THERMALLY STIMULATED CURRENT STUDY OF THE MICROSTRUCTURE OF PEEK

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Thermally Stimulated Current (TSC) spectroscopy and Differential Scanning calorimetry (DSC) have been applied to the characterization of the microstructure of Poly (Ether Ether Ketone)/ PEEK. the dielectric relaxation spectra show two modes, dependent upon crystallinity:

* for the mode stuated in the vicinity of the glass transition temperature, two components have been distinguished and attributed to the molecular mobility in the 'true amorphous phase' and in the 'rigid amorphous region'.

* below 0°C, two sub-modes appear, situated around −110°C and −75°C, due to the two different crystal entities, beads and laths.

Introduction

Properties of thermostable thermoplastic polymers like Poly (Ether Ether Ketone) (PEEK) depend largely upon crystallinity [1, 2]. The aim of this work is to characterize the molecular mobility in PEEK, as a function of crystallinity. Thermally Stimulated Current/TSC spectroscopy and Differential Scanning Calorimetry/DSC have been used for the characterization.

Materials and methods

PEEK with 10% crystallinity (PEEK/10) supplied by ICI, has been studied. A comparative study was carried out with 28% crystallinity samples (PEEK/28).

The DSC thermograms were obtained on a DSC7 from Perkin-Elmer, with a scanning rate of 20 deg·min^{-1}. The TSC study [3] was performed on a TSC/RMA spectrometer from Solomat.

Results

DSC curves

DSC curves of PEEK/10 (solid line) and PEEK/28 (dashed line) are reported on Fig. 1. To see the glass transition of PEEK/28, the correspondant curve has been multiplied by 5.
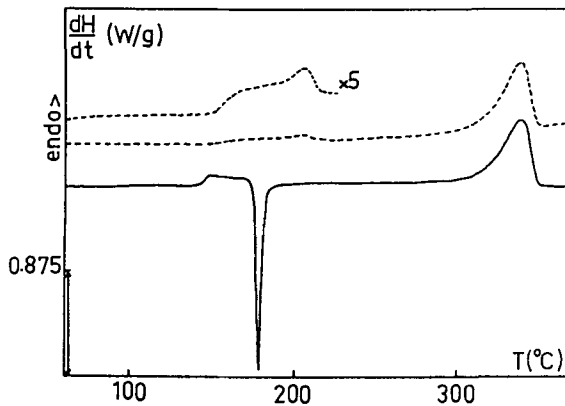
Fig. 1 DSC curves for PEEK/10 (—) and PEEK/28 (----)

Glass transition temperatures T_g and values of the variation of the heat capacity at T_g, ΔC_p, are reported in Table 1. As expected, we can note that T_g increases with the crystallinity, contrary to ΔC_p [4].

Table 1 DSC parameters of the glass transition

	PEEk / 10	PEEK / 28
$T_g/°C$	145	157
$\Delta C_p / J·g^{-1}K^{-1}$	0.28	0.10

The cold crystallization appears at 179°C, for PEEK/10. This phenomenon does not occur for PEEK/28.

For the two samples, melting peak appears around 338°C, with a heat of fusion is 38.5 J·g^{-1}.

Complex TSC spectra

We have reported the complex TSC spectra of PEEK/10 (solid line) and PEEK/28 (dashed line) for High Temperature/HT (around T_g) and low temperatures/LT (below 0°C), respectively in Figs 2 and 3. Data were obtained with a polarization field $E = 8.10^5$ V·m^{-1}, a polarization time $t_p = 2$ min, and a polarization temperature of 160° and 20°C, respectively for HT and LT spectra.
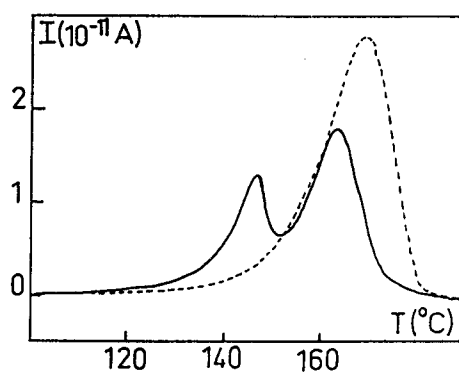

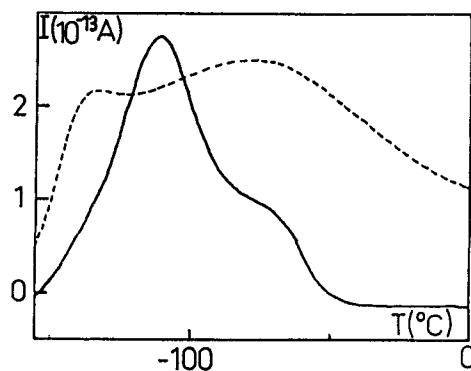Fig. 2 Complex TSC spectra at HT for PEEK/10 (—) and PEEK/28 (----)

Fig. 3 Complex TSC spectra at LT for PEEK/10 (—) and PEEK/28 (----)

At high temperature, for PEEK/10, two relaxation peaks appear situated at 145° and 162°C. For PEEK/28, only one peak can be observed around 170°C.

These relaxation modes have been associated with the dielectric manifestation of the glass transition owing to their proximity with the DSC glass transition temperature.

At low temperature, for PEEK/10, we can see the existence of two sub-modes located around −110° and −75°C. For PEEK/28, the higher sub-mode only appears around −75°C. It is interesting to note that the intensity of the higher sub-mode increases with the crystallinity.

Fine structure of TSC spectra

All the complex TSC spectra have been resolved into elementary spectra, using the fractional polarization method [3]. Elementary peak can be well described using a single relaxation time $\tau(T)$, obeying an Arrhenius equation $\tau(T) = \tau_o \exp[\Delta H / kT]$, where τ_o is the preexponentail factor, ΔH the activation enthalpy and k the Boltzmann constant. For PEEK/10 (open points) and PEEK/28
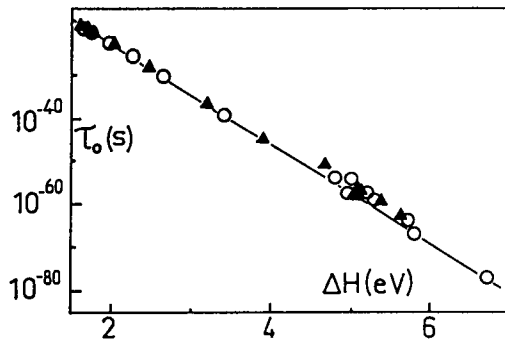

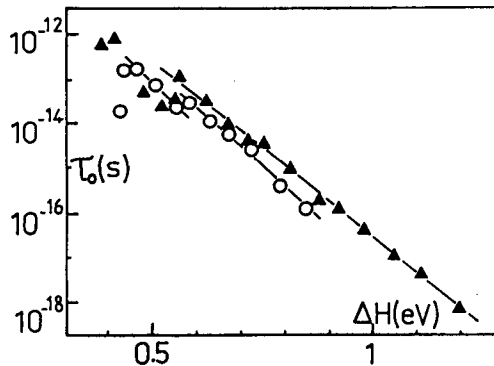Fig. 4 τ_o as a function of ΔH at HT for PEEK/10 (o) and PEEK/28 (▲)

Fig. 5 τ_o as a function of ΔH at LT for PEEK/10 (o) and PEEK/28 (▲)

(filled triangles), the values of τ_o as a function of ΔH have been reported in Fig. 4 and Fig. 5, respectively for the HT and LT modes. For some complex relaxation mode, elementary peaks are characterized by relaxation times following a compensation law $\tau(T) = \tau_c \exp[\Delta \dfrac{H}{k}(\dfrac{1}{T} - \dfrac{1}{T_c})]$. So, a compensation temperature T_c and a compensation time τ_c can be defined [3]. Tables 2 and 3 give the compensation para-meters for PEEK/10 and PEEK/28 respectively.

Table 2 Compensation parameters for PEEK/10

	LT		HT	
$T_c/°C$	208	300	161	–
τ_c / s	$1.4 \cdot 10^{-8}$	$4.2 \cdot 10^{-9}$	2	–

Table 3 Compensation parameters for PEEK/28

	LT		HT	
$T_c/°C$	–	364	165	–
τ_c / s	–	$2.3 \cdot 10^{-9}$	2	–

Discussion

Molecular mobility at high temperature

The complex TSC spectra associated with the glass transition is constituted of two submodes: the lower temperature sub-mode and the upper temperature sub-mode, respectively labelled T_{gl} and T_{gu}, according to the nomenclature of Boyer [5].

For the sub-mode associated with T_{gl}, the magnitude of the peak increases contrary to the crystallinity. Moreover, T_{gl} is characterized by a compensation law: this behavior is attributed to cooperative movements liberated at the glass transition. The maximum of ΔH is 6.7 eV for PEEK/10. It decreases up to 5.1 eV for PEEK/28. According to the model of Hoffmann-Williams-Passaglia [6], those magnitudes reflect the maximum length of mobile units.

For the sub-mode associated with T_{gu}, the magnitude of the peak increases with the crystallinity. T_{gu} is characterized by activation enthalpy equal approximately to 5 eV: elementary processes do not obey a compensation law. So, T_{gu} has been associated with the 'rigid' amorphous region constrained by crystallites, that is, the interface between amorphous and crystalline regions [7-9].

Molecular mobility at low temperature

The LT relaxation mode of PEEK/10 shows the existence of two sub-modes responsible for a main peak situated at $-110°C$ and a shoulder around $-75°C$. It is important to note that in the PEEK/28, the increasing of crystallinity favours the second mode at $-75°C$. According to previous study of PEEK morphology [10, 11], these two sub-modes have been associated to two different crystal entities: bens and laths, and they will be designated as β_b and β_1, respectively in the order of increasing temperature. The analysis of the fine structure shows that corresponding compensation phenomena have parameters remaining of the same order of magnitude: τ_c is much smaller than for the processes around T_g, and T_c is in the range of crystallization-melting temperatures. We can conclude that the mobile entities belong to the crystalline regions and the corresponding movements are localized.

Conclusion

PEEK samples have been investigated by the Thermally Stimulated Current spectroscopy. Around the glass transition temperature, the dielectric relaxation mode shows the existence of two amorphous phase:
    * a 'true amorphous phase' with cooperative movements
    * a 'rigid amorphous phase' constrained by crystallites.
Below $0°C$, two sub-modes appear. Owing to their values of compensation parameters, they have been associated with localized movements in two different crystalline regions: beads and laths.

References

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Zusammenfassung — Zur Beschreibung der Mikrostruktur von Poly(Ether-Ether-Keton)/PEEK wurden TSC und DSC angewendet. In Abhängigkeit von der Kristallinität zeigen die Dipolrelaxationsspektren zwei Arten:

* in der Nähe der Glasumwandlungstemperatur konnten zwei Komponenten unterschieden und der Molekülbeweglichkeit in der 'echten amorphen Phase'und in der 'starren amorphen Region' zugeordnet werden.

* unter 0°C erscheinen wegen der zwei Kristallgebilde Perlen und Zäpfchen bei −110° und −75°C zwei Unterarten.