A study of the glass transition in the amorphous interlamellar phase of highly crystallized poly(ethylene terephthalate)

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Abstract
The glass transition of poly(ethylene terephthalate) (PET) crystallized for 4 h at temperatures between 413 and 453 K was studied. Secondary crystallization processes were monitored by differential scanning calorimetry and the glass transition of the remaining interlamellar amorphous phase was studied by thermally stimulated depolarization currents measurements. Non-isothermal window polarization is employed to resolve the relaxation in modes with a well-defined relaxation time that is subsequently adjusted to several standard models. An analysis of experimental results reveals that cooperativity can be disregarded in the modelization of data. The evolution of modes during secondary crystallization, once primary crystallization has been completed, gives more weight to lower energy modes. As a consequence, secondary crystallization tends to lower the glass transition temperature of the amorphous interlamellar phase, although remaining noticeably higher than in amorphous samples. The evolution of calorimetric scans of the glass transition is simulated from the obtained results and shows the same behaviour. Regarding the glass transition temperature of the material, it can be concluded that primary and secondary crystallization act in opposite directions even though the effect of secondary crystallization is much smaller. The interpretation of these results in terms of current views about secondary crystallization is discussed.

1. Introduction
Poly(ethylene terephthalate) (PET) is a widely used semi-crystalline polymer. Just to mention a few applications, it is used to manufacture films, tapes, mouldings, bottles and engineering components. These applications take advantage of the outstanding chemical resistance, thermal stability and mechanical performance of PET. These properties depend strongly on the microstructure of the material which, in turn, is determined by the crystallization conditions. Not surprisingly, the relevance of PET applications has spurred a lot of interest about the crystallinity of PET.

In PET, as in other semi-crystalline polymers, the crystalline regions are usually found inside spherulites. These spherical semi-crystalline structures grow during crystallization and tend to fill all the available space. The spherulites contain plates of highly ordered polymer chains named crystalline lamellae. An individual lamella tends to form stacks (sometimes called fibres) that radiate from the centre of the spherulite. These stacks are separated by amorphous regions [1]. Although a small amount of amorphous material can exist between the individual lamellae that form the stacks [1], most of the amorphous material in the spherulite is placed between the stacks of lamellae. We will refer to this material as the amorphous interlamellar phase. If the material has a low degree of crystallinity, there is also an interspherulitic amorphous phase. This phase is predated by the spherulites as the crystallinity degree grows.

In addition to the usual crystallization process that takes place when the material is cooled slowly from the melt, PET can also be crystallized by heating from the amorphous state (cold crystallization). This state can be reached if the material is cooled fast enough from the melt (quenching). In fact, the amorphous state can be considered as a supercooled liquid. As
the material is heated, chains gain enough mobility to fold and create lamellae more or less in the same way as in the usual crystallization process [1].

Many studies deal with the kinetics of the crystallization process in polymers [2]. It has been found that the process can take place in two stages, the so-called primary and secondary crystallization. Primary crystallization is a three-dimensional growth process and it is commonly accepted that it corresponds to the development of the spherulites. Instead, secondary crystallization takes place if the sample is annealed at high temperatures once primary crystallization has been completed (this is when spherulites fill up the available space), and occurs inside the amorphous interlamellar regions [2, 3].

There is some controversy over what really is secondary crystallization [3]. It is known that it corresponds to a one-dimensional growth process [2] but its exact nature remains unclear. It has been attributed to different facts such as thickening and rearrangement of the existing lamellae, insertion of new lamellae inside the stacks, insertion of new stacks as ramifications of the existing stacks, creation of randomly oriented new stacks in the interlamellar amorphous phase or connection between stacks with micella structures or folded chains [1–6]. There is certain consensus on the fact that as a result of secondary crystallization a dual population of lamellae is created.

A manifestation of secondary crystallization is a minor low-temperature endothermic peak that can be seen by differential scanning calorimetry (DSC) [6]. This peak appears, when the annealed sample is measured in a non-isothermal scan, at a temperature some degrees higher than the annealing one. It is caused by the fusion of materials crystallized by secondary crystallization during the annealing stage [7].

The presence of crystalline regions in semi-crystalline polymers is also known to affect the glass transition of the material. The glass transition temperature is higher in crystallized samples as a consequence of the isolation of the amorphous phase in multiple portions. We must note that usually it is more difficult to study the glass transition in such systems, as extensive measurable properties (such as enthalpy recovery and volume) are weaker in this case.

It is commonly accepted that the glass transition in polymers is a distributed process. In such processes different parts of the system respond with different relaxation times. A convenient way to study these transitions assumes that the complete relaxation can be modelled by a continuous distribution of relaxation times (DRT). A DRT is thus a set of elementary modes that can reproduce the behaviour of the whole process by the superposition of all of them.

Calorimetry and dilatometry have been thoroughly used to study the glass transition of polymers [1, 8], although some complexity arises in the interpretation of the results because of the distributed nature of the glass transition. Other techniques, such as WAXS or SAXS, are completely unable to detect the amorphous phase in any way [2].

Dielectric techniques have some advantages that make them a worthwhile option. Almost any change in the material modifies its dielectric properties, so it is possible to study a wide range of phenomena at least indirectly. In the case of the glass transition of polar polymers, the change in mobility of the main polymer chain will result in a change in the polarizability of the material. Dynamic electrical analysis (DEA) is a well-known method that is based on the interaction of an external alternating field with the electric dipoles present in the sample [9].

Among the dielectric techniques, thermally stimulated depolarization currents (TSDC) [10] stands out because of its high resolution and low equivalent frequency [11]. TSDC can be used to study the α relaxation and how it is affected by crystallization [12]. This relaxation is the dielectric manifestation of the glass transition [13] and, therefore, the measured current exclusively comes from the depolarization of the amorphous phase [14].

The most interesting feature of TSDC is the ability to resolve a complex relaxation into its elementary components. This is done using a procedure known as relaxation map analysis (RMA) [15]. If the polarizing field, in a TSDC experiment, is on during a large portion of the cooling ramp (conventional polarization) many relaxation processes can be detected in the same thermogram. Instead, if the polarizing field is on in a narrow thermal window, the activated process will behave approximately in an elementary way and will be well described by a single relaxation time τ (see section 2 for details on a TSDC measurement).

An analysis of the α relaxation by TSDC thus gives information about the relaxation time, both its mean value, its distribution and cooperativity. A complete and more detailed explanation of the whole process can be found in a previous work of our group [16].

The aim of this work is to study the glass transition in highly crystallized PET and, more specifically, how it is affected by the secondary crystallization on the amorphous interlamellar phase. TSDC was applied to cold-crystallized PET samples and the α relaxation was studied. Also, DSC scans were performed to monitor the secondary crystallization process. This kind of study is complementary to the ones focused on the crystalline phase. For this reason, it can give some clues about some controversial points on the morphology of highly crystallized PET, especially on the mechanism that gives rise to secondary crystallization.

2. Experimental

Experiments were carried out on commercial PET, supplied by Autobar, 300 μm thick sheets. As received, the material was almost amorphous with less than 3% crystallinity degree. From previous works [17] it is known that Tg for this polymer is approximately 353 K and that cold crystallization takes place above 373 K.

The samples were cut into squares of 2 cm sides. Some samples were reserved for as-received measurements and the other ones were annealed. Each sample was annealed for 4 h at one of the following temperatures: 413, 423, 433, 443 and 453 K. After annealing, the samples were quenched to room temperature. These samples were used to perform DSC and TSDC measurements.
Calorimetric measurements were made with a Mettler TC11 thermoanalyzer equipped with a Mettler-20 differential scanning calorimeter module. The calorimeter was previously calibrated with metallic standards (indium, lead, zinc). To obtain DSC curves, 20–25 mg portions of the samples were sealed in aluminum pans. Scans begin at 313 K and end at 573 K and are performed at a heating rate of 2.5 K min\(^{-1}\). In some experiments, additional thermal treatment was performed in the calorimeter previously to the scan.

The samples for TSDC measurements were prepared by coating 1 cm diameter Al electrodes on both sides of the sample by vacuum deposition. TSDC measurements were carried out in a non-commercial experimental setup, controlled by a Eurotherm-2416 temperature programmer. The temperature, during measurements, was measured to an accuracy of 0.1 K by a J-thermocouple located inside the electrodes (in direct contact with the sample). A Keithley-6512 electrometer was employed for the current intensity measurements.

Most TSDC experiments have been performed using the non-isothermal windowing polarization (NIW) method. According to this method, the sample is continuously cooled from the initial temperature \(T_i\) to the storage temperature \(T_s\) and the polarizing field is applied during the cooling ramp when the temperature of the sample reaches \(T_p\) and switched off at \(\Delta T = 2\) K below \(T_p\). In some experiments, referred to as conventional polarization in the text, \(\Delta T\) has been enlarged significantly, in order to record the relaxation as a whole in spite of not having a unique relaxation time.

The sample remains at \(T_s\) for a short storage time \(t_s\) and then it is heated at a constant rate while the TSDC discharge is recorded. The experiment ends at a final temperature \(T_f\). Usually, this final temperature is taken as the \(T_i\) of the following experiment. This implies that for a given sample the \(T_i\) of an experiment should be lower than the \(T_i\) of the previous one, in order to ensure that no relaxation activated in previous experiments is recorded. Since \(T_i\) values are chosen so that the whole \(\alpha\) relaxation is recorded, experiments proceed from higher to lower polarization temperatures.

In all the experiments, \(V_p = 800\) V, \(T_s = 303\) K, \(t_s = 5\) min and the cooling and heating rate is 2.5 K min\(^{-1}\). \(T_i\) and \(T_f\) have values between 363 and 398 K, well above \(T_E\) but, anyway, much lower than the annealing temperature, so several experiments can be performed on the same sample without modifying crystalline morphology.

### 3. Results and discussion

#### 3.1. Calorimetric characterization

First we will consider the DSC scan of the as-received material, presented in figure 1. The plot presents data from just above \(T_E\) until the complete fusion of the sample. The crystallization peak can be seen clearly at about 393 K. At 398 K most of the crystallization process was completed, although the process has a long tail that extends onwards. No other feature can be observed in the scan until the fusion peak. This is a broad peak with a maximum at about 525 K.

When the annealed material is measured by DSC, see figure 2, the crystallization peak disappears since this process has already taken place during the preparation of the sample. Instead, a smaller but broader endothermic peak appears at a slightly higher temperature than the annealing one. As we consider samples with a higher annealing temperature, the peak appears at progressively higher temperatures. Although the temperature at which the crystallization process ends in the as-received material is unclear, as seen in figure 1, the new peak is not due to the fraction of the tail that remains above the annealing temperature. Otherwise it should have an exothermic sign.

Figure 3 shows the DSC scans, which correspond to this minor endothermic peak, with different previous annealing times at 433 K. Interestingly, the area of the peak is greater for longer annealing times, although most of the process takes place in the first half hour. It can be safely concluded that it is due to the fusion of some structure grown during the annealing stage. More specifically, secondary crystallization [2] during the annealing stage is the most probable cause of the new endothermic peak [3, 7].

The glass transition of crystallized samples is scarcely observable by DSC because the interlamellar amorphous phase yields a much weaker signal than the fully amorphous material.
Figure 3. Power for mass unit of treated samples during DSC scans at 2.5 K min$^{-1}$ heating rate. Samples were annealed at 433 K for 15 min (curve a), 30 min (curve b), 1 h (curve c), 2 h (curve d) and 4 h (curve e). The scale has been adjusted to show just the minor endothermic peak.

Figure 4. Experimental TSDC spectra of the $\alpha$ relaxation obtained by NIW polarization at different $T_p$ from 349 K (curve a) to 371 K (curve l) in 2 K increment steps. The sample was annealed at 433 K for 4 h.

Figure 5. Experimental TSDC spectra of the $\alpha$ relaxation obtained by NIW polarization at different $T_p$ from 349 K (curve a) to 371 K (curve l) in 2 K increment steps. The sample was annealed at 433 K for 4 h.

It can be seen in these measurements that the glass transition of the remaining amorphous fraction of the annealed material shows up at higher temperatures and is far more symmetrical than in the case of the almost fully amorphous sample.

3.3. Relaxation map analysis

Further information relative to the glass transition can be obtained performing a RMA [15]. In fact, one of the main advantages of the TSDC technique is that it allows one to study on its own the parts of the mechanism (modes) that give rise to the relaxation as a whole [16]. To perform the RMA, NIW polarization is employed through a broad range of polarization temperatures in order to study modes with well-defined relaxation time in each TSDC experiment. An example of this kind of measurement is shown in figure 5, where 10 modes around the maximum of the relaxation are plotted for the sample annealed for 4 h at 433 K.

If the relaxation mechanism has first order kinetics, the calculated depolarization current of each mode can be obtained from the equation

$$J(T) = \frac{P_0}{\tau(T)} \exp \left[ -\frac{1}{\beta} \int_{T_0}^{T} \frac{dT}{\tau(T)} \right],$$

(1)

where $P_0$ is the initial polarization of the sample, $\tau(T)$ is the relaxation time of the process, $T_0$ is the initial temperature of the experiment and $\beta$ is the heating rate. To modelize the TSDC spectrum $J(T)$, the relaxation time of the $\alpha$ process was evaluated according to several phenomenological models, that are usually applied to calorimetric and dilatometric measurements. The various kinetic parameters involved were evaluated fitting $J(T)$ by computational methods to the experimental data. A complete and more detailed explanation of the whole process can be found in a previous work [16].

The TSDC measurements of the annealed samples were fitted to different models: Arrhenius, Vogel–Tammann–Fulcher (VTF) and Tool–Narayanaswamy–Moynihan. In figure 6 a comparison of the obtained results is presented.
The best results are obtained with the Arrhenius model, as the high symmetry of the peaks suggest. In this model the relaxation time $\tau$ is assumed to obey the equation

$$\tau(T) = \tau_0 \exp \left( \frac{E_a}{RT} \right),$$

where $E_a$ is the activation energy of the process and $\tau_0$ the pre-exponential factor. It must be noted that this model assumes isolated dipoles and therefore does not take cooperativity into account.

The VTF model, given by the equation

$$\tau(T) = \tau_0 \exp \left( \frac{E_w}{R(T - T_\infty)} \right),$$

is not able to significantly improve the results of the Arrhenius model. In fact both fittings are very close, with Arrhenius performing better at low temperatures. Both models are equivalent for $T_\infty = 0$. In our case, the obtained value for $T_\infty$ is about 110 K lower than $T_g$, which is a sign that cooperativity can be disregarded. Although there is an overall marginal improvement, it does not justify the inclusion of an additional parameter.

Also, the Tool–Narayanaswamy–Moynihan model [18] was employed to modelize the TSDC spectrum, as in [16], but the non-linearity parameter was found to be 1. As in previous cases, this value represents a non-cooperative relaxation. For this value of the parameter the model is equivalent to the Arrhenius one and identical results are obtained. For this reason it has not been plotted in figure 6.

Apart from the activation energy and the pre-exponential factor, the relative importance (weight) of each mode $N$ can be obtained from the total area of the peak, this is $P_0$, through [15]

$$N = P_0 \tau_p,$$

where $P_0$ is multiplied by $\tau_p$ to take into account the intrinsic dependence of static polarizability on temperature.

**Table 1.** Fits for samples annealed 4 h at 433 K.

| $T_p$ (K) | $\tau_p$ (s) | $E_a$ (eV) | $P_0$ (C) | $N/N_{\text{max}}$ |
|----------|--------------|-----------|-----------|-------------------|
| 369      | $2.80 \times 10^{-10}$ | 3.71  | $1.87 \times 10^{-10}$ | 0.637             |
| 367      | $3.91 \times 10^{-10}$ | 3.68  | $2.11 \times 10^{-10}$ | 0.715             |
| 365      | $4.01 \times 10^{-10}$ | 3.66  | $2.35 \times 10^{-10}$ | 0.792             |
| 363      | $1.94 \times 10^{-10}$ | 3.67  | $2.57 \times 10^{-10}$ | 0.860             |
| 361      | $1.14 \times 10^{-10}$ | 3.52  | $2.82 \times 10^{-10}$ | 0.939             |
| 359      | $3.35 \times 10^{-10}$ | 3.47  | $2.93 \times 10^{-10}$ | 0.969             |
| 357      | $2.34 \times 10^{-10}$ | 3.26  | $3.02 \times 10^{-10}$ | 0.996             |
| 355      | $2.56 \times 10^{-10}$ | 2.96  | $3.05 \times 10^{-10}$ | 1.00              |
| 353      | $1.35 \times 10^{-10}$ | 2.68  | $2.93 \times 10^{-10}$ | 0.954             |
| 351      | $1.17 \times 10^{-10}$ | 2.40  | $2.66 \times 10^{-10}$ | 0.862             |
| 349      | $2.65 \times 10^{-10}$ | 2.16  | $2.36 \times 10^{-10}$ | 0.761             |
| 347      | $1.30 \times 10^{-10}$ | 1.96  | $2.01 \times 10^{-10}$ | 0.642             |
| 345      | $8.66 \times 10^{-14}$ | 1.76  | $1.67 \times 10^{-14}$ | 0.532             |
| 343      | $1.36 \times 10^{-10}$ | 1.60  | $1.37 \times 10^{-10}$ | 0.433             |
| 341      | $7.64 \times 10^{-14}$ | 1.48  | $1.09 \times 10^{-14}$ | 0.342             |
| 339      | $1.07 \times 10^{-10}$ | 1.46  | $8.52 \times 10^{-10}$ | 0.267             |
| 337      | $9.10 \times 10^{-10}$ | 1.39  | $6.27 \times 10^{-10}$ | 0.195             |
| 335      | $1.43 \times 10^{-10}$ | 1.43  | $4.28 \times 10^{-10}$ | 0.132             |

Nevertheless, at the polarization temperature range employed this correction is very small.

While it is clear that the effect of primary crystallization is an increase in the value of $T_g$, the effects of secondary crystallization on $T_p$ remain largely unknown. To study this issue we have performed RMA on samples annealed at five temperatures at which it has been checked, in the previous section, whether secondary crystallization takes place.

In table 1 we present the results for each mode of the $\alpha$ relaxation for the sample annealed at 433 K. It is given as an example of the results obtained. The results for the other annealing temperatures are not presented in the table form since they are more easily grasped from the presented figures.

The results of $P$ in front of $E_a$ for each annealing temperature are plotted in figure 7. This figure reveals that the $\alpha$ relaxation is composed of the superposition of modes with a wide range of activation energies centred at 3 eV.

We can discuss the results only in terms of the activation energy because the compensation law [15] is fulfilled, as it can
be seen in figure 8. This law states a linear relationship between the activation energy and the logarithm of the pre-exponential factor, so it is exactly the same to discuss our results in terms of either quantity.

A significant plot, \( \frac{N}{N_{\text{max}}} \) in front of \( T_p \), can be seen in figure 9. This figure allows a comparison between data that correspond to samples previously annealed at different temperatures. High energy modes, which are excited at higher polarization temperatures, tend to lose importance as samples are annealed at higher temperatures while low energy modes, which correspond to lower polarization temperatures, gain relative weight.

It is interesting to plot the polarization temperature at which a mode is activated in front of the activation energy of the mode. This plot can be seen in figure 10. From this plot it can be inferred that the modes that reproduce this relaxation have activation energies between 1.25 and 3.75 eV approximately. It is clear that no modes exist with activation energies outside this range.

3.4. Comparison with the glass transition in fully amorphous PET

These results can be compared with those obtained from amorphous PET in a previous work [16] whose RMA is reproduced in figure 11. The most striking difference between the amorphous and crystallized samples lies in the overall shape of the discharge peak, which is much less symmetric in the case of the amorphous material. This lack of symmetry leads to unsatisfactory results if the Arrhenius equation is used to modelize the discharges, opposite to the results obtained with annealed samples. For the amorphous samples the VTF and the TNM models provide a significantly closer fit to experimental data [16]. As a consequence, it can be inferred that cooperativity is much lower in the crystallized samples than in the amorphous ones.

Another significant difference between the results of amorphous and annealed samples arose in the calculated activation energies. In the case of annealed samples this parameter is between 1.25 and 3.75 eV approximately, as stated...
above, and a clear upper limit can be inferred from figure 10. In the case of amorphous samples no upper limit seems to be present with significant contribution from modes with an activation energy of 8 eV and even higher [16]. Although the obtained values may not be directly comparable because different models have been used to fit each of the curves, the presence of this cutoff in annealed samples is significant. This behaviour may be a consequence of the limited distance range in which interactions between molecules can propagate during the glass transition, due to the fractioning of the interlamellar amorphous phase.

This interpretation is also coherent with the observed evolution of modes due to secondary crystallization. In this case modes with higher activation energies do not disappear, but low energy modes gain relative weight. Taking into account all these observations, it seems clear that during secondary crystallization some changes occur in the amorphous interlamellar phase that slightly lower the glass transition temperature, unlike primary crystallization that clearly raises the glass transition temperature. These changes will be discussed in section 3.6.

3.5. Modelization of DSC curves

The analysis of TSDC data allows us to predict the shape that would have a calorimetric curve obtained from the glass transition of the interlamellar amorphous phase. This can be done through the fictive temperature, which represents, for a non-equilibrium system, the temperature at which the same system at equilibrium would have the same structural conformation.

To calculate the evolution of the fictive temperature, we assume that the structural relaxation is a first-order distributed process. This means that the fictive temperature of each mode evolves according to the relaxation time determined in the RMA, as

$$\frac{dT_i}{dt} = \frac{T - T_{fi}}{\tau_i},$$

where $\tau_i$ is the relaxation time and $T_{fi}$ is the fictive temperature of mode $i$. Since the thermal history is known and in part goes over $T_g$, we can easily solve equation (5) for each mode, taking into account that $T_{fi} = T$ when $T > T_g$. In our calculation, $\tau_i$ is obtained by fitting the TSDC curves to the Arrhenius model.

The fictive temperature of the system as a whole, $T_f$, is calculated as the weighted mean of the fictive temperature of all the modes, using $N_i$ as the weight of each mode [16].

Once $T_f(t)$ is calculated for a given thermal history that corresponds to the DSC scan that is being simulated, the normalized calorific capacity $C_p^n$ can be obtained with [19]

$$C_p^n = \frac{dT_f}{dT}.$$  

Calculated DSC scans at a heating rate of 2.5 K min$^{-1}$ are presented in figure 12 for differently annealed samples. It can be seen that $T_g$ slightly shifts towards lower temperatures with respect to the crystallized samples annealed at lower temperatures, but anyway remaining higher than in the amorphous samples.

![Figure 12](image1.png)  

**Figure 12.** Calculated $C_p^n$ of the glass transition assuming a 2.5 K min$^{-1}$ heating rate and material annealed for 4 h from 413 K (curve 1) to 453 K (curve 3) in 20 K increment steps.

![Figure 13](image2.png)  

**Figure 13.** Experimental TSDC spectra of the $\alpha$ relaxation of samples annealed for 4 h at 413 K (a), 433 K (b) and 453 K (c), obtained by conventional polarization.

This can also be drawn in a more direct way looking for the temperature at which the $\alpha$ relaxation as a whole yields a larger current [13], as seen in figure 13. It can be seen that in the samples annealed at higher temperatures the maximum current, and therefore the glass transition, takes place at slightly lower temperatures. The area of the peaks is also lower for the samples annealed at higher temperatures. This can be due to a decrease in the amorphous fraction, a decrease in its polarizability or due to a combination of both factors.

3.6. Consequences of second crystallization in the glass transition

Up to this point we have presented the effects of secondary crystallization on the glass transition of the amorphous interlamellar phase. However, we can take this discussion one step further and analyse the capability of the existing models on secondary crystallization to explain these effects.

It can be inferred, as it is generally assumed, that secondary crystallization takes place in the amorphous
interlamellar phase (between the stacks of lamellae). Our results track the glass transition of the amorphous fraction present in the material, which is located mainly between the existing stacks (referred to as interlamellar amorphous phase in this work). The fact that secondary crystallization affects the glass transition of this amorphous fraction so strongly indicates that it takes place basically in these regions. The formation of new lamellae, from the very scarce amorphous fraction present between the lamellae inside the existing stacks [1], does not seem to be, thus, the main contribution to secondary crystallization.

Other models have been suggested to explain secondary crystallization in these polymers; thickening or rearrangement of the existing lamellae or creation of new stacks as ramifications of the existing stacks [5] and creation of randomly oriented new stacks in the interlamellar amorphous phase [1, 3] or connection between stacks with micella structures or folded chains [6]. According to the presented evolution of the glass transition of annealed samples in this work, all of them are compatible with the observed decrease in the α peak with annealing. However, the creation of randomly oriented new stacks in the interlamellar amorphous phase can probably better explain the observed decrease in the relative weight of high activation energy modes when annealing takes place at higher temperatures. In any case we think that only if these new crystalline structures are small enough to be considered randomly and homogeneously distributed, can they effectively affect the relaxation time distribution as a whole.

4. Conclusions

The minor low-temperature endothermic peak that appears in the annealed samples before the main fusion peak should be attributed to the fusion of the fraction of the material that has been crystallized during annealing by secondary crystallization. This crystallized fraction is prone to melting at a slightly higher temperature than the one at which it has been crystallized.

On the other hand, TSDC experiments do not reach the annealing temperature in any case, so the effect of secondary crystallization on the glass transition can be analysed by means of TSDC data.

The results from curve fitting to the Arrhenius model show modes with a limited interval of activation energies in all the cases. The values obtained range from 1.25 eV for low temperature modes to 3.75 eV for the modes that appear at higher temperatures. For any given activation energy, the pre-exponential factor is found easily since the compensation law is fulfilled.

The Samples crystallized at higher temperatures show as well a decrease in the fraction of high activation energies modes (those that respond at higher temperatures) in comparison with those modes of lower activation energies. The overall weight of the modes is thus shifted towards lower activation energies. Secondary crystallization would explain this behaviour since it would increase movement restrictions in the amorphous phase.

TSDC experiments show that secondary crystallization produces a slight displacement of $T_g$ towards lower temperatures. This can be seen both directly, because the dynamic value of $T_g$ can be associated with the maxima of TSDC plots, and indirectly, reproducing calorimetric data from the obtained dielectric parameters.

Although secondary crystallization has been investigated by many means, its influence on the dielectric properties of the amorphous interlamellar phase allows us to favour some of the descriptions that have been given to the phenomena, in particular those related to the growth of structures in the interlamellar amorphous phase.

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