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Dielectric relaxation phenomena in PEEK [1]

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Abstract

Molecular movements in poly(ether-ether-ketone) have been investigated by thermally stimulated currents (TSC). The TSC spectra have been analyzed as a function of crystallinity. Around −80°C, two sub-modes are observed: the lower temperature sub-mode has been attributed to localized cooperative movements in the crystallizable amorphous phase; and the upper temperature sub-mode has been located in the crystalline phase. The magnitude of the corresponding compensation line increases with the ratio of crystallinity. Around the glass transition temperature (145°C), the existence of two sub-modes has been shown: the lower temperature sub-mode has been attributed to the dielectric manifestation of the glass transition and the cooperative movements have been assigned to the "true amorphous region" of PEEK; the upper temperature sub-mode is dependant upon crystallinity. Regardless of the preceding sub-mode, the activation enthalpies of the constituting elementary processes are practically constant. This sub-mode has been attributed to the "rigid amorphous region", constrained by the crystallites.

INTRODUCTION

Poly(ether-ether-ketone) or PEEK is a high performance thermoplastic thermostable semi-crystalline polymer. Its specific high toughness and satisfactory thermal resistance stem from the microstructure of its amorphous and crystalline phases. Many reports have been devoted to the crystalline phases [1–4] and special attention has been paid to the influence of microstructural details such as spherulite size, ratio of crystallinity and orientation [5]. The study of annealing [6] has also shown the importance of structural reorganization.

The aim of this work was to characterize the microstructure of the amorphous phase. The influence of the ratio of crystallinity on the coupling

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of the crystalline and amorphous phases was investigated. Differential scanning calorimetry (DSC) was used as a reference technique for determination of the transition spectra. Experiments were performed on a Perkin-Elmer DSC 7 and the thermograms were recorded at a scanning rate of 20 K $\min^{-1}$. The characterization of PEEK was done with thermally stimulated current (TSC) spectroscopy and the experiments were performed on a TSC/RMA spectrometer from Solomat.

PEEK was supplied by ICI in the form of sheets with a thickness of 0.25 mm; the ratio of crystallinity was 10% (PEEK/10). A compensation study with sheets having 28% ratio of crystallinity (PEEK/28) was carried out.

DSC THERMOGRAMS

The DSC thermograms of PEEK/10 (solid line) and PEEK/28 (broken line) are shown in Fig. 1.

For the melting, the temperature of the maximum (338°C) and the heat of fusion (38.5 J g^{-1}) are the same for the both samples.

The peak characteristic of the cold crystallization appears at 179°C, but only for PEEK/10: PEEK/28 does not crystallize with the scanning rate used.

At the glass transition, from the heat flow dH/dt, we have deduced the variation of the heat capacity at the step, ΔC_p, and the rigid amorphous fraction $fr = 1 - \Delta C_p/\Delta C_p^0$, where ΔC_p^0 is the heat capacity of a completely amorphous sample [7]. Those values together with T_g are reported in Table 1. It is interesting to note the increase in T_g when the ratio of crystallinity increases: in contrast, ΔC_p decreases, as expected.

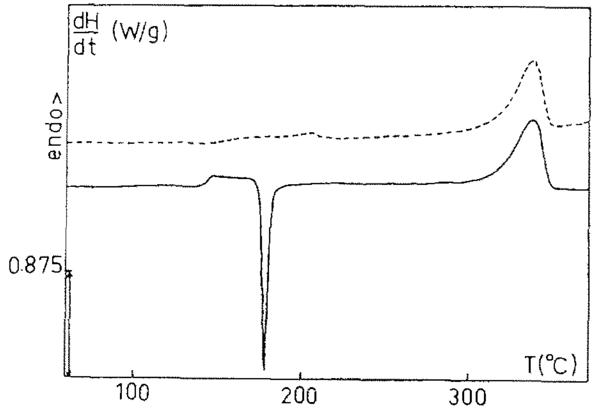

Fig. 1. DSC thermograms: —, PEEK/10; ---, PEEK/28.

TABLE 1

DSC parameters of the glass transition

	PEEK/10	PEEK/28
T_g/°C	145	157
ΔC_p/J $g^{-1}K^{-1}$	0.28	0.10
fr%	8	63

COMPLEX TSC SPECTRA

Low temperature

Complex TSC spectra of PEEK/10 (solid line) and PEEK/28 (broken line) have been obtained after polarizing the sample at 20°C for 2 min, under 8×10^5 V m^{-1} (Fig. 2).

For PEEK/10, the observed spectrum is complex, with a peak at −110°C and a shoulder around −75°C. For PEEK/28, only one peak is well-resolved, at around −75°C.

High temperature

Figure 3 shows the complex TSC spectra of PEEK/10 (solid line) and PEEK/28 (broken line). The polarization conditions were: field, $E = 8 \times 10^5$ V m^{-1}; time, 2 min; temperature, 160°C.

For PEEK/10, there are two well-resolved relaxation peaks on the complex TSC spectrum: the lower temperature peak is located at around 145°C, the higher temperature peak at 162°C. For PEEK/28, only one peak appears at around 170°C. It should be noted that the polarization peak may

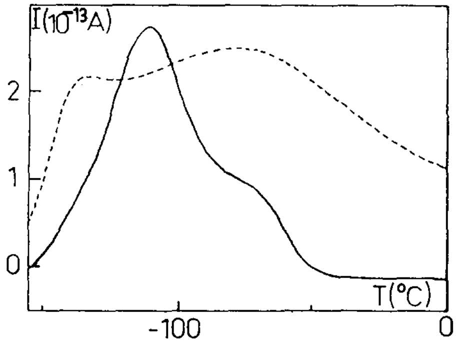

Fig. 2. Complex TSC spectra at low temperature: —, PEEK/10; ---, PEEK/28.

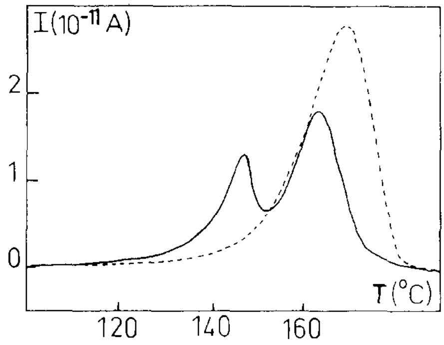

Fig. 3. Complex TSC spectra at high temperature: —, PEEK/10; ---, PEEK/28.

appear above the polarization temperature, according to the relative values of the activation parameters.

These relaxation modes are situated in the vicinity of the DSC glass transition temperature; they have been associated with the dielectric manifestation of the glass transition of PEEK.

For a more thorough investigation of these observations the degree of crystallinity, the fine structure of the complex relaxation spectra was explored.

FINE STRUCTURE OF COMPLEX SPECTRA

The complex TSC spectra were resolved into elementary spectra using the technique of fractional polarizations [8]. The electric field strength was the same as that of the complex spectra; the temperature window was 10°C and the polarization temperature was also shifted by 10°C at low temperature and by 5°C at high temperature.

Each elementary TSC peak can be described using a model with a single relaxation time τ, obeying an Arrhenius equation

$$\tau(T) = \tau_o \exp\frac{\Delta H}{kT} \tag{1}$$

where τ_o is the pre-exponential factor, ΔH the activation enthalpy, k the Boltzmann constant and T the temperature.

For both samples, some peaks isolated successively are characterized by relaxation times following a compensation law

$$\tau(T) = \tau_o \exp\left\{\frac{\Delta H}{k}(T^{-1} - T_c^{-1})\right\} \tag{2}$$

where T_c is the compensation temperature and τ_c the compensation time.

DISCUSSION

Low temperature

The two sub-modes were resolved using the technique of fractional polarization, and a compensation low is apparent for each sub-mode (Fig. 4). Compensation parameters are reported in Table 2.

β_a-relaxation
For the sub-mode situated at −110°C, in PEEK 10, the compensation temperature is in the vicinity of the crystallization temperature: it has been associated with cooperative movements in the amorphous crystallizable phase. Therefore, it is denoted β_a.

According to the DSC thermogram (Fig. 1), the sample with 28% crystallinity can crystallize no further: this explains the absence of the β_a sub-mode in the dielectric characterization of PEEK/28.

β_c-relaxation
In both samples, the sub-mode situation around −75°C is characterized by a compensation temperature at around the melting temperature of PEEK: this relaxation mode, which has been denoted β_c, has been associated with localized movements into the crystalline phase. The

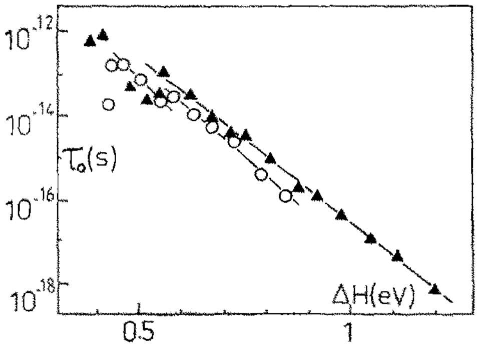

Fig. 4. τ_0 as a function of ΔH for elementary peaks isolated at low temperature: ○, PEEK/10; ▲, PEEK/28.

TABLE 2

Compensation parameters for PEEK, at low temperature

	PEEK/10		PEEK/28	
	β_a	β_c	β_a	β_c
T_c/°C	208	301	–	362
τ_c/s	1.4×10^{-8}	4.2×10^{-9}	–	2.5×10^{-9}

magnitude of the corresponding compensation line increases with the crystallinity rate (Fig. 4).

High temperature

The glass transition of PEEK has been observed by differential scanning calorimetry in the vicinity of 145°C. This value of T_g is consistent with values given in the literature [4].

The dielectric relaxation mode associated with the glass transition has been studied by thermally stimulated current spectroscopy. It is composed of two sub-modes: the lower temperature sub-mode and the upper temperature sub-mode.

Lower glass transition/relaxation

This is practically situated at the DSC glass transition temperature; its magnitude is higher for the lower degree of crystallinity (10%).

The elementary processes are characterized by relaxation times following a compensation law, eqn. (2). Table 3 shows the values of the compensation parameters for PEEK/10 and PEEK/28.

The values of τ_o are reported as a function of ΔH in Fig. 5. It is important to note here that the range in variation of ΔH is 6 eV for PEEK/10 and 4.7 eV for PEEK/28. This behavior is characteristic of cooperative movements liberated at the glass transition temperature.

TABLE 3.

Compensation parameters for PEEK, at high temperature

	PEEK/10	PEEK/28
T_c/°C	161	165
τ_c/s	2	2

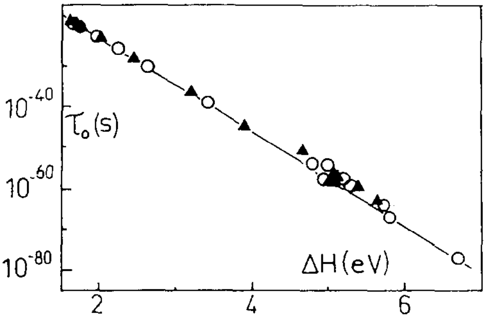

Fig. 5. τ_o as a function of ΔH for elementary peaks isolated at high temperature: ○, PEEK/10; ▲, PEEK/28.

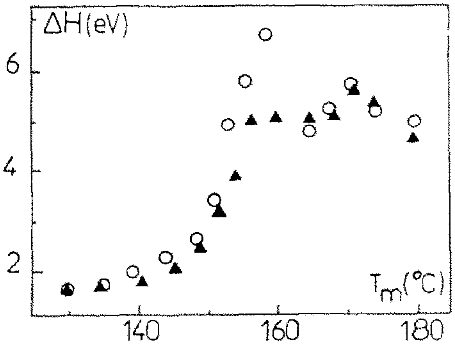

Fig. 6. ΔH as a function of T_m for elementary peaks isolated at high temperature: ○, PEEK/10; ▲, PEEK/28.

Figure 6 shows the variation of ΔH as a function of T_m for PEEK/10 (open circles) and PEEK/28 (solid triangles). The activation enthalpy levels off at 6.7 eV in PEEK/10 and at 5.1 eV in PEEK/28 for increasing temperatures.

In the Hoffman–Williams–Passaglia model [9], these values reflect the maximum length of the mobile units. Thus, they are indicative of the range of local order.

This lower glass relaxation has been associated with the dielectric manifestation of the lower glass transition T_{g_l}, according to the nomenclature of Boyer [10].

Upper glass transition/relaxation

The magnitude of this sub-mode increases with the degree of crystallinity and with the rigid amorphous fraction. At the same time, it is shifted towards higher temperatures.

Analysis of the elementary processes indicates that this sub-mode is composed of processes with activation enthalpies of the same order of magnitude, around 5 eV (see Fig. 6).

Thus, it has been associated with the existence of "rigid domains" constituting the interface between amorphous and crystalline regions [7, 11], and characterized by the rigid amorphous fraction *fr*. This sub-mode has been assigned to the dielectric manifestation of the upper glass transition T_{g_u} in the Boyer nomenclature [10].

CONCLUSION

The microstructure of PEEK has been investigated by the thermally stimulated current spectroscopy.

The dielectric relaxation mode observed below 0°C shows the existence of two sub-modes: β_a, situated at around −110°C, is associated with movements in the crystallizable amorphous phase and, therefore is highly dependent upon the ratio of crystallinity; β_c, centered at −75°C, is characteristic of movements in the crystalline phase, and the magnitude of its compensation line and the ratio of crystallinity in the sample increase together.

The dielectric relaxation mode associated with the glass transition shows the existence of two amorphous phases: the "true amorphous phase" is characterized by cooperative movements following a compensation law, with parameters indicative of local order; and the "rigid amorphous phase" corresponds to amorphous regions constrained by crystallites. Because the metastability of this phase is strongly dependent on thermal history, it might play an important role in the variation of the final properties of PEEK.

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