Dielectric spectroscopy and thermally stimulated discharge current in PEEK film

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Abstract: The complex permittivity of films of polyether ether ketone (PEEK) has been investigated over a wide range of frequency. There is no relaxation peak in the range of 1Hz to 10^5 Hz but in the low-frequency side (10^{-4} Hz) there is an evidence of a peak that also can be observed by thermally stimulated discharge current measurements. That peak is related with the glass transition temperature (T_g) of the polymer. The activation energy of the relaxation was found to be 0.44 eV, similar to that of several synthetic polymers. Space charges are important in the conduction mechanism as shown by discharging transient.

Keywords: dielectric loss; thermally stimulated discharge current; polymer; activation energy; glass transition temperature.

Introduction

Polyether ether ketone (PEEK) is an aromatic polyether. It has been developed by I. C. I. Petrochemicals and Plastic Division as a high-temperature engineering thermoplastic [1]. Because of the symmetry of the benzene rings along the polymer backbone, PEEK offers mechanical strength and from the characteristic of almost linear chemical structure, the polymer has a crystalline phase.

PEEK is also resistant to an extraordinary range of chemicals and has very low emission of smoke and toxic fumes when exposed to a flame [2]. Due to characteristics such as: melting point over 300 ºC; low dielectric loss; resistance to attack by several chemical solvents and insulating properties, PEEK has considerable applications as an engineering material [3]. Nowadays there is high interest for the use of PEEK as a matrix for ferroelectric-ceramic/polymer composites as non-destructive testing sensors.

Although PEEK has already been used as insulating material and its electrical and dielectric properties have been reported [4, 5], this paper reports results of dielectric spectroscopy in the wide frequency range of 10^{-5} Hz to 10^5 Hz and the nature of the thermally stimulated discharge current (TSDC) in the temperature range from 10 ºC to above glass transition temperature (T_g) is analyzed.

Experimental

Commercial samples of 25 mm PEEK film were used in this work. Polyether ether ketone is an engineering thermoplastic with high performance. It belongs to a class of polyaryletherketone (PAEK) which are characterized by the presence of benzene rings linked with oxygen and ketone groups. The chemical structure of PEEK is shown in figure 1. The pair of ether linkages – O – in the chain backbone gives to the PEEK's chain flexibility and ability to crystallize [2].
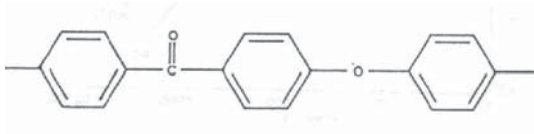
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Figure 1. Chemical formula of polyether ether ketone (PEEK) from I.C.I.

The samples were cleaned with alcohol and aluminium electrodes of circular area of 1.0 cm diameter were deposited onto both sides of the samples. The dielectric data were taken using an impedance analyzer model HP 4192A in the frequency range of 20 Hz to 10^5 Hz. For the medium frequency range of 5 x 10^{-2} Hz to 10 Hz, a Lock-In amplifier model EG&G 7265 was used. In the low frequency range of 10^{-5} Hz to 3 x 10^{-2} Hz the time domain technique of the measurement of discharge current with subsequent Hamon [6] approximation method were used.

For discharge current measurement, the PEEK film was placed in an evacuated chamber and a Keithley 247 high voltage supply was used to charge the sample at a field of 10^6 V/m for a period of 27 hours. The discharge current was measured for 3.0 hours. For the thermally stimulated discharge current (TSDC) measurement a TSC measuring system form Toyo Seiki, with a temperature controlled chamber was used and the currents were monitored with a Keithley 610 C electrometer suitably fed to a microcomputer.

Results and discussion

Figure 2 shows the behavior of the complex permittivity for PEEK at room temperature. The low-frequency (10^{-5} Hz to 10^{-2} Hz) data of the dielectric loss (e²) were calculated from transient discharge current measurement, using the following equation,

$$\varepsilon^2 = \frac{I_d}{2\pi f C_0 V} \tag{1}$$

where I_d is the discharge current measured for 3 h after charging the sample for 27 h with a 10^5 V/m electric field, f = 0.1/t is the Hamon [6] frequency,

C_0 is the capacitance of measuring electrodes without the sample and V is the charging voltage. Considering that the measurement of the discharge current start 5 sec. After the removal the applied voltage and short-circuit the electrodes, the frequency range obtained is 2 x 10^{-2} Hz to 9 x 10^{-6} Hz due to Hamon approximation (f = 0.1/t).
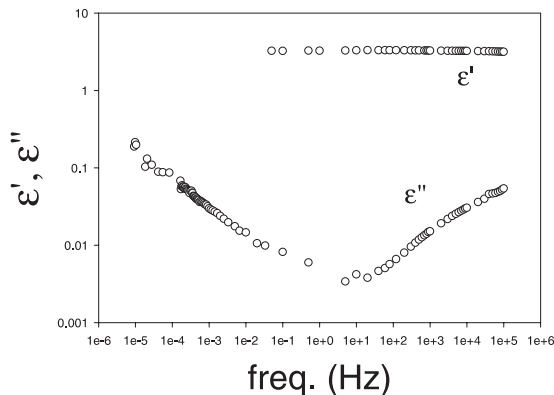

Figure 2. Dielectric behavior of PEEK film at room temperature.

The low-frequency permittivity (ε') values can be calculated using the well-known Kramers-Kronig relation [7]. In the frequency range of 10^{-2} Hz to 10 Hz both ε' and ε'' were obtained experimentally using a lock-in amplifier. A sinusoidal voltage was applied to the sample and both the in-phase and 90 ^{0}C out-of-phase currents were measured. The permittivity and dielectric loss were calculated by [8],

$$\varepsilon' = \frac{t I_y}{\omega \varepsilon_0 A V} \tag{2}$$

$$\varepsilon'' = \frac{t I_x}{\omega \varepsilon_0 A V} \tag{3}$$

where t is the sample thickness, ω is the angular frequency, A is the electrode area, V the applied voltage, $\varepsilon_0 = 8,85 \times 10^{-12}$ F/m is the vacuum permittivity, I_x and I_y are the quadrature and in-phase currents, respectively.

From 20 Hz to 10^6 Hz the conventional bridge can be used with very good accuracy and the complex permittivity can be obtained by measuring the capacitance of the sample as a function of the frequency.

It can be seen from figure 2 that no loss process is centered in the frequency range of 1.0 to 10^5 Hz. The increase of e' at high frequency indicates that the loss process might be occurs in the frequency range (MHz) outside the frequency range of the present work. The absence of loss peak in that frequency range is compatible with the flat behavior of the permittivity.

On the low-frequency side there is an evidence of a peak around 10^{-4} Hz in the dielectric loss (e"). This peak might be related with the glass transition of the polymer. Actually, the relaxation at low-frequency due to glass transition (a relaxation) can be seen by thermally stimulated discharge current (TSDC) measurements. Figure 3 shows a typical TSDC spectrum. The sample was poled with 10^7 V/m electric field for 30 min at 150 °C. The sample was cooled at 0 °C under applied field and after 30 min with the electrodes short-circuited, the discharge current was measured with a heating rate of 1 degree/min. The a relaxation related with the glass transition was observed at 90 °C.
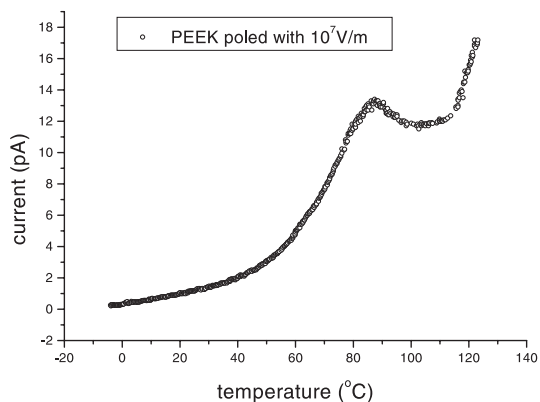
According to Van Turnhout [9] the peak observed in TSDC spectrum is related with the peak observed in dielectric loss by,

$$\omega = \frac{E_a}{hkT^2} \tag{4}$$

where w is the angular frequency, E_a is the activation energy of the process, h is the reciprocal of heating rate, $k = 1.38 \times 10^{-23}$ J/K is the Boltzmann constant and T is the temperature of maximum current in TSDC measurement.

The activation energy was calculated using the initial rise method [9]. The Arrhenius equation is:

$$I = I_0 \exp[\frac{-E_a}{kT}] \tag{5}$$

and from the slope of the ln[I] x 1/T plot in figure 4, the value of $E_a = 0.44$ eV was found for the dipolar transition. That value of activation energy is in the range of the insulating polymers such as: polyethylene terephthalate (0.62 eV) [10], polypropylene (0.75 eV) [11] and low-density polyethylene (0.60 eV) [12].

Using equation 4 and $E_a = 0.44$ eV, $k = 1.38 \times 10^{-23}$ J/K, h = 60 sec/degree and T = 365 K, the corresponding peak in dielectric loss occurs at 1.0×10^{-4} Hz as observed in figure 2.

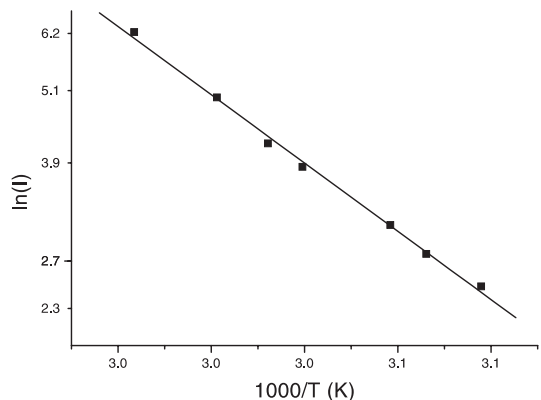**Figure 3.** Thermally stimulated discharge current (TSDC) for PEEK poled at 150 °C for 30 min.

Figure 4. Plot of ln(I) x 1000/T, using the initial rise method from TSDC measurement.

Figure 5 shows typical discharging transients for different temperatures. For all temperatures the discharge current obey the empirical law:

$$I(t) = A(t)t^{-n} \qquad (6)$$

where I(t) is the current at time t after the removal of the electric field, A(t) is a temperature dependent material constant and n is an index roughly equal to 1. The change in the slope at low frequency (long time) is an indicative of a low-frequency dispersion (LFD) [13] that can be better observed in the dielectric loss data. The increase of the dielectric loss values at low frequency is usually indicative of an ionic or electronic space charge mechanism [12] which is responsible for mask the peak in dielectric loss spectrum.
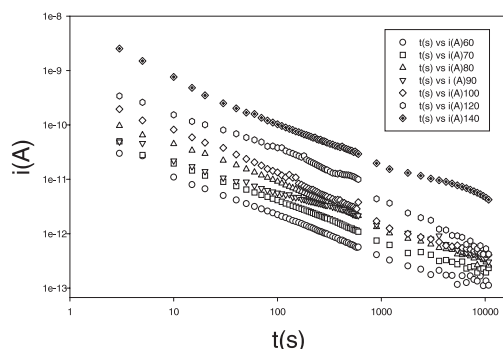

Figure 5. Discharging currents in PEEK. Sample charged with 10^5 V/m for 27 h

Some experiments are in progress in our lab to provide an analysis of the temperature and field dependence of the conduction currents in PEEK films. Also the TSDC spectra in low-temperature range should be done for better understanding of the conduction mechanism.

Conclusions

An analysis of the dielectric loss and the thermally stimulated current spectra in PEEK films show a relaxation process in low-frequency range related with the glass transition temperature. It would appear from low-frequency dielectric loss and discharging transient that space charges are important to understand the conduction mechanism in the polymer and deserve more attention for a comprehensive explanation of the process.

Acknowledgement

W. K. SAKAMOTO. Espectroscopia dielétrica e corrente de despolarização termo-estimulada em filmes de peek

Resumo: A permissividade complexa de filmes de poli(eter-eter-cetona) (PEEK) foram investigados num grande intervalo de frequência. Não foram observados picos de relaxação no intervalo de frequência de 1,0 Hz a 10^5 Hz, mas no intervalo de baixa frequência (10^{-4} Hz) há uma evidência de pico, o qual também pode ser observado com medidas de corrente de despolarização termo-estimulada (TSDC). Este pico está relacionado com a transição vítrea do polímero. A energia de ativação relacionada a esta relaxação dipolar foi obtida e ovalor é $E_a = 0,44$ eV, que é similar à energia de ativação de muitos polímeros sintéticos. As cargas espaciais se mostraram importantes no mecanismo de condução como evidenciado nas medidas da corrente de despolarização.

Palavras-chave: perda dielétrica; corrente de despolarização termo-estimulada; energia de ativação; temperatura de transição vítrea.

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