



STUDY OF THE SPACE CHARGE RELAXATION IN POLY ETHER ETHER KETONE (PEEK)

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Abstract

The relaxation of space charge is studied by the dielectric modulus formalism in poly(ether ether ketone) (PEEK). The obtained data suggest a prevailing ohmic conduction in one specimen and interfacial polarization effect, known as the Maxwell-Wagner-Sillars polarization. The interfacial relaxation taking place at the interface between the crystalline inclusions and the amorphous matrix. It's attributed to the trapping of ionic charges at the interface between crystalline lamellae and the amorphous matrix. The conductivity must be attributed to the increasing mobility of the carriers.

Keywords : Space charge; Electric modulus; Interfacial relaxation; Poly(ether ether ketone).

1. Introduction

In the area of structural composites, engineering thermoplastics are considered as potential replacements for thermosetting matrices. Thermoplastics usually offer a relative ease of processing together with enhanced toughness while overcoming deficiencies in end-of-use temperature and solvent resistance which are typically attributed to thermosets. One candidate for structural composite applications is poly(ether-ether-ketone) (PEEK). The successful application of PEEK in composites requires a detailed knowledge of how processing conditions and material history influence [1-2] the resultant semi-crystalline morphology and how this morphology ultimately impacts bulk properties (mechanical strength, chemical and thermal resistance, long-term stability, etc.).

When an electrical field is applied across a parallel-plate capacitor containing a dielectric, the various atomic and molecular charges that are present in the dielectric are displaced from their equilibrium positions and the material is said to be polarised. Different polarisation mechanisms can occur, including dipole orientation, extrinsic free charges or intrinsic charge migration, electrode polarisation, and, in heterogeneous or composite systems, the Maxwell-Wagner-Sillars (MWS) interfacial polarisation. In our studies, we focus our attention on the frequency region in which the contribution of migrating charge carriers dominate the dielectric response.

We have presented elsewhere [3-4] a study of the interfacial relaxation found in model composite constituted of amorphous thermoplastic polymer matrices and spherical glass inclusions.

The effect of the diameter, the volume fraction and the surface coating of glass beads on the interfacial relaxation characteristics have been studied .

A previous study of PEEK by dielectric spectrometry [5] show the dependence of the dielectric relaxation with crystallinity. Three relaxation processes take place in the polymer : the α glass transition, the α_c relaxation in amorphous PEEK which not present in semicrystalline polymer, and the MWS interfacial relaxation due to polarization of the amorphous-crystalline interface The intensity of the interfacial relaxation is shown to be sensitive to annealing conditions and is related to the morphological features. the aim of this paper is to study the space charge relaxation mechanisms in these poly(ether-ether-ketone) by dielectric relaxation spectroscopy.

2. Experimental

Commercial amorphous PEEK (Stabar K200) was purchased from ICI on the form of 250 μ m-thick films. The PEEK samples were used as-received or isothermally crystallised from the glass at two temperatures (160 and 320°C) and for various annealing times varying from 30min to 25h.. Measurements of the dielectric parameters were performed with the 20-10kHz-frequency range and $-150 + 500^\circ\text{C}$ temperature range Dielectric Thermal Analyser (Rheometrics Scientific) with a heating rate of $2^\circ\text{C}/\text{min}$. A circular gold electrode (1cm-diameter) was sputtered on both surfaces of the sample in order to insure good electrical contacts with the gold-plated measuring electrodes. From 240 to 330°C,

the isothermal step method was used, in which data were collected isothermally at several frequencies increasing temperature at 10°C steps.

3. Results and discussion

At low frequencies and at temperatures above the glass transition temperature, the increase of the imaginary part of the permittivity due to ionic conduction in PEEK is so dramatic that it masks the interfacial relaxation (figure 1.a). To overcome this difficulty it has been decided to introduce the electric modulus which has been proposed for the description of systems with ionic conductivity.

The electrical modulus is the reciprocal of the permittivity, $M^*=(\epsilon^*)^{-1}$, was introduced by McCrum et al. [6] and Macedo et al. [7] to study interfacial polarization phenomena. From the physical point of view, the electrical modulus

corresponds to the relaxation of the electric field in the material when the electric displacement remains constant, so that the electric modulus represents the real dielectric relaxation process [8-10]. It must be emphasized that the complex permittivity and the complex electric modulus contain the same information. It is possible, however, to present this information more clearly by the appropriate choice among these functions.

The interest of the dielectric modulus formalism arises from the fact that in the case of the conductive processes that are observed at low frequencies, the loss factor exhibits a sharp monotonic increase whereas the imaginary part of the electric modulus show a peak [7], so that this function is suitable to study the space charge relaxation phenomena, as they are reflected by changing in this peak [11].

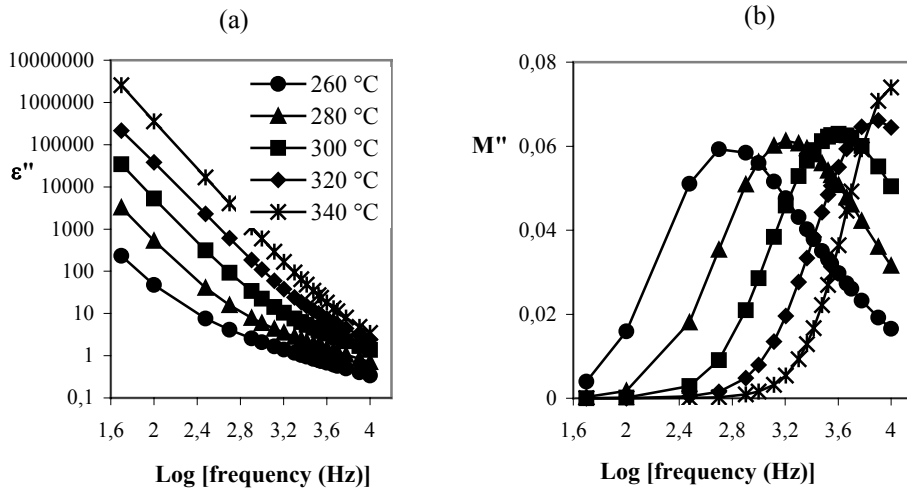


Figure 1 : Isothermal runs of the loss factor ϵ'' (a) and the imaginary part of the dielectric modulus M'' (b) versus frequency for the PEEK crystallized isothermally at 160°C for 25h.

In the case of the imaginary part of the dielectric modulus (figure 1.b), a new relaxation peak appear around 250°C. This relaxation is attributed to the trapped ionic charges at the interface between the amorphous and the crystalline regions of the polymer (interfacial relaxation). A similar behaviour was found for poly methyl methacrylate (PMMA) [12]. The results obtained in the temperature range studied indicate that the peak arising from the contribution of the conductive processes shifts to higher frequencies with temperature.

The interfacial relaxation ensues from the fact that a significant difference does exist in the values of the permittivities and conductivities of at least two distinct phases of the material. In our case, it is thought that the respective electrical characteristics of the rigid and mobile fractions of the amorphous phase should not be different

enough to allow charge carriers to be trapped at a rigid-mobile boundary. On the contrary, due to their differences in density the interface between the crystalline and the amorphous zones of the polymer must be the actual location of the blocking of the charges

Isothermal dielectric experiments were also performed and a typical curve in the complex plane is reported in figure 2.a for semi-crystalline PEEK at 290°C. The curves are shaped as skewed arcs that can be fitted by the Havriliak-Negami equation [13] :

$$\epsilon^*(\omega)=\epsilon_{\infty}+\frac{\epsilon_s-\epsilon_{\infty}}{(1+i\omega\tau)^{\alpha}\beta} \quad (1)$$

where ϵ_s and ϵ_{∞} are the dielectric constants on the low- and high-frequency sides of the relaxation, α is the symmetric and β the asymmetric broadening

parameters, τ is the central relaxation time and ω is the radial frequency. Low-frequency points are

excluded from the fitting as they are only related to ionic characterisation.

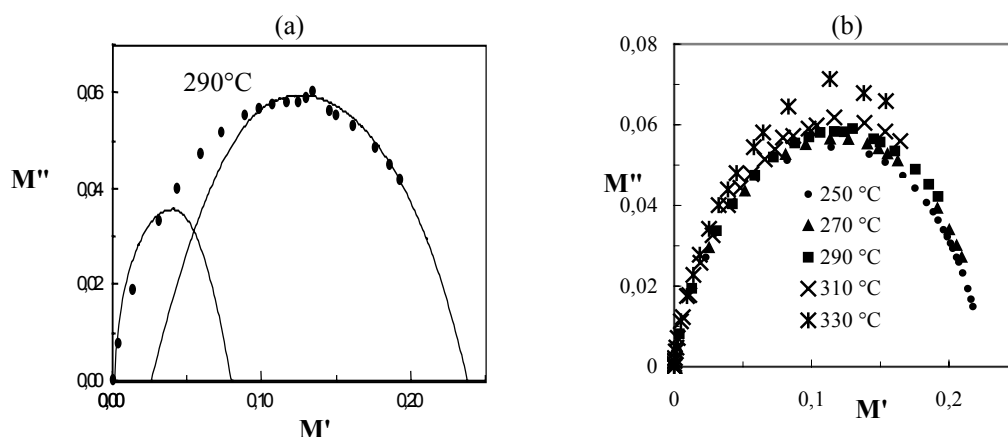


Figure 2 : Cole-Cole plot of the PEEK crystallized: (a) at 320°C for 1h (solid curve denotes best fits according to the Havriliak-Negami equation), (b) at 320°C for 25h.

Low frequency points results from ionic conductivity. The data at low frequencies (low M') fit the semicircle quite well, they are only related to ionic characterisation [11,14]. At higher frequencies, interfacial relaxation effects make additional contribution to M'' . It should be emphasized that this “conductivity relaxation” (low frequencies) is a result of algebraic properties of conductivity and does not provide information about interfacial relaxation in PEEK. Since known interfacial relaxation in composites are always broader than the Debye model, these tests tell us that this peak in M'' (at low frequencies) probably does not belong in that category.

The experimental points shift towards lower M' and M'' as temperature is increased (figure 2.b). This behaviour is related to important effects of conduction. When the temperature is increased, the electrical properties are frequently dominated by conduction. The rise in the conductivity must be attributed to the increasing mobility of the carriers, as the temperature increased.

4. Conclusion

At high temperatures the electric behavior of PEEK is strongly influenced by its conductive properties. The model of Havriliak Negami is adequate to explain the conductive properties of this material at temperatures above the glass transition. The dependance on the temperature of the conductivity can be associated with a rise of the mobility with temperature.

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