The Optical and Electrical Properties of Low Density Polyethylene Films in CuSO$_4$ Solution

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الخواص البصرية والكهربية لشرائح من البولي-إثيلين منخفضة الكثافة
فى محلول كبريتات النحاس

صباح النعيمى

قسم الفيزياء ـ جامعة قطر ـ قطر

في هذا البحث تمت دراسة تأثير غمر شرائح رقيقة من مادة البولي-إثيلين المنخفضة الكثافة بمحلول 10% من كبريتات النحاس لفترات زمنية مختلفة على الخواص البصرية والكهربية لها. تم قياس طيف الامتصاص البصري للشرائح في مدى الأطوال الموجية: 1100nm→200 ، وبعد ذلك تم حساب قيم فجوات الطاقة البصرية وعرض ذيول الطاقة عند فترات زمنية مختلفة. أما قياسات معامل التوصيل للتيار المتردد، فقد تمت في مدى الترددات: 10^5Hz→10^2 ، وبعد ذلك تم تحليل هذه القياسات لتعطي نتائج عن الثابتين: معامل التوصيل للتيار المستمر، وثابت العزل البصري. من خلال نتائج هذه الدراسة لوحظ ما يلي: (1) وجود الانتقالات البصرية المباشرة وغير المباشرة. (2) زيادة فجوات الطاقة المباشرة وغير المباشرة بزيادة زمن غمر الشرائح. (3) يقل عرض ذيول الطاقة بزيادة زمن الغمر. (4) يقل معامل التوصيل للتيار المستمر بينما يزداد ثابت العزل البصري ، وذلك بزيادة زمن الغمر. قد يرجع تفسير هذه النتائج إلى أن أيونات الكبريتات تكون قد سببت اضمحلال مادة البولي-إثيلين المنخفضة الكثافة بمرور الزمن.

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ABSTRACT

The optical and electrical properties of pure and treated low density polyethylene (LDPE) were investigated. These measurements have been carried out at various times of immersion for LDPE films in 10% solution of $CuSO_4$. The optical absorption spectra were measured in the wavelength range $200 \rightarrow 1100$ nm. The optical energy gaps and energy bandwidth of the tail of localized state (E_{opt} and ΔE) were calculated at different times of exposure to $CuSO_4$. The a.c. conductivity was studied in frequency range $10^2 \rightarrow 10^5$ Hz. The data of a.c. conductivity were analyzed to obtain the d.c. conductivity (σ_{dc}) and the optical dielectric constant (ε'_∞). The results of this study show that: (1) Direct and indirect optical transitions exist, (2) Direct and indirect energy gaps increase as the exposure time increases, (3) The Urbach energy band tail decreases as time increases, (4) The d.c. conductivity decreases, while the dielectric constant increases as time increases. These results could be explained by the fact that sulfate ions have caused formation of voids and degradation of the LDPE as time increased.

Introduction

The state of Qatar constitutes aggressive environments for concrete durability. Qatar is characterized by adverse geomorphic and climatic conditions such as severe ground ambient salinity. On the other hand chloride and sulfate salts extensively contaminate the ground water and moisture laden environment. These conditions may lead to some thermal changes in plastics and may cause dry shrinkage cracking. The amount of chloride and sulfate in the shallow coastal areas are 20% or more greater than those in open seas. LDPE plastics FD 0274 is good in processability and transparency. It is well known by its resistance to chemicals, water, and anticorresive. Its cost is low, easily colored, and can be supplied abundantly. Therefore, it is used to insulate and shear wires and cables [1].

The study of the optical absorption spectra in solids provides essential information about the band structure and the energy gap in both crystalline and noncrystalline materials [2,3]. The lower energy part of the absorption spectra gives information about the atomic vibrations and higher energy part of the absorption spectra gives knowledge about electronic status in the normal materials. LDPE is used widely as an electrical insulation material because of its low dielectric loss and its superior breakdown strength [4-6]. The physical properties of any plastic depend on the length of the molecular chains [7]. The greater the length of these chains the stronger and tougher the plastic will be. As soon as the chain is broken the plastic begins to become fragile and if the process proceeds to a sufficient extent, the plastic becomes so brittle that it breaks up under the action of such erosive forces as wind, rain and waves into very small particles.

The work here focuses on the study of the effect of sulfate ions content on the cross linking of LDPE FD 0374 by investigating the optical and electrical properties.

Experimental

Samples Preparation

The material used in the present investigation was LDPE grade FD 0374 produced by QAPCO, Qatar. The material has the following properties: melt flow index 3.3-3.8 g/10 min, density 0.923 g/cm^3, and its crystalline melting temperature is $115\,^\circ C$.

Samples (or films) of LDPE were shaped as discs with diameter of 2.5 cm and thickness of 0.1→ 0.3 cm using the compression molded method at 30 Mpa and 165 °C for 20 minutes [8]. Then, they were immersed into aqueous solution of 10 % CuSO₄ by weight for different intervals of time.

Optical Measurements

The absorption measurements of LDPE films were made using UV 160 Shmadzu spectro-photometer in the wavelength range 200→ 1100 nm. The optical density was directly measured.

Electrical Measurements

For electrical measurements, LDPE films were pasted with silver electrodes using silver dag, then inserted into a special holder [9]. The measurements were performed in the frequency range of 10^2Hz → 10^5Hz, operating at 0.8 volt, using Hioki 3520 LCR tester at room temperature.

Results and Discussion

Optical Results

Figure 1 shows the optical absorbance of pure and treated samples (or films) of LDPE with solution of 10 % CuSO₄ at different intervals of time. It is clear from this figure that the structure of absorption spectra curves changed: the absorbance decreases as the wave length increases and the absorbance for treated samples is slightly shifted up regarding the pure at the same wave length.
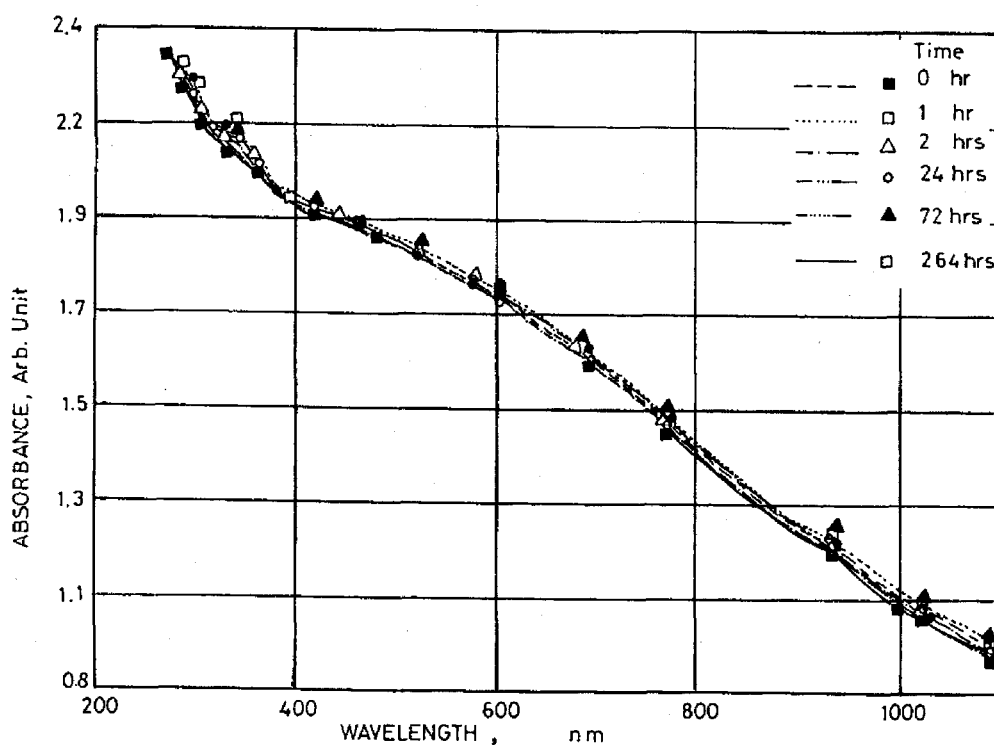

Figure 1: Spectral absorbance distribution for LDPE exposed to 10% CuSO₄ solution at different times of exposure.

This behavior could be due to the penetration of sulfate ions into LDPE's textures and the formation of voids [10].

The absorption coefficient $\alpha(\omega)$ at angular frequency ω is given by [11-14]:

$$\alpha(\omega) = b \, (Abs/t) \qquad (1)$$

where b is a constant, Abs is the absorbance, and t is the thickness of the sample.

The variation of the absorption coefficient as a function of photon energy was used to study the optical induced transition affect. This study gave some information about the structure and the optical energy gap in many disordered materials, which follow the Urbach rule [15].

$$\alpha(\omega) = B \exp\left(\frac{\hbar\,\omega}{\Delta E} \right) \qquad (2)$$

where ΔE is the energy bandwidth tail of localized states in the normally forbidden band gap and B is the correlation constant. Rewriting equation (2) in the following form:

$$\Delta E = (\hbar\omega) \ln B - (\hbar\omega) \ln \alpha \qquad (3)$$

This will allow us to obtain a relationship between the energy width of the band (ΔE) and the absorption coefficient $\alpha(\omega)$ at fixed frequency. By calculating the absorption for each sample at a fixed frequency, we obtained the results that link the energy width of the band (ΔE) with treatment time as shown in Figure 2. From this figure, we can deduce that the energy width of the band (ΔE) decreases as time increases.
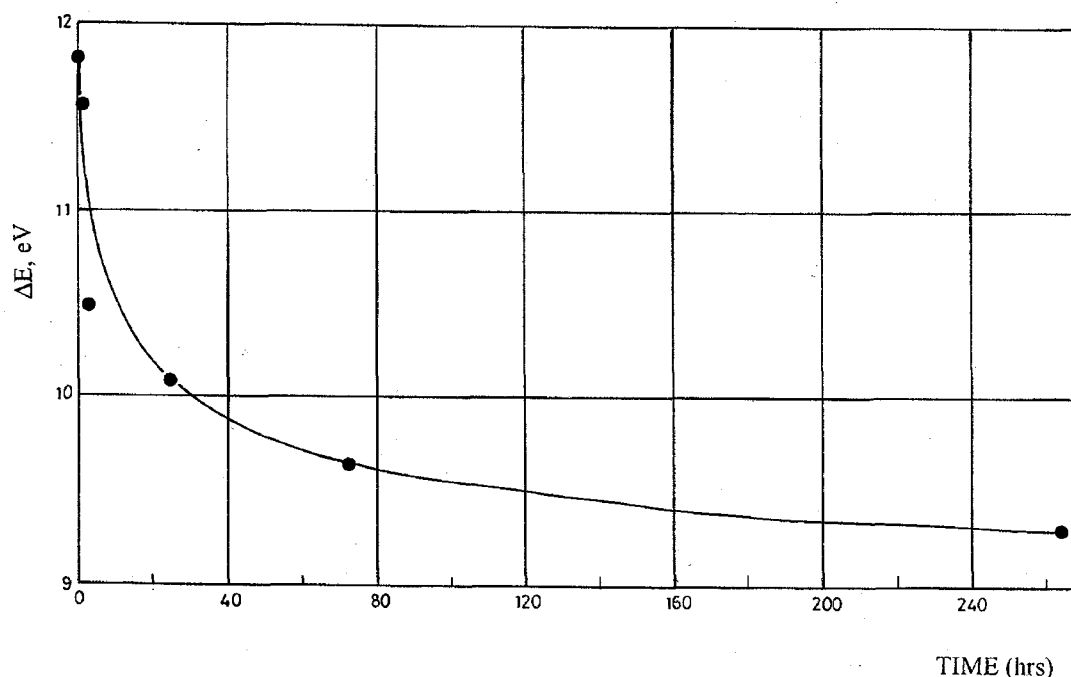

Figure 2: The dependence of the band energy tail (ΔE) on time of exposure to 10% $CuSO_4$ solution.

Urbach formula, which was applied for many amorphous materials, has been modified to a more general form by Mott, Davis and Tauc [11-14]:

$$\alpha(\omega) = C\,(\hbar\omega - E_{opt})^n \tag{4}$$

where n = 1/2 for direct transition, n = 2 for indirect transition

The variation of (α^2) with ($\hbar\omega$) for different samples gives the optical energy gap for the allowed transition and can be obtained by extrapolating the linear portion of the curves to $\alpha^2=0$. This extrapolation gives the values of direct energy E (optical direct), which are shown in Figure 3 as a function of time of treatment. Also the extrapolation of the curves to ($\alpha^{1/2}=0$) gives the indirect energy. The obtained values of E (optical indirect) are shown in Figure 4 as a function of time of treatment. Figure 3 shows that the energy of transition of direct optical energy transition increases as the exposure time increases. Also, figure 4 shows that the energy of transition of indirect optical transitions increases as the exposure time increases.

Therefore, we can conclude that both mechanisms of transitions exist, as found in previous studies [16], and immersion of samples in sulfate might lead to increase in degree of degradation [10].

Electrical Results:

Many dielectric functions have been used to describe the frequency dependent properties of materials. Among the most important ones are the complex dielectric constant, ε and the complex impedance, Z. These functions may be expressed as [17]:

$$\varepsilon = \varepsilon' - i\varepsilon'' \tag{5}$$

$$Z = Z' - iZ'' \tag{6}$$

where ε' and ε'' are the real and imaginary parts of the dielectric constant, Z' and Z'' are the real and imaginary parts of the impedance of the sample.

The a.c. conductivity $\sigma(\omega)$ as a function of frequency ω at fixed temperature can be expressed as [18]:

$$\sigma(\omega) = A\,\omega^s \tag{7}$$

where A is a constant and s is a parameter characterized by the frequency. The above equation was found to hold for several low mobility amorphous and crystalline materials [19,20].

Using the computer analysis for the electric conductivity at different frequencies, one can obtain the d.c. impedance at zero frequency (Z_o) for different times of treatment. The obtained results are illustrated in Figure 5. From this figure it is clear that impedance (Z_o) increases with the time of treatment, which might be attributed to the fact that upon immersion of LDPE into 10% $CuSO_4$ solution, creation of voids has taken place. Using the geometrical factor of the sample we can calculate the d.c. conductivity with time as shown in Figure 6. From this figure we find that d.c. conductivity decreases with time and this behavior could be explained by increasing the degree of degradation [10].

Figure 7 shows the dependence of the static dielectric constant upon the time of treatment, where it increases with time.

One of the most common causes of dielectric dispersion in inhomogeneous materials is due to electrode barriers; however the measured values should depend on the thickness of the samples if the area remains constant. If the carrier is hoping along a random path then both the dielectric polarization and the d.c. conductivity can arise by the same mechanism. Such random path model suggests that the loose peak will be masked by d.c. conductivity, but at low frequency one should observe a frequency independence static dielectric constant. The over all agreement of data with the model based on the distribution on conductivity relaxation time suggests that the local inhomogenuity is within the material.
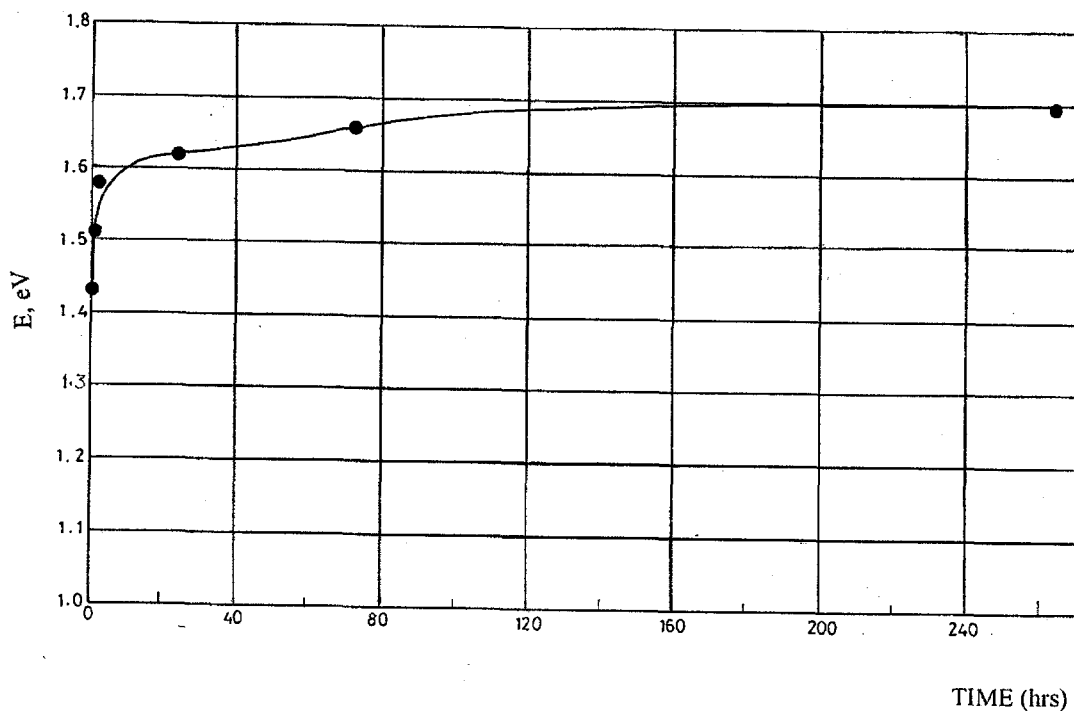
Figure 3: The dependence of variation of the direct optical energy on the time of exposure to 10% $CuSO_4$ solution.
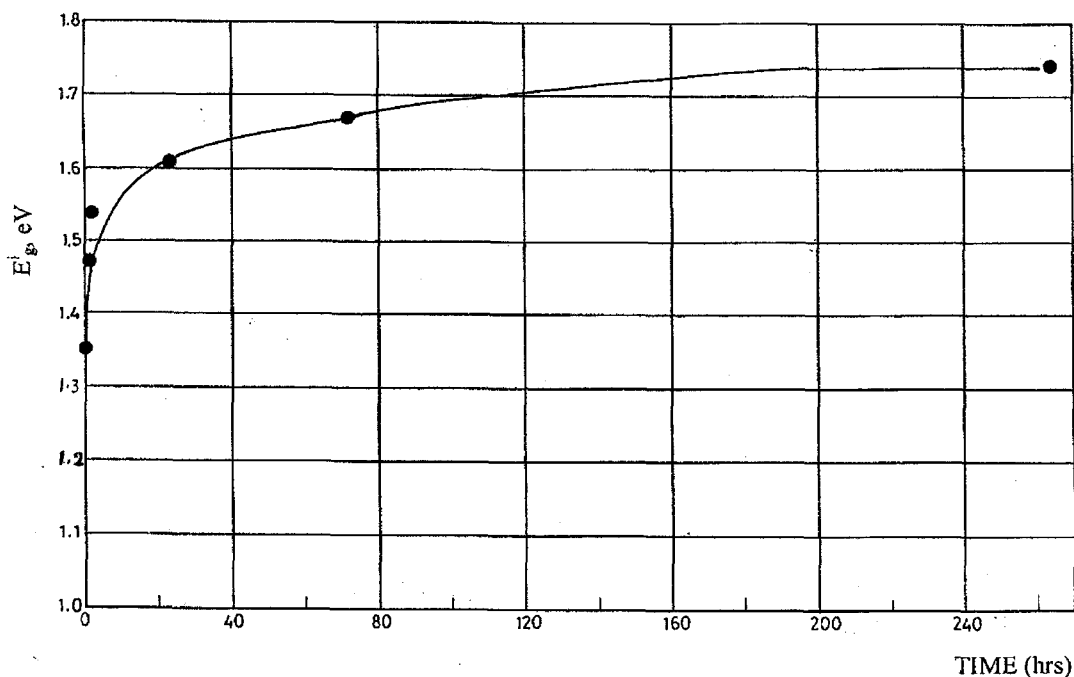

Figure 4: The dependence of variation of the indirect optical energy on the time of exposure to 10% $CuSO_4$ solution.
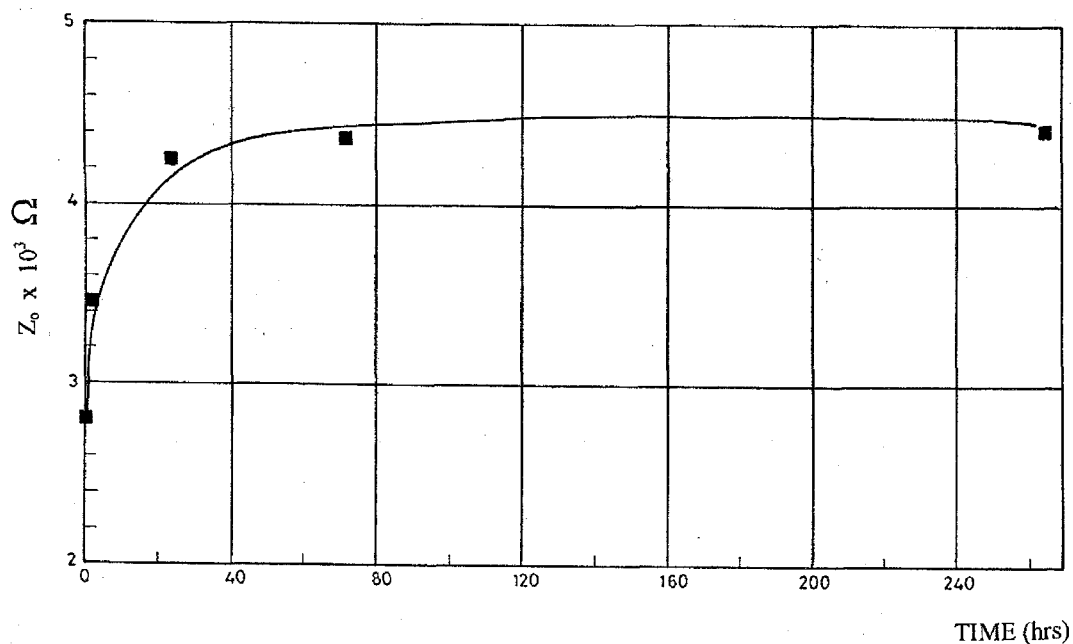
Figure 5: The dependence of the variation of the d.c. impedance (Zo) on the time of exposure to 10% CuSO4 solution.
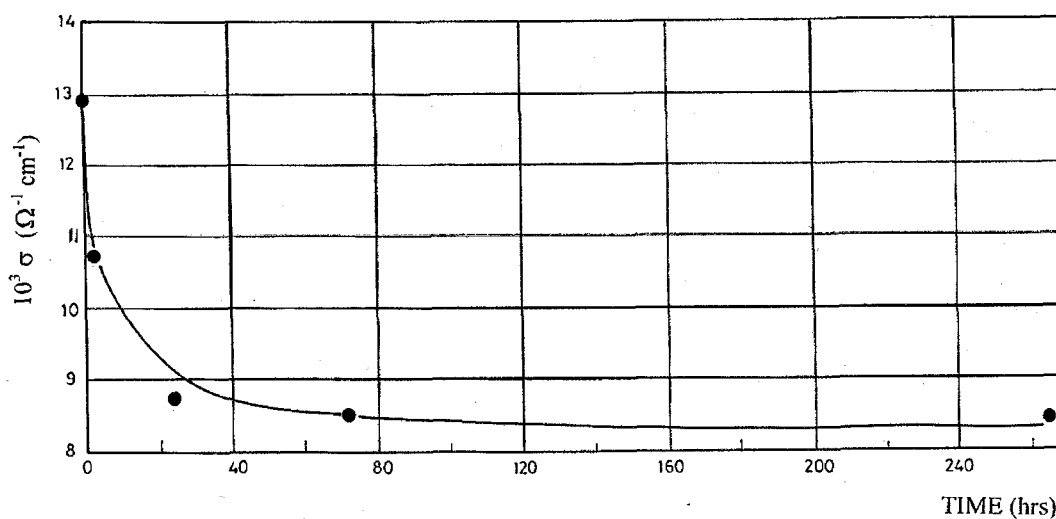

Figure 6: The d.c. conductivity dependence on the time of exposure to 10% CuSO$_4$ solution.
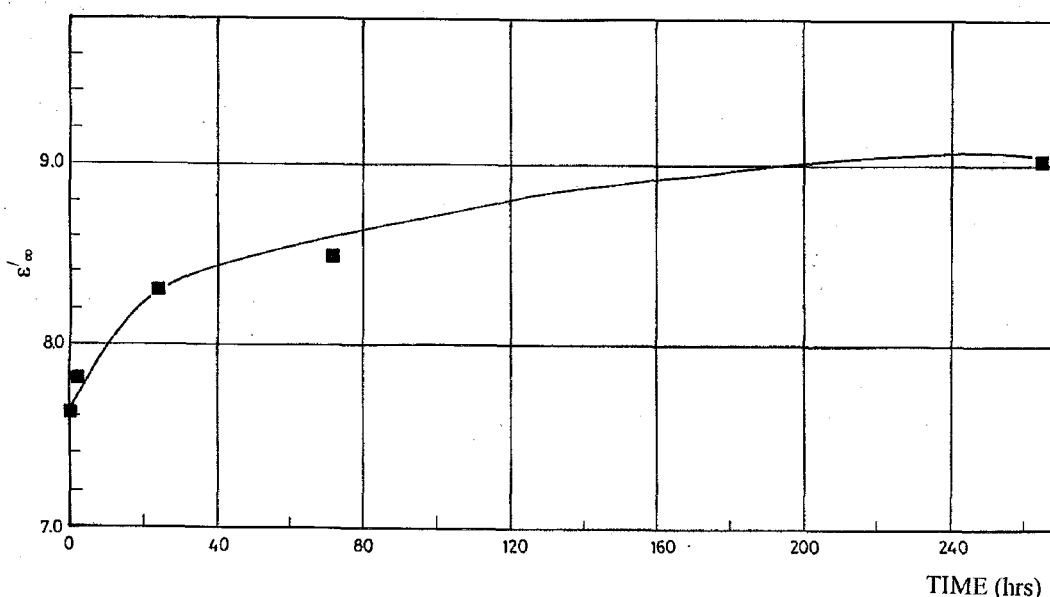
Figure 7: The dependence of the variation of static dielectric constant (ε'_∞) on the time of exposure to 10 % $CuSO_4$ solution.

Conclusions

The investigations of the effect of sulfate ions on optical and electrical properties of LDPE show that:

Both mechanisms of direct and indirect optical transitions exist for treated LDPE films with 10% of $CuSO_4$ solution over different intervals of time.

As the time of treatment increases, the optical energy gaps of transitions increase, while the energy band tail decreases.

When the time of treatment increases, the electrical d.c. conductivity decreases and the static dielectric constant increases.

These results could be due to the fact that sulfate ions cause formation of voids and degradation for LDPE as time goes by.

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