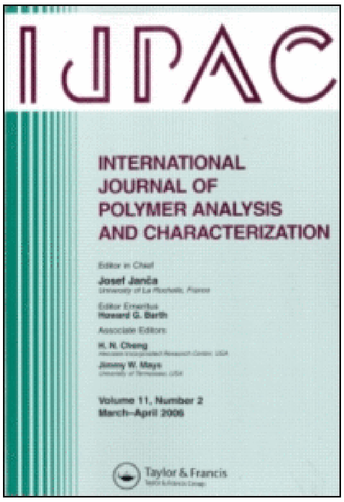


International Journal of Polymer Analysis and Characterization
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713646643

Study of Quenched Poly Ethylene Naphatalate (PEN) Using the Three-Phase Model by Differential Scanning Calorimetry (DSC)

N. Doulache[a]; M. W. Khemici[ab]; A. Gourari[a]; M. Bendaoud[a]
[a] Physics Faculty, University of Science and Technology Houari Boumediene, USTHB, Algiers, Algeria
[b] Sciences Faculty, University M'Hamed Bougara, Boumerdès, Algeria

To cite this Article Doulache, N. , Khemici, M. W. , Gourari, A. and Bendaoud, M.(2010) 'Study of Quenched Poly Ethylene Naphatalate (PEN) Using the Three-Phase Model by Differential Scanning Calorimetry (DSC)', International Journal of Polymer Analysis and Characterization, 15: 1, 7 — 17

To link to this Article: DOI: 10.1080/10236660903299259

URL: http://dx.doi.org/10.1080/10236660903299259

International Journal of Polymer Anal. Charact., 15: 7–17, 2010

ISSN: 1023-666X print
DOI: 10.1080/10236660903299259

STUDY OF QUENCHED POLY ETHYLENE NAPHATALATE (PEN) USING THE THREE-PHASE MODEL BY DIFFERENTIAL SCANNING CALORIMETRY (DSC)

N. Doulache,[1] M. W. Khemici,[1,2] A. Gourari,[1] and M. Bendaoud[1]
[1]*Physics Faculty, University of Science and Technology*
Houari Boumediene, USTHB, Algiers, Algeria
[2]*Sciences Faculty, University M'Hamed Bougara, Boumerdès, Algeria*

In order to optimize the use of some materials in electronic and microelectronic fields, the study of some of their properties is very important. Among these materials, we cite poly (ethylene naphtalate), PEN, which the description with a three-phase model is necessary to explain some of its dielectric behaviors, such as, for example, the α relaxation peak. A thermal treatment by quenching the material in ice water at different temperatures has allowed us to obtain various partially crystalline poly ethylene naphtalate. DSC measurements have been carried out from **40°** ***to*** **290°C** ***in order to characterize the glass transition, melting point, and crystallinity of the obtained semicrystalline PEN. The results show the presence of a crystalline phase and a part of the amorphous phase that does not participate in glass transition, called the rigid amorphous phase. This later is more important in PEN than the one present in PET.***

Keywords: DSC; Poly (ethylene 2,6-naphtalate); Poly (terephthalate); Three-phase model

INTRODUCTION

Poly (ethylene terephthalate), PET, and its concurrent poly (ethylene 2,6-naphtalate), PEN, are some of the most widely used polymers in packaging applications because of their high performance such as mechanical properties, transparency, and easy processing. These properties are also suitable for technological applications, for instance in commercial recipients and capacitor miniaturization.[1–3]

The difference between PEN and PET is that a double aromatic ring of naphtalene group is present in PEN, whereas there is a single one in PET. In fact, this difference provides a higher stiffness to the macromolecular chain of PEN

Submitted 1 April 2009; revised 1 September 2009; accepted 2 September 2009.

Presented at the 21st International Symposium on Polymer Analysis and Characterization held 22–24 June 2009 at the Tomas Bata University in Zlin, Zlin, Czech Republic. The authors would like to express their gratitude to A. Boukemidja of Sonatrach firm and R. Maghniz of Lab Solutions firm for helpful collaboration.

Correspondence: M. W. Khemici, Physics Faculty, University of Science and Technology Houari Boumediene, USTHB, B.P. 32, El-Alia, 16111, Algiers, Algeria. E-mail: khemici@gmail.com

and hence yields better thermomechanical properties and presents higher thermal stability than PET.

During amorphous PET heating process from its glassy state, by using the differential scanning calorimetry (DSC) method, a broad and weak glass-rubber transition appears at around 80°C. This is about 45°C lower than PEN's glass-rubber transition.[4–6] An endothermic peak corresponding to the melting process is observed at $T_m = 257°C$, which is about 10°C lower than PEN's T_m.[4–6] Furthermore, at around $T_c = 130°C$, an exothermic peak corresponding to the crystallization process is observed. T_c in PET is 70°C lower than PEN's T_c.[4–6]

PET and PEN can be obtained in the amorphous state by rapid quenching from their melting temperature in ice water.[3] When the quenching is performed from T_Q temperature lower than T_m, the positions and intensities of the endothermic and exothermic peaks are changed. Thus, partially crystalline PET and PEN are obtained with various degrees of crystallinity.

The two semicrystalline polymer structures can be explained with a two-phase model in which the materials are described without a transitional region between crystalline and amorphous domains. However, in the past 20 years, there have been several attempts to describe easily such polymers; a three-phase model taking into account the rigid amorphous fraction has been proposed.[7–11]

The third phase of this model is a transitional region located between crystalline and mobile amorphous regions; it is called the rigid amorphous fraction and it can be characterized easily by calorimetric measurements, because it does not participate in the glass transition of the amorphous phase (called the amorphous mobile phase). PET is one of polymers for which the three-phase model has successfully described the thermal behavior. Some authors have shown, in various annealed PET, that the amount of the rigid amorphous fraction must be considered as a measure of the coupling between the crystalline and amorphous phases, and recently Arnoult et al.[12] proposed the investigation of the coupling between the rigid amorphous fraction and the mobile amorphous one.

Although many works have described PET behavior using the three-phase model, the description of PEN by this model remains, to our knowledge, poor. For this reason, the aim of this work is to describe the influence of quenching on the thermal behavior of PEN by using the three-phase model.

EXPERIMENTAL SECTION

Biaxially stretched film of PEN (125 μm thickness) was supplied by Goodfellow (U.K.). Commercial PET film (55 μm thickness) was supplied by Dupont de Nemours (Luxembourg). Low crystallinity degree samples were obtained by rapid quenching of the molten materials in ice water. Samples with various degrees of crystallinity were prepared by quenching materials from different temperatures T_Q lower than the melting temperature. Thus, we obtained different degrees of crystallinity χ_c as shown in Table I.

Calorimetric measurements were performed with a TA instruments Q-10. The temperature of the instrument was calibrated with indium and lead standards, and only the indium sample was used for heat flow calibration.

The sample was placed in a sealed aluminum pan. The mass of fragments should have a maximum contact area between the sample and the pan. A mass

Table I. Crystallinity degree χ_C for various quenching temperatures T_Q for PET and PEN

T_Q (°C)	270	250	240	230	220	210	200	190	180	170
χ_C (%) PET	14.26	14.33	15.29	17.34	22.62	32.90	39.60	44.47	44.29	45.81
T_Q (°C)	280	250	240	225	210	200	170	140	–	–
χ_C (%) PEN	5.56	6.94	8.84	15.82	29.38	34.72	35.86	35.86	–	–

higher than 5 mg has proved to be acceptable. DSC curves were obtained from 10 mg samples at 10°C/min controlled heating rate.

The crystallinity degree deduced from a DSC thermogram is given by the following equation[11]:

$$\chi_c = 100 \times \frac{\Delta H_m - \Delta H_c}{\Delta H_0} \tag{1}$$

where ΔH_m and ΔH_c represent the area of the exothermic and endothermic peaks respectively. ΔH_0 is the extrapolated heat of fusion for a pure crystal. In this work, we used $\Delta H_0 = 126.7\,\mathrm{J/g}$ for PET[5] and 103.4 J/g for PEN.[13]

The amorphous mobile fraction χ_{am} is given by the following equation:[12]

$$\chi_{\mathrm{am}} = 100 \times \frac{\Delta C_p}{\Delta C_{p0}} \tag{2}$$

where ΔC_p and ΔC_{p0} are jumps at the glass transition temperature T_g of the thermal heat capacity for the semicrystalline and the wholly amorphous samples respectively.

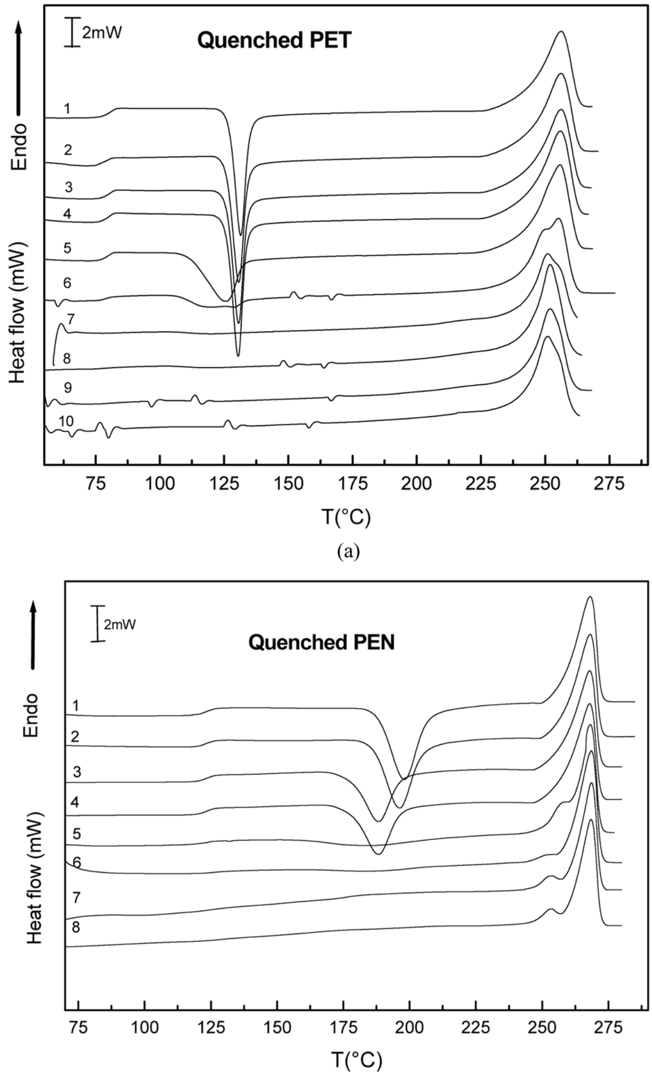
Thermally stimulated currents (TSC) were measured with a dielectric spectrometer developed in our laboratory. To obtain a global TSC spectrum, the sample is polarized by a static field E_p at the polarization temperature T_p for a time Δt_p. The sample is then quenched from T_p to the freezing temperature $T_0 \ll T_p$. At T_0, the field is removed and the sample is short-circuited. The depolarization current is then recorded as the temperature is increased at a heating rate $q = 7°\mathrm{C/min}$, resulting in a complex TSC spectrum.

RESULTS AND DISCUSSION

DSC measurements were carried out from 40° to 290°C in order to characterize the glass transition, melting point, and crystallinity of quenched PET and PEN.

Figures 1(a) and (b) show the results obtained for samples quenched at different temperatures T_Q. The glass transition of the materials is clearly observable in the scan corresponding to the sample with low degree of crystallinity and lies approximately at 80°C for PET and 124°C for PEN. During the crystallization process, an important heat transfer between the sample and the environment is observed because of polymer chains move toward lower energy configuration.

The exothermic crystallization process of PET and PEN with low crystallinity degrees can be observed in DSC curves, T_Q up to 190°C (PET) and 200°C (PEN), at temperatures around 130°C and 198°C respectively. For PEN, this peak has a



(a)

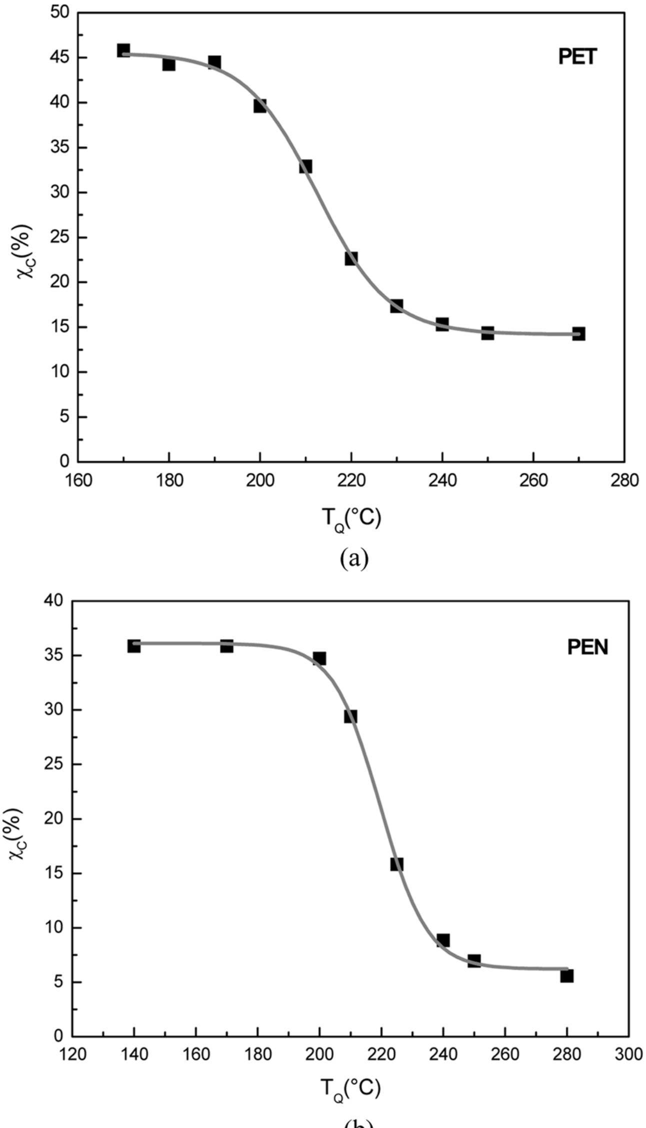
(b)

Figure 1. DSC scans at 10°C/min. Samples were previously quenched from different temperatures T_Q lower than the melting temperature: (a) PET, T_Q (°C): 270 (1), 250 (2), 240 (3), 230 (4), 220 (5), 210 (6), 200 (7), 190 (8), 180 (9), 170 (10); (b): PEN, T_Q(°C): 280 (1), 250 (2), 240 (3), 225 (4), 210 (5), 200 (6), 170 (7), 140 (8).

tendency to shift towards the low temperatures and to become broader for low values of T_Q.

The melting process took place at about 257°C for PET and 268°C for PEN. The enthalpy of this process corresponds to the melting of the entire crystal part of the samples and remains constant for each sample.

The appearance of a small endothermic peak in PEN can be seen in Figure 1(b) (curves 5–8). Pre-melting processes occur in materials when T_Q decreases. These processes are identified in DSC curves by an increase of the small endothermic peak area and its shifting towards higher temperatures. The same phenomenon has been observed in treated PEN by using the thermal step simulation (TSS) method,[5] and it has been explained by the fact that this behavior is related to the important changes in the ρ relaxation associated with free charge in the material.[14]



(a)

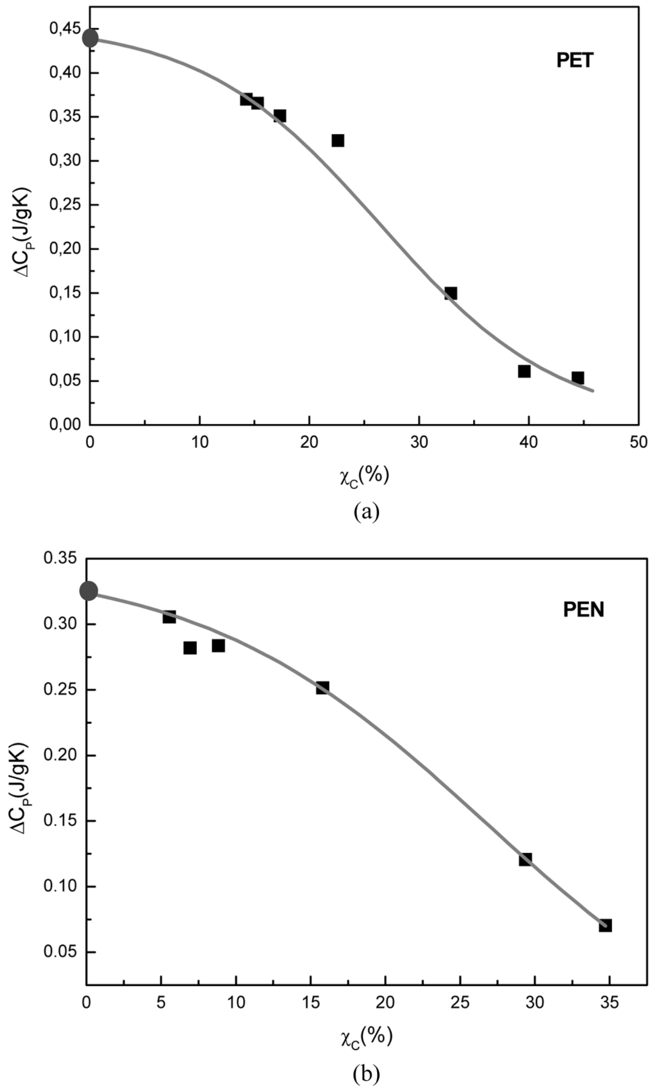
(b)

Figure 2. Evolution of the crystallinity degree χ_c vs. T_Q for quenched samples: (a) PET and (b) PEN.

The variations of χ_c versus the temperature T_Q reported in Figures 2(a) and (b) show a sigmoidal decrease of χ_c for each sample (PET and PEN). For PET, a wholly amorphous material could not be obtained. Also, the minimum χ_c deduced from the curve shown in Figure 1(a) and by using Equation (1) was close to 14%.

Recently, Arnoult et al.[12] tried to prepare a wholly amorphous PET, but the minimal value of χ_c that was obtained was close to 7%. The lower value of χ_c (5%) was obtained by Schmidt-Rohr et al.[15]

For PEN, the lower degree of crystallinity that we can obtain is approximately 5%. The same value was found by Canadas et al.[14] For every temperature $T_Q >$



(a)

(b)

Figure 3. Difference of thermal heat capacities ΔC_p between liquid and glassy states at T_g vs. χ_c: (a) PET and (b) PEN.

240°C, χ_c remains constant for each sample. For T_Q included between 240° and 190°C for (PET) and between 240° and 200°C for (PEN), a crystalline phase will appear. For $T_Q < 190°C$ (PET) and $T_Q < 200°C$ (PEN), the crystallinity degree the of sample remains practically constant and close to 46% (PET) and 36% (PEN).

Quantitative information on the amorphous phase evolution is given by the variations of heat capacity at glass transition. Figure 3(a) represents the variations of ΔC_p versus χ_c for PET. It shows an important decrease between $\chi_c = 15\%$ and $\chi_c = 38\%$, and after that it remains constant. The same evolution was noticed for

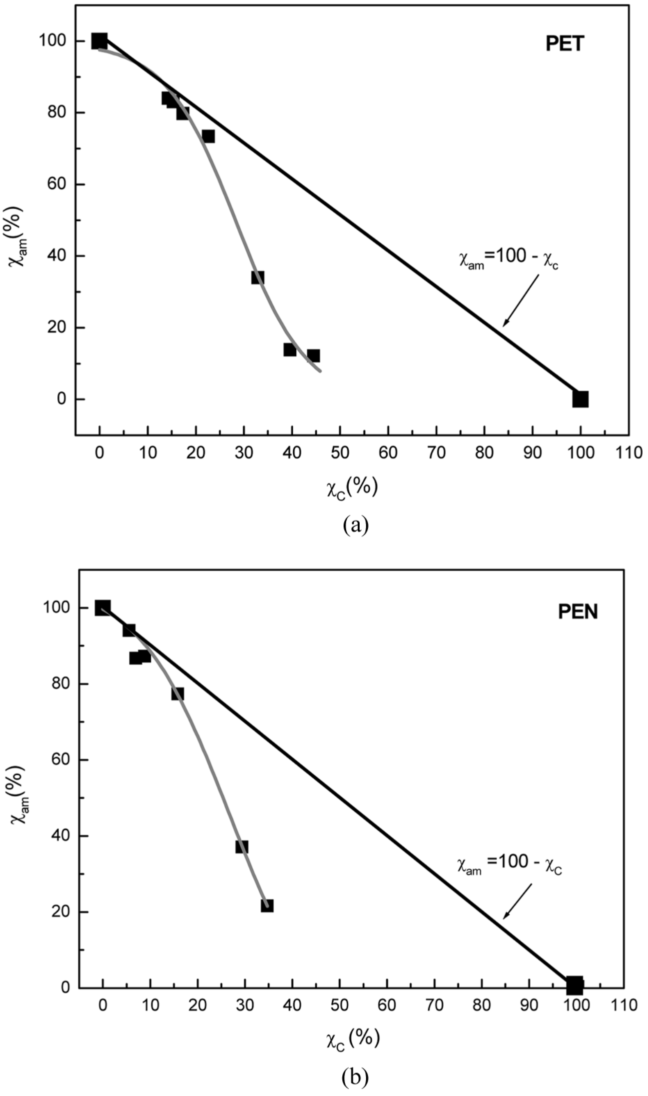
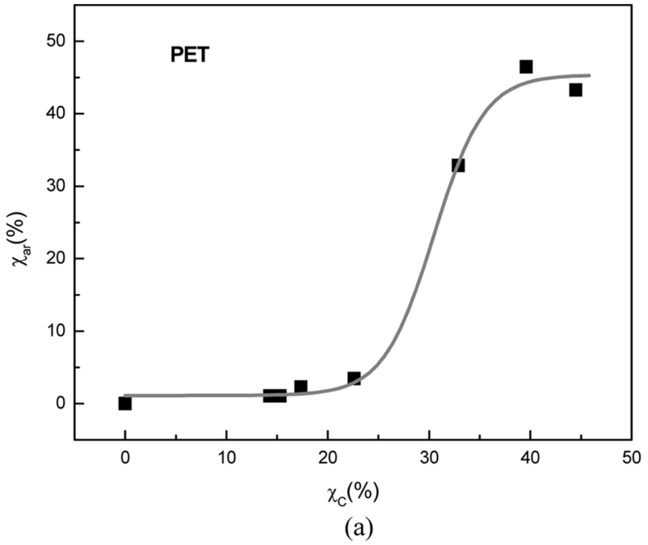


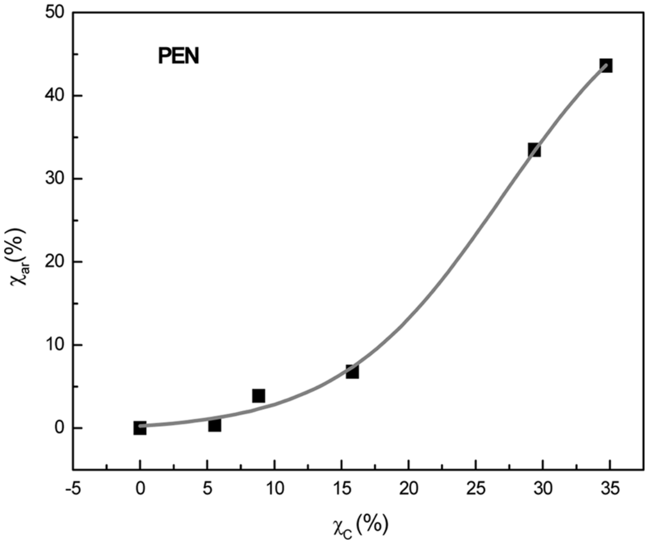
Figure 4. Evolution with χ_c of the mobile amorphous phases rate χ_{am} for quenched samples: (a) PET and (b) PEN.

PEN (Figure 3(b)): an important decrease of ΔC_p is observed between $\chi_c = 6\%$ and $\chi_c = 35\%$. However, in the case of PEN and for χ_c up to 34%, we were able to observe the glass transition on DSC curves. For this reason, the constancy of ΔC_p values was not observable as it was the case in the PET.

Since we have not obtained wholly amorphous materials, the values of ΔC_{p0} used in the present work were deduced by extrapolation of the curves shown in Figures 3(a) and (b). The obtained values were equal to 0.440 J/gK and 0.325 J/gK for PET and PEN, respectively. These values are in good agreement with those found



(a)



(b)

Figure 5. Percentage of rigid amorphous fraction as a function as χ_c: (a) PET and (b) PEN.

in the literature. For PEN, Zouzou[16] found $\Delta C_{p0} \approx 0.328\,\mathrm{J/gK}$. For PET, Arnoult et al.[12] used the value of $\Delta C_{p0} \approx 0.405\,\mathrm{J/gK}$ suggested by the ATHAS database.

In Figures 4(a) and (b), we have reported the variations of χ_{am} versus χ_c for both polymers at the glass transition. Its decrease is very important when χ_c increases, and the data are not aligned with the straight line whose equation is: $\chi_{\mathrm{am}} = 100 - \chi_c$. Thus, we can deduce that a part of the amorphous phase does not participate to the glass transition, and a rigid amorphous fraction should be taken into account for PET and PEN. This fraction is considered as a third element

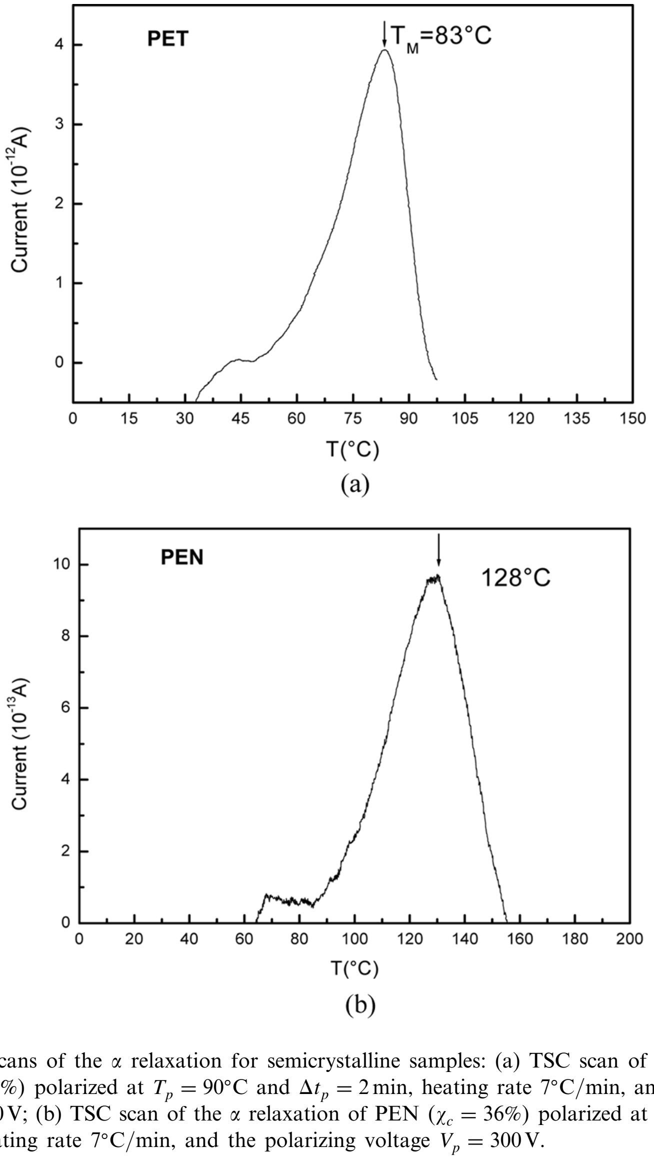


Figure 6. TSC scans of the α relaxation for semicrystalline samples: (a) TSC scan of the α relaxation of PET ($\chi_c = 46\%$) polarized at $T_p = 90$°C and $\Delta t_p = 2\,\mathrm{min}$, heating rate 7°C/min, and the polarizing voltage $V_p = 100\,\mathrm{V}$; (b) TSC scan of the α relaxation of PEN ($\chi_c = 36\%$) polarized at $T_p = 130$°C and $\Delta t_p = 2\,\mathrm{min}$, heating rate 7°C/min, and the polarizing voltage $V_p = 300\,\mathrm{V}$.

of a three-phase model according to the equation $\chi_{\mathrm{ar}} = 100 - \chi_c - \chi_{\mathrm{am}}$, where, χ_{ar} describes the contribution of the rigid amorphous fraction.

Figures 5(a) and (b) display the variations of χ_{ar} versus the crystallinity degree χ_c. After performing a comparison between the two obtained figures, it can be deduced that the rigid amorphous fraction is more important in PEN than in PET.

For example, for the same degree of crystallinity $\chi_c = 20\%$ we obtain $\chi_{\mathrm{ar}} = 2\%$ (PET), $\chi_{\mathrm{ar}} = 13\%$ (PEN) and for $\chi_c = 34\%$ the values are $\chi_{\mathrm{ar}} = 37\%$ (PET) and $\chi_{\mathrm{ar}} = 43\%$ (PEN). These results are in good agreement with the structure of the two polymers. Indeed, PEN is an aromatic polyester in which the benzene group of PET is replaced by a naphthalene group. Then, the double aromatic cycle present in PEN provides a higher stiffness to the macromolecular chain of PEN. For this reason, PEN's rigid amorphous fraction χ_{ar} is more important than PET's.

In order to confirm this result, the thermally stimulated current technique was used. Figure 6(a) displays the TSC spectrum of PET in a semicrystalline form ($\chi_c = 46\%$). In the temperature range from 0° to 100°C it shows a relaxation located at $T_M = 83°\mathrm{C}$, which is attributed to the dielectric manifestation of the glass transition (α relaxation). The maximum intensity of the obtained peak is approximately 4×10^{-12} A.

Figure 6(b) represents the TSC peak of PEN ($\chi_c = 36\%$). It shows (in the temperature range from 0° to 160°C) a relaxation located at $T_M = 128°\mathrm{C}$ attributed to the dielectric manifestation of the glass transition with a maximum intensity of about 0.9×10^{-12} A.

The comparison between the two obtained peaks revealed that, although the crystallinity degree of PEN is lower than PET's, the maximum intensity of the TSC peak of PET is higher than PEN's. This result can be explained by the fact that the amorphous mobile fraction, which contributes to the α relaxation, is more important in PET. In other terms, the amorphous rigid fraction in PEN is more important than the one present in PET, because a double aromatic cycle is present in PEN.

CONCLUSION

We have reported on the effect of the quenching process of PET and PEN in ice water from T_Q temperatures that are lower than the melting temperature T_m, by calorimetric measurements. According to the results of the present study, it can be concluded that:

- The quenching process reveals an intermediate phase between the mobile phase and the crystalline one. It is the rigid amorphous phase.
- A quantification of these three phases revealed that the rigid amorphous phase rate χ_{ar} present in PEN is higher than the one of PET; this difference is justified by the aromaticity virtues increased in PEN, which tends to rigidify its macromolecular chains. This result justifies the fact that the glass transition temperature of PEN is higher than PET's.

Also, it should be noted that the quenching process induces the appearance of a pre-melting peak in the PEN. This is absent in the PET case.

REFERENCES

1. Yasufuku, S. (1996). Application of poly(ethylene naphtalate) films to electrical and audio-visual uses in Japan. *IEEE Elec. Insul. Mag.* **12**(6), 8–14.
2. Clelland, I. W., and R. A. Aprice. (1993). Precision film capacitors for high frequency circuits. In *Technical Papers of the 8th International High Frequency Power Conversion Conference*, Ventura, USA. pp. 279–291.
3. Kattan, M., E. Dargent, and J. Grenet. (2004). Relaxations in amorphous and semi-crystalline polyesters. A study by thermally stimulated depolarization. *J. Therm. Anal. Calorim.* **76**(2), 379–394.
4. Aref-Azar, A., F. Arnoux, F. Biddlestone, and J. N. Hay. (1995). Physical ageing in amorphous and crystalline polymers. Part 2. Polyethylene terephthalate. *Thermochim. Acta* **273**, 217–229.
5. Canadas, J. C., J. A. Diego, J. Sellarès, M. Mudarra, and J. Belana. (2000). Cold crystallization effects in free charge relaxation in PET and PEN. *Polymer* **41**, 8393–8400.
6. Benrekaa, N., A. Gourari, M. Bendaoud, and K. Ait-hamouda. (2004). Analysis of thermally stimulated current and effect of rubbery annealing around glass-rubber transition temperature in polyethylene terephthalate. *Thermochim. Acta* **413**, 39–46.
7. Dargent, E., C. Cabot, J. M. Saiter, J. Bayard, and J. Grenet. (1996). The glass transition: Correlation of DSC and TSDC investigations. *J. Therm. Anal. Calorim.* **47**(3), 887–896.
8. Danch, A., and W. Osoba. (2003). Structural relaxation of the constrained amorphous phase in the glass transition phase. *J. Therm. Anal. Calorim.* **72**, 641–650.
9. Hourston, D. J., and M. Song. (1998). Temperature modulated differential scanning calorimetry. Some comments on the rigid amorphous fraction in semi crystalline poly(ethylene terephthalate). *J. Therm. Anal. Calorim.* **54**(2), 651–657.
10. Alseben, M., and C. Schick. (1994). The melting of polymers: A three-phase approach. *Thermochim. Acta* **238**, 203–227.
11. Kattan, M., E. Dargent, and J. Grenet. (2002). Three phase model in drawn thermoplastic polyesters: Comparison of differential scanning calorimetry and thermally stimulated depolarization current experiments. *Polymer* **43**, 1399–1405.
12. Arnoult, M., E. Dargent, and J. F. Mano. (2007). Mobile amorphous phase fragility in semi-crystalline polymers: Comparison of PET and PLLA. *Polymer* **48**, 1012–1019.
13. Cheng, S. Z. D., and B. Wunderlich. (1988). Glass transition and melting behavior of polyethylene-2,6-naphthalene dicarboxylate. *Macromolecules* **21**, 789–797.
14. Canadas, J. C., J. A. Diego, J. Sellarès, M. Mudarra, J. Belana, R. Diaz-Calleja, and M. J. Sanchis. (2000). Comparative study of amorphous and partially crystalline poly(ethylene-2,6-naphthalene dicarboxylate) by TSDC, DEA, AMA and DSC. *Polymer* **41**, 2899–2899.
15. Schmidt-Rohr, K., W. Hu, and N. Zumbulyadis. (1998). Elucidation of the chain conformation in a glassy polyester, PET, by two-dimensional NMR. *Science* **280**(5364), 714–717.
16. Zouzou, N. (2000). Etude de la mobilité moléculaire du PEN destiné à la fabrication des condensateurs: Influence de la microstructure. Ph.D. diss. University Paul Sabatier, Toulouse, France.