) $= A\omega^s$. The results are discussed according to the correlated barrier hopping CBH mechanism from which the Coulomb well barrier of charge carriers (W_M) was calculated. For the dye-doped samples, the hematoporphyrin IX chloride mixed sample showed the larger value of (W_M) compared with the others. At all frequencies, ε' values for doped samples are higher than that of pure one. This is due to a free volume enhancement offered by the large size of the dye molecule. Also, the addition of dyes to PMMA causes an increase in the intensity of the loss peak (ε'') accompanied by a shift in its position. The effect of chemical structure of investigated dyes on the electrical properties is discussed.

Keywords: Polymethylmethacrylate; Phthalocyanine; Ni-phthalocyanine; Hematoporphyrin IX chloride; DC-electrical conductivity; AC-electrical conductivity; Dielectric permittivity; Dielectric loss

1. Introduction

Organic dye–polymer composites have received considerable attentions from many researchers [1] and have been considered as candidates for new photodetectors [2] and solar concentrators [3]. An approach to overcome the cost of solar electrical energy is to concentrate as much light as possible on high efficiency solar cells. Compared with other concentrators, polymethylmethacrylate (PMMA) is a transparent, polar, highly strong amorphous polymer [4]. Therefore, it can be used as a substrate for the fluorescent species of organic laser dyes [5]. Phthalocyanines and metallophthalocyanines are organic materials which have many applications in several fields, such as green and blue dyes and pigments, sensing elements in chemical sensors and photovoltaic cells elements [6]. In this work we use a group of these dyes as luminescent spices in solar concentrator's devices. In these devices solar energy is absorbed and concentrated by total internal reflection to the edge of the device, where it is converted into electricity using a solar cell facing the edge [7]. One of the most important requirements for LSC is a large Stokes shift, which is known to be a function of the dielectric constant (ε') and the refractive index (n) of the substrate [8,9]. So, we concentrate to study the electrical and dielectric properties of PMMA free and mixed with three laser dyes: phthalocyanine, nickel-phthalocyanine and hematoporphyrin IX chloride.

2. Experimental

Polymethylmethacrylate (PMMA) was prepared by polymerizing methylmethacrylate (MMA) in the presence of benzoylperoxide as initiator at 443 K for 7 h. The formed

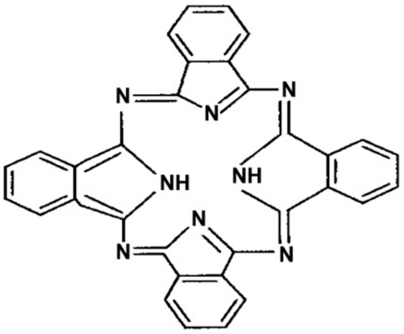
---

E-mail address: safenazr@yahoo.com

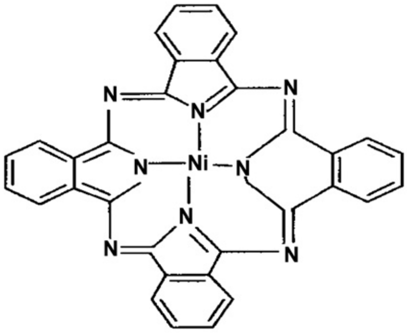
0143-7208/$ - see front matter © 2006 Published by Elsevier Ltd.
doi:10.1016/j.dyepig.2006.06.031

polymer was left for several hours at room temperature to evaporate the solvent off. Phthalocyanine and Ni-phthalocyanine were supplied by Stren chemicals company (U.S.A.), whereas hematoporphyrin IX chloride was obtained from Ciba-Giegy. Plate samples of thickness $\simeq 0.02$ cm and dye concentration of 10^{-4} mol L^{-1} were prepared by casting method where the dye was homogeneously diffused in the precast polymer. The chemical structure of dyes investigated is shown in Fig. 1. In the text the three dyes were abbreviated as PTH, Ni-PTH and HEM, respectively.

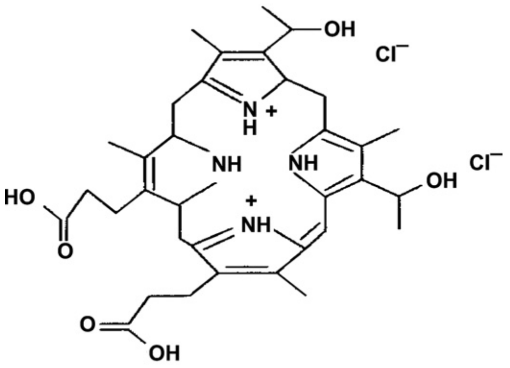
The AC-conductivity, dielectric constant ε' and dielectric loss ε'' as a function of temperature and frequency were measured. This is carried out using programmable automatic LCR meter (PM636 Philips) at frequencies of $1-10^3$ kHz and temperature range of 298–403 K.



Phthalocyanines



Nickel-Phthalocyanines



Hematoporphyrin IX Chloride

Fig. 1. The structure of dyes under investigation.

3. Results and discussion

3.1. Electrical conductivity

The DC-electrical conductivity (σ_{DC}) of pure PMMA and PMMA–dye samples are shown in Fig. 2. Generally, for all investigated samples the conductivity was found to increase with temperature. According to Lewis concept the presence of carbonyl group (C=O) in PMMA may be acted as an electron donor group [10]. So the electrical conduction in pure PMMA may occur by the electron jumping (hopping or tunneling) between filled and empty sites localized in the energy band gap. As shown in Fig. 2 the PMMA has low conductivity values and behaves as an insulator material, the conductivity values for all polymer–dye samples are higher than that of the pure PMMA. This indicates that the introducing dye in the polymer matrix may act as localized centers affecting the conduction process [7] in PMMA.

The activation energy, E_a, under DC-field was calculated using the equation:

$$\sigma = \sigma_0 \, e^{\frac{-E_a}{2k_B T}} \tag{1}$$

where k is the Boltzmann's constant and σ_0 is the conductivity at infinity temperature. The data obtained are listed in Table 1. From which it can be seen that E_a values for doped samples are lower than that of pure one. This refers to the facilitating of the conduction process through the presence of dye molecules, which either lie in the energy gap or act as donor and acceptor sites. These sites facilitate the hopping of electrons between valence and conduction bands.

The total measured AC-conductivity (σ_{total}) can be expressed according to [11]:

$$\sigma_{total} = \sigma_{AC}(\omega) + \sigma_{DC} \tag{2}$$

where σ_{DC} is the DC-conductivity and $\sigma_{AC}(\omega)$ is the polarization conductivity which depends on the measuring frequency according to [11]:

$$\sigma_{AC}(\omega) = A\omega^s \tag{3}$$

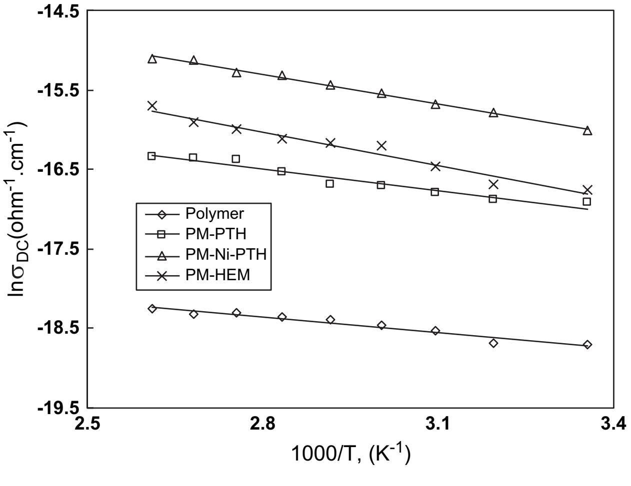


Fig. 2. Effect of temperature on DC-electrical conductivity for all investigated samples.

Table 1
DC- and AC-conductivity data for all investigated samples

Samples	E_a (eV)	Temp. Range[c] (K)	σ_{DC}[a] ($\mathrm{Ohm^{-1}\,cm^{-1}}$)	W_M (eV)	σ_{AC}[b] ($\mathrm{Ohm^{-1}\,cm^{-1}}$)
PMMA	0.79	343–383	1.1×10^{-8}	0.29	4.4×10^{-8}
PM–PTH	0.37	343–363	7.6×10^{-8}	0.62	2.2×10^{-6}
PM–Ni-PTH	0.23	363–383	2.3×10^{-7}	0.05	2.2×10^{-6}
PM–HEM	0.49	313–333	1.1×10^{-7}	0.25	2.8×10^{-6}

[a] σ_{DC} at 363 K.
[b] σ_{AC} at 363 K and frequency of 50 kHz.
[c] Temperature range at which the activation energy, E_a, was calculated.

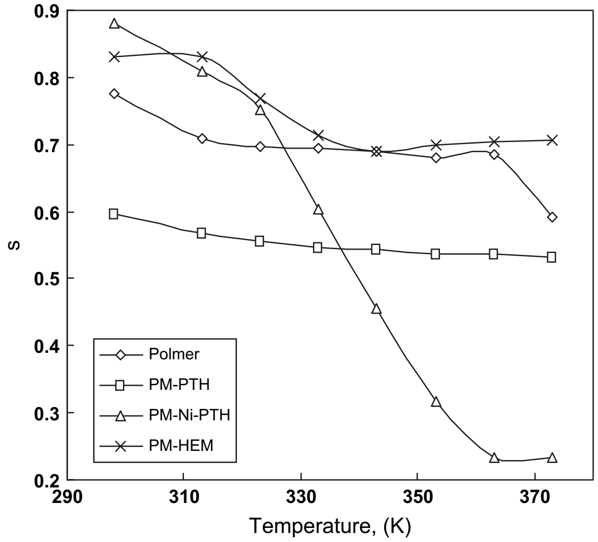


Fig. 4. Effect of temperature on s value for all investigated samples.

where A is a constant, ω is the angular frequency and s is an exponential power of frequency. For all investigated samples σ_{AC} increases with increasing temperature and frequency, typical plot is given in Fig. 3. The values of the exponent s were obtained from the slopes of the straight lines for all investigated samples at different temperatures using the logarithmic form of Eq. (3). Fig. 4 shows that, s values are decreased with increasing temperature. This indicates that hopping mechanism is dominated in these samples [12,13]. For pure PMMA, PTH and HEM-mixed samples, at lower temperature, the exponent s is close to unity and is slightly dependent on temperature. It seems that these samples behave as insulting materials [1]. This is attributed to that PMMA exhibits an amorphous structure which contains imperfections such as impurities or dangling bonds at point defects. This may lead to create levels within the band gap (localized states) [14]. Electrons created in PMMA are trapped in pairs at defect sites. The Coulomb repulsion energy between electrons being out weighed by an energy gain associated with lattice distortion [1]. Moreover, in our samples, the Van der Waal's bonds between neighbouring molecules give rise to very narrow allowed bands with corresponding high effective masses in the energy gap. The charge carriers of this band together with the presence of disorder contribute further to the process of localization. These localized centers can give rise to hopping transport. At higher temperature, in addition to hopping transport, the reduced internal viscosity of the material allows the dipoles to rotate freely and dielectric polarization seems to have taken place. The total charge then includes the homocharge and heterocharge produced due to the rotation of the permanent dipoles [1].

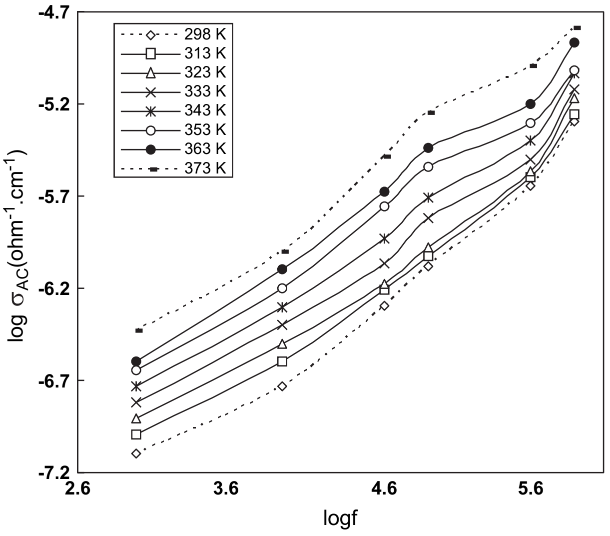


Fig. 3. Effect of frequency on AC-electrical conductivity for PM–Ni-PTH.

According to the correlated barrier hopping model [15], CBH, the Coulomb well barrier of charge carriers (W_M), which are separated by interstice R can be calculated by equating [15]:

$$s = 1 - \left\{ \frac{6 k_B T}{W_M} \right\} \tag{4}$$

From Table 1 it can be seen that the highest values of W_M are assigned to PTH dye mixed sample compared with the other dyes. The high potential barrier exhibited in this sample acts to hinder charge carrier transport and this is responsible for its lower conductivity.

The temperature dependence of AC-conductivity for pure PMMA and polymer–dye sample at different frequencies are shown in Fig. 5. For pure PMMA the σ_{AC} values increase with frequency and temperature till $T = 373$ K before starting to decrease with further heating. This can be explained according to the fact that AC-conductivity arises from the rapid transitions between localized states of charged species such as electrons or dipoles. The drop in σ_{AC} at 383 K is attributed to either a phase transition in the sample or due to thermal energy distributing the dipoles formed in the sample. This agrees with that reported by others [7]. The results also showed that its conductivity values are comparatively low. This could be interpreted on the basis that the dipole in long chain polymer is not quite free to rotate. But it is constrained to assume discrete orientations with respect to its nearest-neighbours. As the side acrylate group of PMMA is strongly disordered structurally in the amorphous state, comparatively weak polarization may result from hopping of charge carriers. This

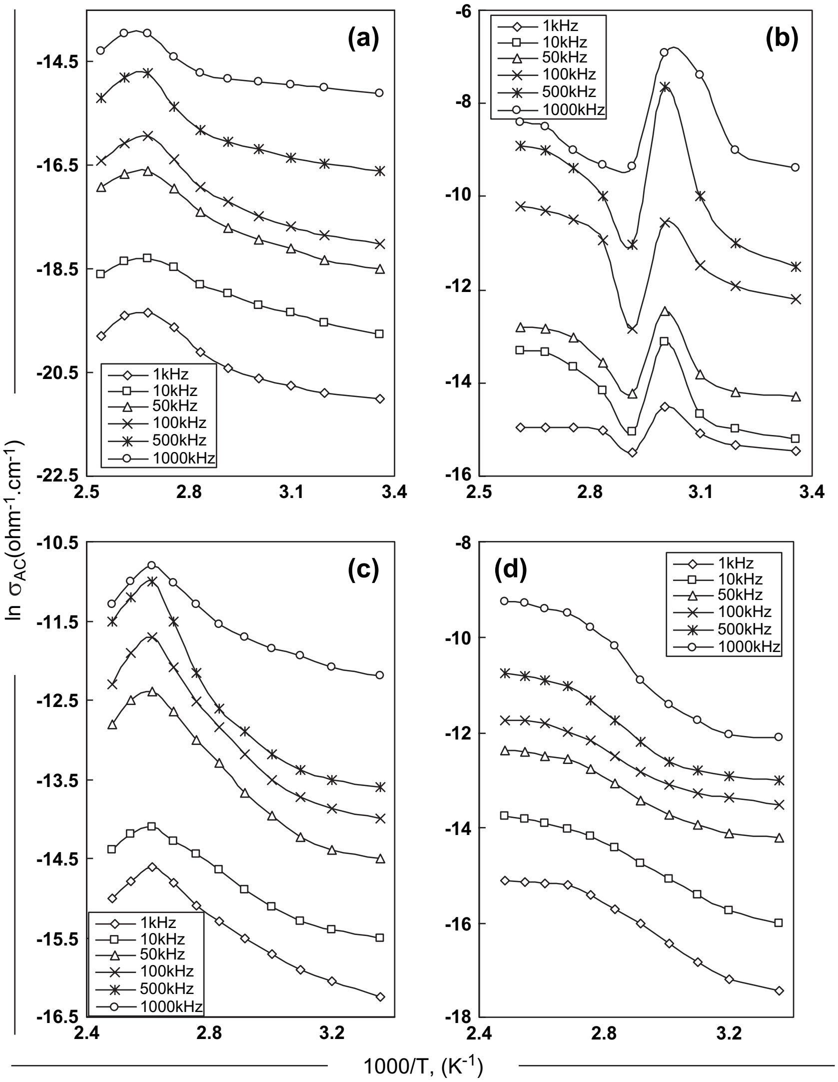


Fig. 5. Effect of temperature on AC-electrical conductivity (at different frequencies) for PMMA (a), PM–PTH (b), PM–Ni-PTH (c) and PM–HEM (d).

perhaps accounts for the low value of AC-conductivity of this polymer [16].

The plot of ln σ_{AC} vs. $1/T$ for all polymer–dye samples exhibits the same trend as that of the pure PMMA. σ_{AC} increases slowly with temperature in the range (298–333 K), while the increase becomes very high at higher temperatures. Generally, for all doped samples σ_{AC} was found to be higher than that of σ_{DC} referring to the presence of polarization effect, Table 1. The σ_{AC} values of dye–polymer samples are higher than those obtained for pure PMMA; this can be attributed to the large dipole of dye content. The drop in σ_{AC} value at $T = 333$ K for PTH and at $T = 393$ K for Ni-PTH-mixed sample indicates that at these temperatures, thermal energy disturb the dipole arrangement occurred in the samples or a phase transition has occurred to a phase of lower conductivity value [7]. Also the increase in the oscillation field accompanied with increasing frequency will lead to an increase in the polarization of the samples appearing in that the form of conductivity increases.

3.2. Effect of temperature on dielectric permittivity

The temperature dependence of permittivity (ε') for pure PMMA and doped samples at different frequencies are shown in Fig. 6. For our polymer, ε' shows a maximum at $T = 373$ K. This is because, by increasing the temperature the orientation of the molecule is facilitated and thereby increases the permittivity up to a maximum value. Further increase in the temperature is accompanied by a decease in ε'. This can be attributed to the intensified thermal oscillations of the polymer molecules which disturb the orderliness of their orientations. The results show also a decrease in ε' with increasing frequency. This can be attributed to the lag of dipole oscillations behind those of the field at high frequencies. On the other hand, higher the frequency of the applied field, the more the thermal energy needed to disturb the ordered dipoles [7]. For all polymer–dye samples ε' values increase, at all frequencies, by adding dye. This can be attributed to either the enhanced mobility of the motion of polymer molecule or due to the rotation

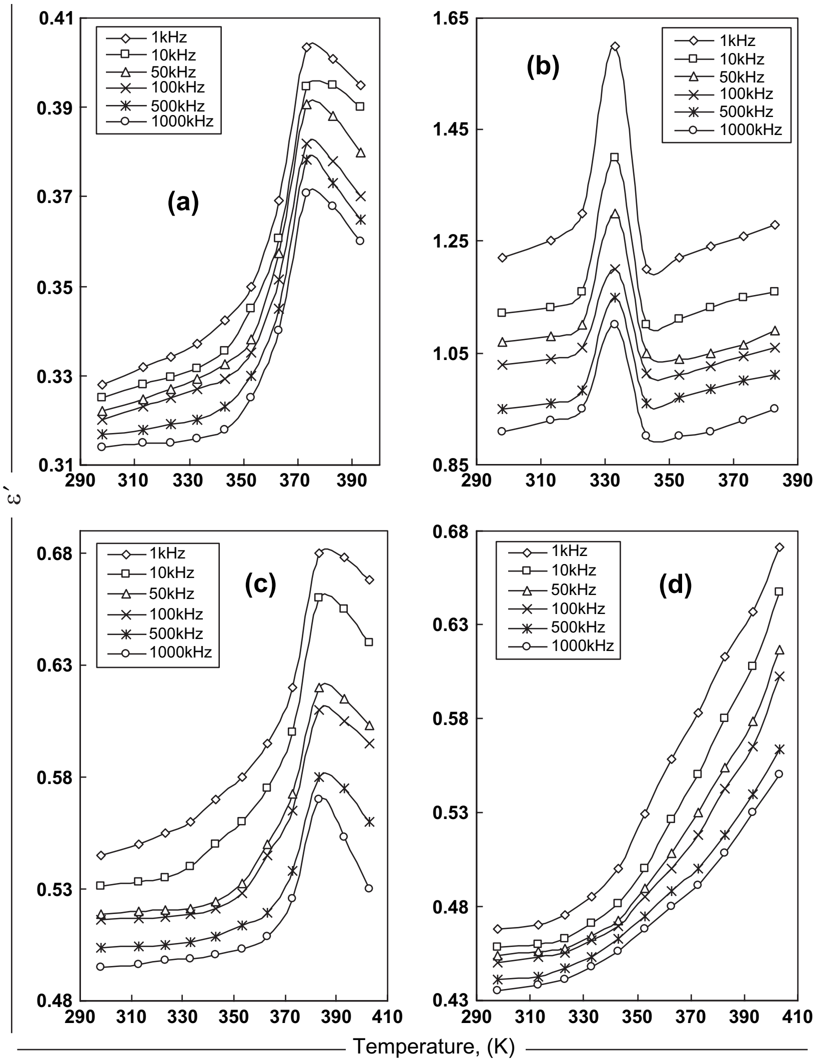


Fig. 6. Effect of temperature on dielectric constant for PMMA (a), PM–PTH (b), PM–Ni-PTH (c) and PM–HEM (d).

of the side acrylate group of the host polymer. This is casued due to a free volume enhancement offered by the large size of the dye molecule [17].

3.3. Temperature dependence of dielectric loss

Two types of dielectric relaxations have been established for ester polymer [5]: (1) glass–rubber transition (α-relaxation) due to micro-Brownian motion of the main chain segments; (2) glass–glass transition of amorphous polymer (β-relaxation), which is attributed to the rotation of the ester side group –COOR about the C–C bond which links the ester group to the main chain of the polymer. The variation of the dielectric loss (ε'') as a function of temperature at different frequencies for all investigated samples are shown in Fig. 7. For pure PMMA, Fig. 7a, only a single peak in $\varepsilon''-T$ curves at $T = 373$ K is observed. This could be assigned to αβ process where the side groups cooperate with the backbone motions in micro-Brownian [17]. Fig. 7 shows that the addition of dyes to PMMA causes an increase in the intensity of the loss peak accompanied by a shift in its position to lower temperature values, (333 K) for PTH-mixed sample, compared with that of the pure PMMA. This can be attributed to an increase in the dipole concentration by the addition of dye molecules, which causes such effect not only via its own polarity but also by changing the nature of the relaxation process (enhancement of its α-character). The existence of hydrogen-bonding interaction between the ester side group and the acidic hydrogen atoms of hydroxylic group in the case of HEM-mixed sample hinders the β-relaxation (the internal rotation of the side group) [18]. This causes the disappearance of the maximum in this sample. Moreover, the addition of Ni-PTH dye to PMMA shifts the position of this peak to higher temperature (383 K). Also the addition of this dye hinders the movement of polymer molecules as they orient themselves following the applied field [17]. Therefore, it can be said that the predominate mechanism of polarization is a deformational one caused

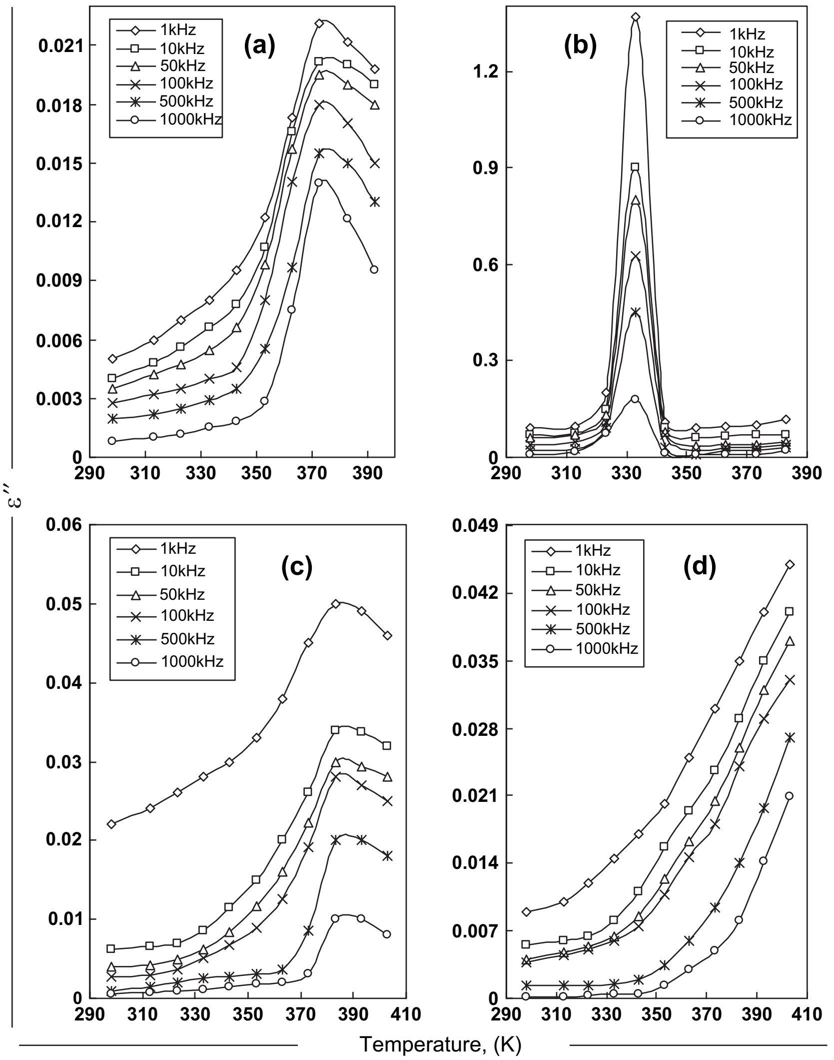


Fig. 7. Effect of temperature on dielectric loss for PMMA (a), PM–PTH (b), PM–Ni-PTH (c) and PM–HEM (d).

by the displacement of charges with respect to each other in the direction of the electric field in which, the relaxation phenomena in amorphous materials are divided into four types of losses: conduction losses, dipole relaxation loss, deformational loss and vibrational loss. At the higher temperature range, deformational loss and vibrational loss are more pronounced.

4. Conclusions

Studying electric and dielectric properties of some luminescent solar collectors using phthalocyanine, Ni-phthalocyanine and hematoporphyrin IX chloride laser dyes shows that the conductivity values for all polymer–dye samples are higher than that of the pure PMMA. The correlated barrier hopping CBH mechanism was found to be the dominating conduction mechanism in these samples. The hematoporphyrin IX chloride mixed sample showed higher value for potential barrier (W_M) compared with the others. The ε' values for doped samples are higher than that of pure PMMA. This is due to a free volume enhancement offered by the large size of the dye molecule. The addition of dyes to PMMA causes also an increase in the intensity of the loss peak (ε'') accompanied by a shift in its position.

Acknowledgements

The author wishes to thank all the staff members and colleagues at Chemistry Department, Faculty of Science, Benha University, Egypt for their cooperation during this work.

References

[1] El-Shahawy MA. Polym Test 2000;19:821.
[2] Grachev AV, Ischenko AA, Kareva EI, Kolotkov VV, Leshin IV, Oborotov AF, et al. Appl Spectrosc 1990;52:431.
[3] El-Shahawy MA, Mansour AF. J Mater Sci Electron 1996;7:171.
[4] Perepehko II. An introduction to polymer physics. Moscow: Mir Publishers; 1981.
[5] Batchelder JS, Zewail AH, Cole T. J Appl Opt 1981;20:3733.
[6] Szymczyk I, Abramczyk H. Pure Appl Chem 2004;76:183.

[7] EL-Shahawy MA, Mansour AF, Hashem HA. Indian J Pure Appl Phys 1998;46:78.
[8] Kondepudi R, Srinivasan S. Sol Energy Mater 1990;20:257.
[9] Kondepudi R, Srinivasan S. Indian J Pure Appl Phys 1992;30:389.
[10] Li D, Brisson J. Polymer 1998;39:793.
[11] Tareev B. Physics of dielectric materials. Moscow: Mir Publishers; 1975.
[12] Elliot SR. Philos Mag 1977;36:1291.
[13] Elliot SR. Philos Mag 1978;37:583.
[14] Mott NF, Davis EA. Electronic processes in noncrystalline materials. 2nd ed. Oxford: Clarendon Press; 1979.
[15] Elliot SR. Adv Phys 1987;36:135.
[16] Shukla JP, Gupta M. Indian J Pure Appl Phys 1987;25:242.
[17] EL-Shahawy MA. Polym Test 1999;18:389.
[18] Dionisio MS, Moura-Ramos JJ, Williams G. Polymer 1994;35:1705.