
Study of relaxation and dielectric response of polyimide films

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ABSTRACT. In recent years, polyimides are more and more used as high performance polymers because of their excellent thermal, mechanical and electrical properties. In this work, dielectric properties and relaxation behavior of some Polyimide films were studied on the basis of dielectric constant, dielectric loss and AC conductivity taking into account their variation with frequency and temperature. According to the results, three types of relaxations α , β and γ at decreasing temperature were detected, the origin of these relaxations and the influence of the chemical structure on changes in dielectric and electrical properties were discussed.

RÉSUMÉ. Au cours des dernières années, les polyimides sont de plus en plus utilisés comme des polymères à hautes performances en raison de leurs excellentes propriétés thermiques, mécaniques et électriques. Dans ce travail, les propriétés et la relaxation diélectriques de certains films polyimides ont été étudiés sur la base de la constante diélectrique, le facteur de perte diélectrique et la conductivité AC en tenant compte de leur variation avec la fréquence et de la température. D'après les résultats obtenus, trois types de relaxations α , β et γ à température décroissante ont été détectés, l'origine de ces relaxations et l'influence de la structure chimique sur les variations des propriétés diélectriques et électriques ont été discutées.

KEYWORDS: dielectric relaxation, polyimide, dielectric spectroscopy.

MOTS-CLÉS : relaxation diélectrique, polyimide, spectroscopie diélectrique.

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1. Introduction

Technological development in the field of design of electrical and electronic devices requires more and more to use materials that can withstand the rise in current, temperature and frequency.

Polyimides appear as very interesting for high temperature electrical insulation applications. They have a thermal stability, good resistance radiation, chemical resistance and good mechanical strength (Chisca *et al.*, 2011); it is possible to notice that as Polyimides exhibit slower degradation kinetics than other polymers, this is mainly due to the presence of the imide rings and many aromatic rings within the macromolecular structure of the Polyimide which give them a very high thermal stability (Liaw *et al.*, 2012).

Therefore, it appears very important to understand the behavior of this type of polymer in an electric field with different temperatures and frequencies, in order to explain the origin of the changes that may occur during use of these films.

In our previous article (Benabed *et al.* 2014), we studied the dielectric properties and conduction mechanism in some Polyimide films by dielectric spectroscopy at frequency range of 10^{-2} Hz to 1 MHz over temperature range of -60°C to 240°C , in this work, we want to give a deeper explanation of the dielectric relaxation and AC conductivity in order to establish a relationship between the dielectric and chemical properties of these films.

2. Experimental method

2.1. Polymer characterizations

Thin aromatic Polyimide films with thickness from $50\mu\text{m}$ were used in this study, the films used were characterized by:

2.1.1. Fourier transforms infrared spectroscopy (FT-IR)

Infrared spectroscopic measurements were performed in the range $4000-400\text{ cm}^{-1}$ at a resolution of 1.0 cm^{-1} . The result is shown in Figure 2.

2.1.2. X-ray Diffraction

The device used is a diffractometer X'PERT PRO coupled to a computer system for processing the results obtained and the layout of the spectra.

2.2. Dielectric relaxation spectroscopy

Dielectric relaxation spectroscopy (DRS) measurements in frequency range 10^{-2} Hz to 1 MHz were carried out using a Broad Band Dielectric controller

(NOVOCONTROL) Alpha, Beta Analyzer .The temperature measurement was varied between -60°C to 240°C and was controlled to within $\pm 0,5^{\circ}\text{C}$.

Measurements have been plotted according to the complex permittivity formalism:

$$\varepsilon^* = \varepsilon' - j\varepsilon'' \quad (1)$$

$$\tan\delta = \frac{\varepsilon''}{\varepsilon'} \quad (2)$$

Where ε' and ε'' are respectively the real and imaginary parts of the complex permittivity ε^* .

Jonscher (1983), has compiled the conductivity as a function of frequency in a large number of materials and suggested a "Universal" power law; the static (dc) conductivity has been derived from the (ac) conductivity measurements at low frequency:

$$\sigma_{ac}(\omega) = \sigma'(\omega) = \omega\varepsilon_0\varepsilon''(\omega) = \sigma_{dc} + K \quad (3)$$

Where ω is the angular frequency, K is an empiric parameter witch is a temperature dependent and n represents the high frequency slope of the (ac) conductivity (from 0 to 1) (Jonscher, 1981). The exponent is observed to be within $0.6 < n < 1$ for most materials. The exponent either remains constant or decreases slightly with increasing temperature and the range mentioned is believed to suggest hopping of charge carriers between traps.

The samples of the solid insulations used in this study are shown in Figure 1; circular gold electrodes were sputtered onto the free surface of the samples. The electrodes have a circular shape with a diameter of 16mm.

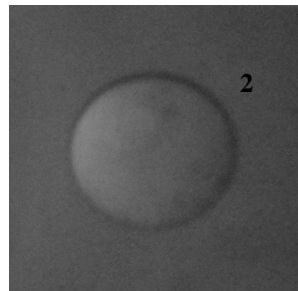


Figure 1. Photo of solid insulation sample PI:1-Polymide film,
2- gold electrode

3. Results and discussion

3.1. Fourier Transform Infrared Spectroscopy

The structure of the Polyimides was confirmed by using Fourier Transform Infrared (FTIR) spectroscopy. The FTIR spectra of the polyimide films showed the absorption bands at about 1780cm^{-1} (C=O asymmetric stretching), 1730cm^{-1} (C=O symmetric stretching), 1378cm^{-1} (C-N stretching) and 721cm^{-1} (C=O bending), which are characteristic for imides rings (Xie *et al.*, 2007). The absorption peak at 1500cm^{-1} , corresponding to the C-C stretching of *p*-substituted benzene (Xu and *al.*, 2004), the peak at $1240\text{-}1270\text{cm}^{-1}$ is attributed to (C-O-C stretching), the absorption bands at about $1070\text{-}1090$ and at $1120\text{-}1140$ corresponding to C-H bending (Ishida and *al.*, 1980), in Figure 2, we illustrated the peaks which characterize the imide groups.

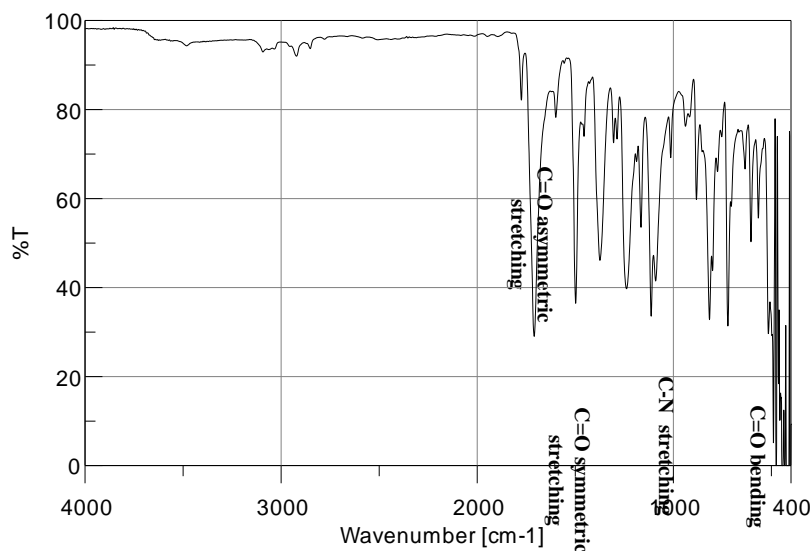


Figure 2. FTIR spectra of PI films

3.2. X-ray diffractogram

Figure 3 shows the X-ray diffractogram (from $2\theta=5^\circ$ to 100°) obtained for the polyimide films of thickness $d=50\ \mu\text{m}$, the patterns are dominated by amorphous envelope and peaks due to some degree of crystallinity, the most intense peak occurs at $2\theta=26,8^\circ$. Polyimide are a class of polymer with planar ring structures which make them very crystalline, and make the charge transfer interaction very easy with a strong capacity for general chain-to-chain polar interaction. The Polyimides are derived from highly disordered soluble precursors and conversion to imide takes

place in a formed structure with high and increasing viscosity (during conversion). But the aromatic Polyimides such as the films in our study tend therefore to be amorphous or to have very low crystallinity (Sroog, 1991).

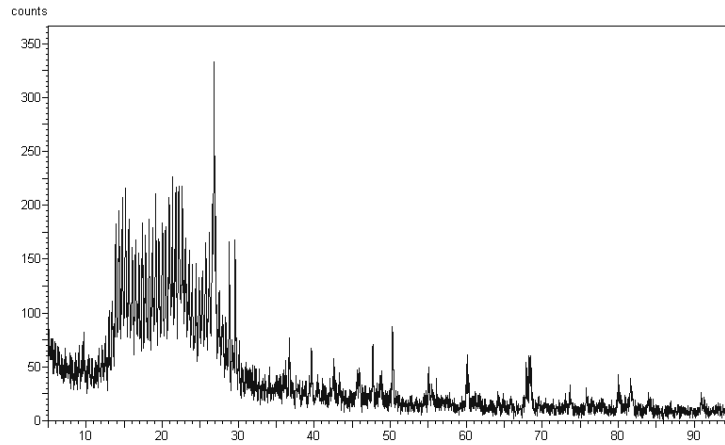


Figure 3. XRD pattern of polyimide films

3.3. Broadband dielectric spectroscopy

3.3.1. Dielectric properties

The experimental results of the study of frequency and temperature dependencies of the overall loss factor $\tan\delta$, real part of the permittivity ϵ' for the samples of PI are illustrated in Figures 4 and 5.

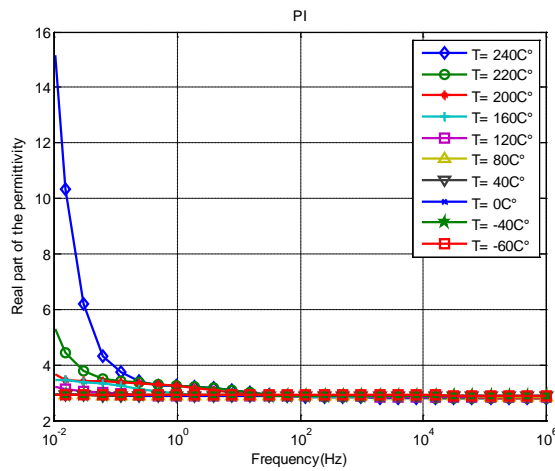


Figure 4. The real part of the permittivity ϵ' of PI as function of frequency for different temperatures

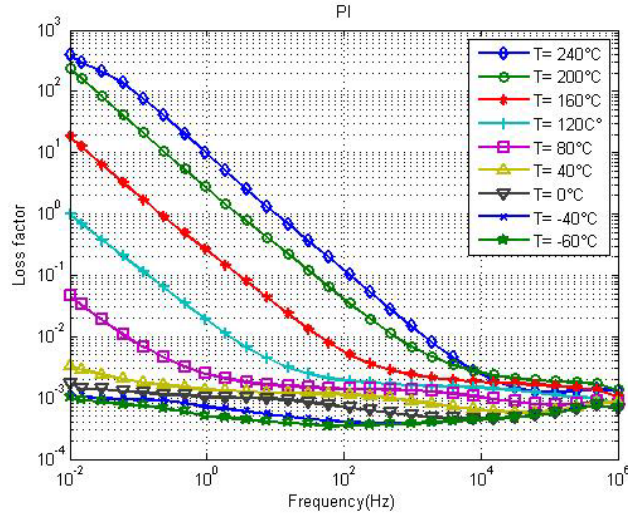


Figure 5. Loss factor $Tan(\delta)$ of PI as function of frequency for different temperatures

From Figure 4 it can be seen that ϵ' remains constant as the frequency increases up to a certain temperature or it increases rapidly which is called the glass transition temperature T_g . The dielectric constant depends upon the ability of the polarizable units in a polymer to orient fast enough to keep up with the oscillations of an alternating electric field. Pham *et al.* (2013) explain that the high values of ϵ' can be attributed to the charge carriers' accumulation at interfaces within the bulk of the sample (interfacial polarization phenomenon) and/or at the interface between the sample and the electrodes (Electrode Polarization - EP).

PI is polar polymer; we note that the temperature has an effect on the permittivity and the dielectric loss. At high frequencies, the shape of the curve $Tan(\delta)$ change due to the intrinsic hopping conductivity.

The polymer becomes highly conductive with the loss factor increasing rapidly. As reminded by Raju (2003), the mechanism is possibly the interfacial polarization with the charge carriers accumulating at the boundaries between the crystalline and amorphous regions.

The increase in dielectric constant ϵ' at low frequencies as shown in Figure 4 is possibly due to the accumulation of charges at the electrodes (Chi, 2004).

In Figures 4 and 5, it can be seen that dielectric constant increase gradually with the increase of temperature at fixed frequency especially at lower frequencies. This increase could be explained by an increase in the motion of dipole molecular chains of Polyimides at high temperatures. At lower temperatures, the dipoles are rigidly fixed in the polymer which make no possibility of dipole orientation by the applied

electric field. As the temperature increases, the dipoles become freer to follow the applied field. As result, the polarization increases and the dielectric constant also increase with temperature (Kum-Pyo Yoo, 2010).

3.3.2. Relaxation identification

Figure 6, represents the variation of the loss factor $\tan(\delta)$ of PI films as function of temperature for different frequencies, the frequencies were chosen to show the dielectric relaxation phenomenon for the very low $f=0,01\text{Hz}$, to very high $f=1\text{ MHz}$.

On the loss factor Figures 6 and 7, it is possible to observe three relaxations process: two sub-glass relaxations (γ and β -transitions), and the glass-rubber α -transition.

The α -transition or relaxation is attributed to the re-orientations of the dipoles due to the segmental motions of the main chains and show up at high temperature, it is assigned to the phase crystalline (Diaham, 2007), the low temperature relaxations are γ and β -relaxations. The β -relaxation which is attributed to the micro-Brownian motions of the side groups accompanied with the local distortions of the main chains and it is associated with the glass transition temperature T_g . The γ -relaxation is assigned to the rotational movement from chemical groups of small dimension in the amorphous phase (Raju, 2003).

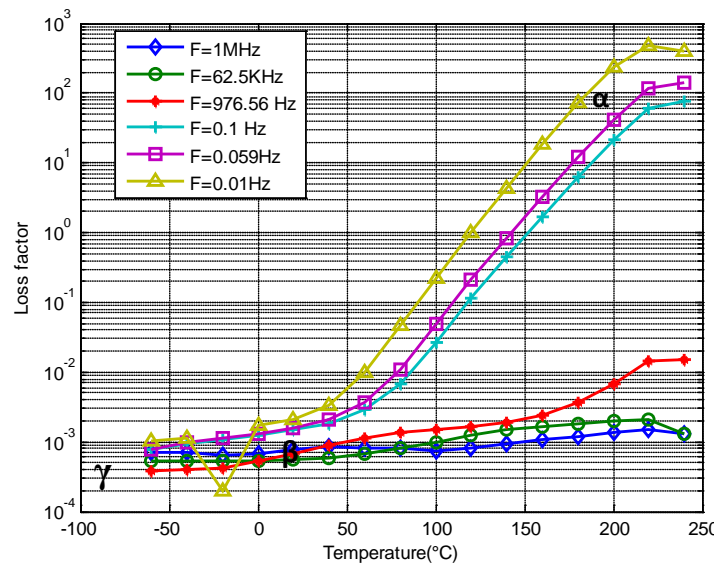


Figure 6. Loss factor $\tan(\delta)$ of PI as function of temperature for different frequencies

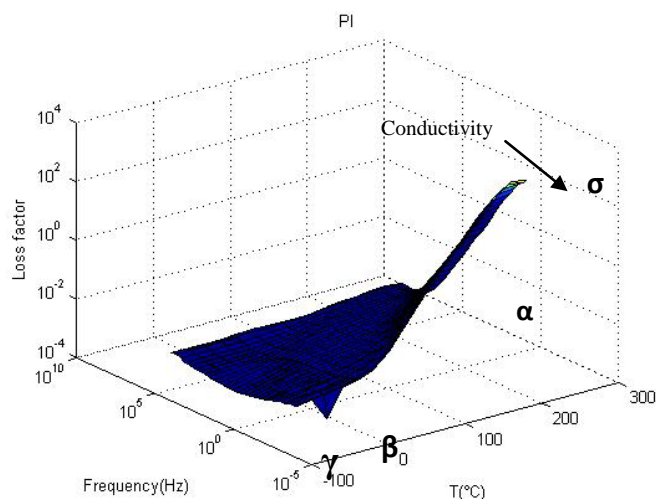


Figure 7. Loss factor $Tan(\delta)$ of PI as function of frequency and temperature

The γ -relaxation shows up at negative temperature region (Chisca *et al.*, 2011) and it is assigned to the small-scale local oscillations of imides rings. The β -relaxation occurs below T_g . There are many explanations regarding the β -relaxation. It has been proposed that the main type of motion is a rotational vibration of small segments of a chain around quasi equilibrium positions. The motion of phenylene and imide rings contributes to the vibration. It has also been reported that the β -relaxation is related to rotation of phenylene and imide groups (Hamciuc *et al.*, 2010).

T_γ is usually in the vicinity of -60 to 0°C , and T_β is observed at 50 to 100°C . Owing to the local character of the sub-glass relaxations, their time-temperature relations can be described by constant activation energy according to the Arrhenius relation.

The last relaxation named α is observed at high temperature starting from 240°C , this phenomenon is higher in magnitude than the two previous ones. It corresponds to the occurrence of the glass transition, and this relaxation is due to a cooperative phenomenon involving micro-Brownian segmental motions of the chain (Diahm *et al.*, 2009).

Numerous studies explain that the presence of residual water in the polymer appears to play an important role in the case of the γ -transition (Xu *et al.*, 1989; Bas *et al.*, 1999), and provide a relationship between water content and the intensity of the relaxation (Xu *et al.*, 1989). The γ -relaxation depends not only on the presence of coupled water molecules, but also may reflect limited motions such as phenyl ring oscillations (Cheng *et al.*, 1995). For the β -transition in Polyimides, several

explanations have been postulated involving motions that while still essentially local in character, encompass larger portions of the repeat unit that respond in a correlated manner (Sun *et al.*, 1992; Arnold *et al.*, 1993). Ngai and Paluch(2004) explain that the origin of the β -relaxation is attributed to small amplitude motions which involve the entire repeat segment in more rigid systems.

Other studies (Sawada and Ishida, 1975; Arnold *et al.*, 1993) have given a relationship between the degree of crystallinity and the amplitude for the expressed relaxations; it was found that for samples with 100% crystallinity the magnitude of β -relaxation is very close to zero. The β -relaxation depends on the chemical structure of the diamine and disappears at 100% crystallinity because the movements introduced during the β -relaxation process occur in the uncrystallized diamines.

In our study, the Polyimides films used have a medium degree of crystallinity, we can note that the amplitude of both α and β -relaxations is related to the amorphous content and it is attributed to the fact that the effective dipole moment in the disordered regions is lowered due to the constraints on motion due to the ordered region (Sawada and Ishida, 1975). And also, in amorphous polymers it seems that the mobile chain segments are in a variety of environments in the spherulite leading an increase of the both α and β -relaxations, and similar behavior would be obtained for polymers having a medium degree of crystallinity (Williams, 1982).

3.3.3. AC conductivity

The frequency and temperature dependence curves of AC conductivity for PI films are shown in Figures 8 and 9.

The real part of conductivity σ' which represents the AC conductivity, remains constant at low frequencies, increasing to a saturation value at high frequency, the low frequency flat part is almost equal to dc conductivity and may not be observed except at high temperatures. Figure 8 demonstrates such conductivity behavior.

On each of these characteristics, two regions differ considerably. At high frequency, AC conductivity changes linearly with frequency. At low frequency, becomes independent of frequency and we can see a horizontal plate which corresponds to the DC conductivity, such a behavior can be described by "Jonscher's universal power law" (see Equation (3)) for several low mobility polymers and even for noncrystalline materials. (Deligöz *et al.*, 2005)

Furthermore, we note that when the temperature increases the amplitude of the DC conductivity also increases and extends towards the higher frequencies. These dielectric materials, as the relaxation time is a thermally activated greatness following behavior, the second reflects the fact that at higher temperature the charge carriers can more easily move in the conduction band: the time for establishment of a steady state becomes shorter and therefore the conduction phenomenon is observed at a higher frequency (Jacobs *et al.*, 2010).

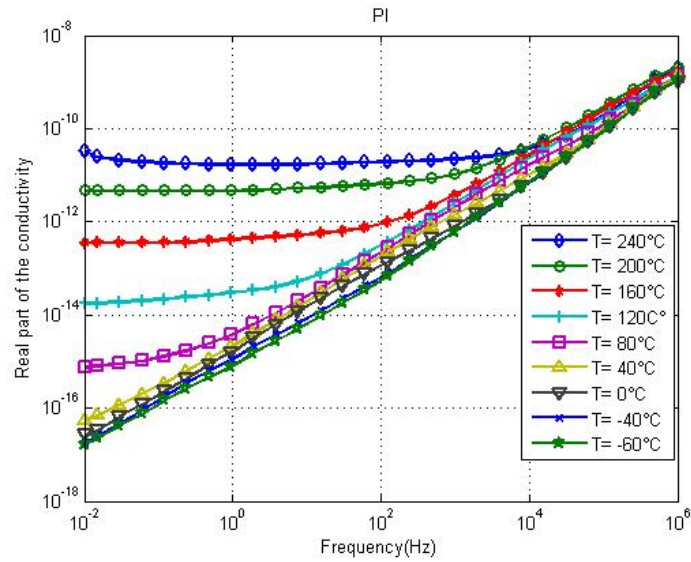


Figure 8. The real part Conductivity $\sigma'(\Omega^{-1}cm^{-1})$ of PI as function of frequency for different temperatures

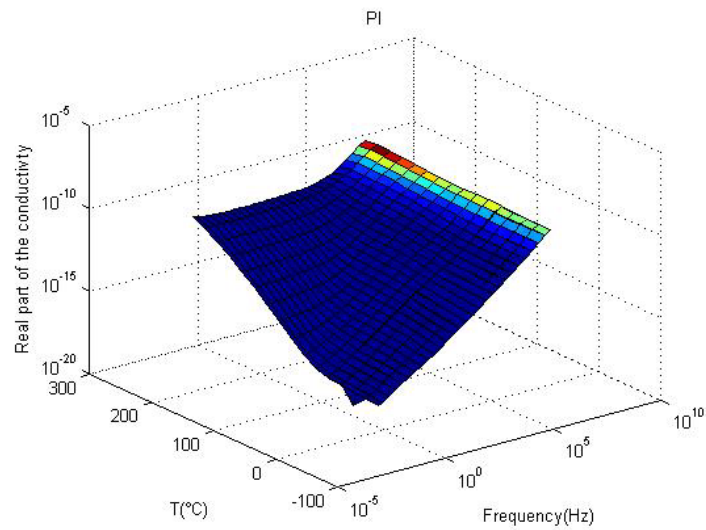


Figure 9. The real part Conductivity $\sigma'(\Omega^{-1}cm^{-1})$ of PI as function of frequency and temperature

The fractional exponent n in (Equation (3)) is used to understand the conduction or relaxation mechanism in insulating materials, n and K the pre-exponential factor were plotted as a function of temperature in figures 10 and 11 respectively.

From Figure 10, we note in our type of polymer that the exponent n (see Equation (3)) decreases with increasing temperature which characterizes electronic conduction via hopping process (Muruganand *et al.*, 2001).

The interaction between the charge carriers participating in the polarization process is characterized by the parameter n . At very low temperatures n is close to the unit value and that implies a Debye case, and as the temperature increases, the interaction increases, leading to a decrease in n .

An interesting feature from Figures 10 and 11 that there are two regions in both figures: the value of n decreases as the temperature increases and attains a minimum near T_c and subsequently it increases with further increase in temperature, conversely the parameter K increases with temperature until a maximum T_m and decreases, the important observation is that $T_c = T_m \approx 160^\circ\text{C}$. The observed minimum at T_c in $n(T)$ and maximum or peak in $K(T)$ implies the strong interaction between the charge carriers and the lattice (Zhigao *et al.*, 1992), other authors found the same results but in ceramic material (Dasari *et al.*, 2011).

From this observation, a conclusion can be drawn that there is a relationship between the two parameters: n and K , there is a lack of information about this relationship, Papathanassiou (2006) discovered that: the ratio $-\log K/n$ is near-constant for different materials, which indicates that the temperature evolution of $-\log K$ is proportional to the temperature evolution of n , with proportionality constant depending on the specific type of material and it is still an open question.

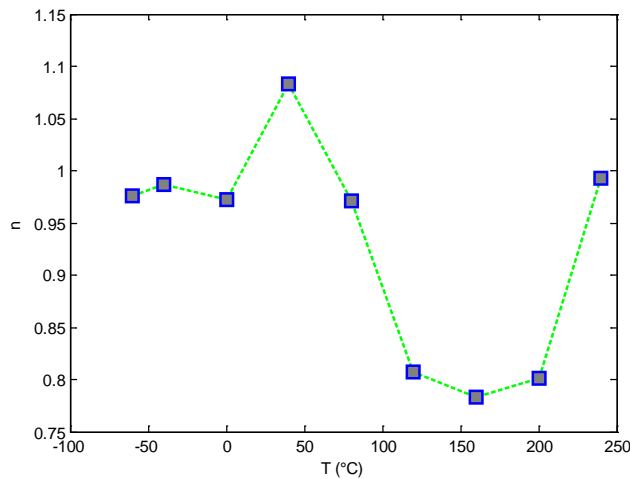


Figure 10. Variation of critical exponent $n(T)$ with temperature

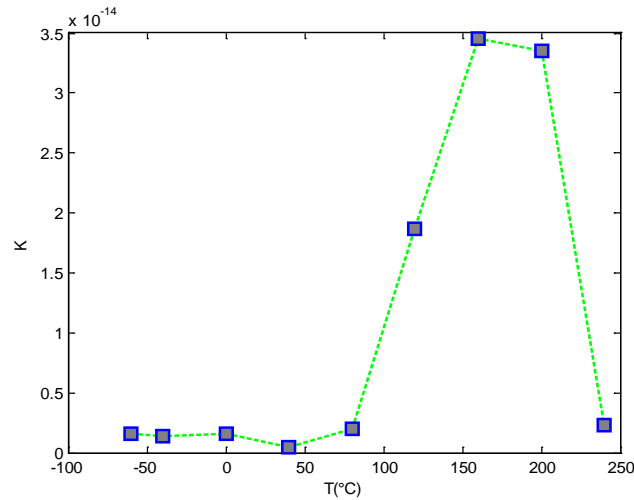


Figure 11. Variation of pre-exponent $K(T)$ with temperature

4. Conclusion

In this work we have presented results of electrical and dielectric studies in Polyimide films with thicknesses from 50 μm , by using of dielectric relaxation spectroscopy (DRS in frequency range 10^{-2} - 10^6 Hz and temperature between -60°C and 240°C .

The obtained results show three relaxations α , β and γ , which contribute to the increasing values of the loss factor $\text{Tan}\delta$, the real part of permittivity ϵ' and the real part of conductivity σ' . This result shows that, at temperatures higher than the glass transition T_g , the charge carrier transport mechanisms are governed by the motions of the polymeric chains.

The amplitude of both α and β -relaxations are related to the amorphous content and it is attributed to the fact that the effective dipole moment in the disordered regions is lowered due to the constraints on motion due to the ordered region.

The frequency dependence of AC conductivity follows the universal power law with a small deviation in the low frequency region due to the electrode polarization effect.

The analysis of the dielectric results and the AC conductivity indicate that the polyimide films in this study represent a better choice for applications in electronic devices because they present low values for dielectric constant about 2.8 at temperature $<220^\circ\text{C}$ for the range frequency values from 10^{-2} to 10^6 Hz, as reminded by Chisca *et al.* (2011), this value is much lower than other Polyimide films cited in (Sroog, 1991) like H polyimide film, which has a dielectric constant of 3.5, and it is one of the most common high performance dielectrics used in microelectronics

applications, and as it is known that lower dielectric constant is one of the most desirable properties for next generation electronic devices (Liaw *et al.*, 2012).

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