



INTERFACIAL RELAXATION IN SEMI-CRYSTALLINE POLYMER

M. Arous^{1,2}, A. Kallel¹, Z. Fakhfakh^{1*}, G. Périer²

¹Laboratoire de Microscopie Electronique (Groupe Diélectrique),
Faculté des Sciences de Sfax, 3038 Sfax, Tunisia

²Laboratoire Matériaux Composites, ESIGEC, Université de Savoie,
73376 le Bourget du Lac, France

* Corresponding author. E-mail : zouheir.fakhfakh@fss.rnu.tn
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Abstract

The semi-crystalline morphology of a series of poly(ether ether ketone) (PEEK) has been investigated as a function of crystallization condition by dielectric relaxation spectroscopy. An interfacial polarization effect, known as the Maxwell-Wagner-Sillars polarization, is clearly evident taking place at the interface between the crystalline inclusions and the amorphous matrix. The intensity of the relaxation is presented in relation to the morphology of the crystalline part which is known to depend on annealing conditions.

Keywords : Interfacial relaxation; Semi-crystalline polymer; Crystallization.

1. Introduction

Poly(ether ether ketone) or PEEK is a high performance thermoplastic thermostable which can be obtained both in amorphous form as well as in semi-crystalline form depending on process conditions. Its specific high toughness and satisfactory thermal resistance stem from the microstructure of its amorphous and crystalline phase. Many reports have been devoted to the crystalline phase [1-2]. The study of annealing [3] has also shown the importance of structural reorganization.

The interfacial relaxation can be seen in heterogeneous system. The origin of this relaxation lies in the presence of intrinsic immobilized free electrical charges in the inclusions. These charges can migrate in the applied electrical field provided the temperature is high enough to ensure some conductivity of the material. These free carriers are then blocked at the interface between the two media of different conductivity and permittivity, leading to the appearance of an interfacial polarization.

The interfacial relaxation characteristics depend on the respective values of the conductivities and permittivities of the conductive part and the insulating part of the composite, and also on the shape of the inclusions [4]. We have presented elsewhere a study of the interfacial relaxation found in model composite constituted of amorphous thermoplastic polymer matrices, filled with spherical glass particles. The effect of the diameter, the volume fraction and the surface coating of glass beads on the interfacial relaxation characteristics have been studied [5-8].

Although the semi-crystalline polymer can be considered as a composite constituted of

crystalline inclusions dispersed in amorphous matrix of the same chemical nature, the aim of this work is of putting in relation the annealing-dependent morphological characteristics of the inclusions in PEEK and the intensity of the interfacial relaxation.

2. Experimental

The polymer used in this study is PEEK Stabar K200 supplied by ICI films in the form amorphous sheets whose thickness is about 250 μm . Semi-crystalline PEEK samples were obtained by annealing as-received films at two temperatures 160°C et 320°C for various keeping times varying from 30 min to 25 h. The crystalline ratio were measured by X-ray Diffractometry. It was obtained from the area of crystalline X-ray diffraction peaks after subtracting the contribution of the amorphous phase. Dielectric measurements were performed on DETA spectrometer (Rheometric Scientific) in the range 80-320°C and at a scan speed of 2°Cmin⁻¹.

3. Results and discussion

Although the dielectric data were taken in isothermal mode, it is much more informative to display the data in isochronal plots versus temperature. The real (M') and imaginary (M'') parts of the dielectric modulus at three decade frequencies are shown in figure 1 for the amorphous and crystallized samples. The M' and M'' spectrums can be divided into two temperature ranges. The first one (100-180 °C) deals with dipolar relaxation, whereas the second one (180-300°C) shows evidence for ionic conduction.

A series of three distinct phenomena can be considered as the sample is heated over the whole temperature range (figure 1.a). The first of them is related to the dipolar relaxation associated with glass transition of the amorphous PEEK. This is the so-called α relaxation which appears at a temperature around 150°C for the frequencies used. The sample being now at a temperature above its glass transition, a non-isothermal crystallization occurs inside the spectrometer

measurement head. An increase of the dissipation factor (α_c) is seen in the 165-180°C range, just following the α relaxation. This relaxation is not present in the case of already crystallized samples (figure 1.b). This second peak has already been reported [9,10] and assigned to the relaxation of the just-crystallized sample whose amorphous part motions are now restricted by the presence of crystals.

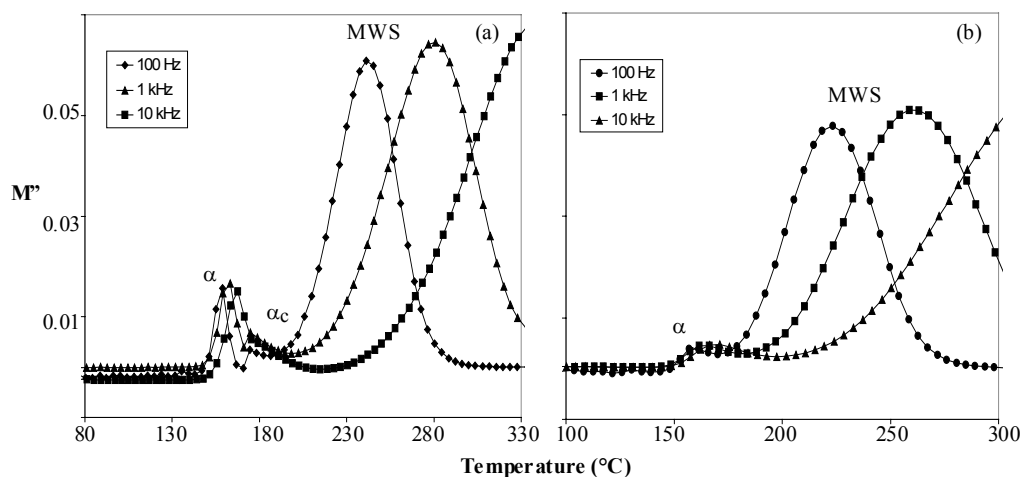


Figure 1 : Isochronal curves of the loss factor ϵ'' for frequencies of 0.1, 1 and 10 kHz :
(a) Amorphous PEEK
(b) 320°C-30min glass-crystallized PEEK.

At temperatures much higher, another relaxation appears in our curves as a plateau around 250°C. This relaxation is attributed to the trapping of ionic charges at the interface between the amorphous and the crystalline regions of the polymer (interfacial relaxation). Space-charge effects [11] as detected by Thermally Stimulated Current technique are related to this interfacial polarization mechanism.

Table 1 reports the measured volumic fraction of the crystalline part of the polymer and the intensity of the interfacial relaxation. In a first reading of these results, and in agreement with literature, it can be said that the 320°C heat treatments seem to give lamellae whose thickness is growing with keeping times as the crystalline volumic fraction is seen to increase.

Concerning the dielectric results, 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. Despite the fact that some further crystallization may occur during the experiment for not fully crystallized samples, the variation of the intensity of the MWS relaxation leads us to believe that this characteristic can be related to the overall amorphous-crystalline interface area.

The intensity of the 320°C-1h and 320°C-2h samples is lower than the intensity of the 160°C-2h one. This can suggest that lamellae resulting from the high-temperature annealing must be less numerous and therefore larger than the low-temperature annealing lamellae.

The crystal volumic fraction increase weakly with the time at 320°C but the intensity of MWS relaxation decrease strongly. This phenomena can not be attributed to an increase in the size or thickness of the lamellae. Rather, it can be put down to an improvement in the order and/or

crosslinking of the polymer chains inside the lamellae [2], leading to a more marked boundary between the amorphous and the crystalline regions, and to more efficient trapping of free charges at the interface. The same result is found in particulate composites where glass beads were

embedded in polystyrene-based matrices [7]. We showed that the presence of a coating layer on the beads surface leads to a more efficient for the blocking of the charges carriers moving in the glass.

Crystallization	Annealing	Crystalline volumic fraction (%)	Intensity of relaxation $\Delta\epsilon = \epsilon_S - \epsilon_\infty$
From the glass	160°C-2h	8.3	51.13
	320°C-30min	26.1	54.71
	320°C-1h	27.6	33.04
	320°C-25h	31.3	31.84

Table 1. Crystalline volumic fractions and intensity of relaxation at 180°C for PEEK with various annealing conditions.

4. Conclusion

Dielectric measurements was used to study the interfacial relaxation in semi-crystalline PEEK. This relaxation is seen in addition to dipolar relaxation and ionic conduction. It's attributed to the trapping of ionic charges at the interface between crystalline lamellae and the amorphous matrix. The intensity of the relaxation is shown to be sensitive to the annealing conditions and is related to the morphological features. This exploratory work shows that the study of the interfacial relaxation can have the potential of providing valuable information on the nature of the crystalline-amorphous interface in semi-crystalline polymers.

References

- [1] D. J. Blundelle, J. D'Nello, *Polymer*, 32 (2) (1991) 304.

- [2] A. Jonas R. Legras, *Macromolecules*, 26 (1993) 813.
- [3] P. Cebe, *J. Mater. Sc.*, 23 (1988) 3721.
- [4] L. K. H. van Beek, in : *Progress in Dielectric* p. 69, Heywood, London (1967).
- [5] G. Perrier, A. Bergeret, *J. Appl. Phys.*, 77 (1995) 2651.
- [6] G. Perrier, A. Bergeret, *J. Polym. Sci. B*, 35 (1997) 1349.
- [7] M. Arous, A. Kallel, Z. Fakhfakh, G. Perrier, *Comp. Int.*, 5 (1997) 137.
- [8] M. Arous, A. Kallel, Z. Fakhfakh, G. Perrier, *J. Phys. Soc. Jap.*, 66 (1997) 3665.
- [9] P. J. Huo, P. Cebe, *Macromolecules*, 25 (1992) 902.
- [10] D. S. Kalika, R. K. Kirshnaswamy, *Macromolecules*, 26 (1993) 4252.
- [11] B. B. Sauer, P. Avakian, H. K. Starkweather Jr, B. S. Hsiao, *Macromolecules*, 23 (1990) 5119.