Glass transition temperature versus structure of polyamide 6

Citation for published version (APA):

DOI:
10.1016/j.tca.2017.09.021

Document status and date:
Published: 10/11/2017

Document Version:
Publisher’s PDF, also known as Version of Record (includes final page, issue and volume numbers)

Please check the document version of this publication:
• A submitted manuscript is the version of the article upon submission and before peer-review. There can be important differences between the submitted version and the official published version of record. People interested in the research are advised to contact the author for the final version of the publication, or visit the DOI to the publisher’s website.
• The final author version and the galley proof are versions of the publication after peer review.
• The final published version features the final layout of the paper including the volume, issue and page numbers.

Link to publication

General rights
Copyright and moral rights for the publications made accessible in the public portal are retained by the authors and/or other copyright owners and it is a condition of accessing publications that users recognise and abide by the legal requirements associated with these rights.

• Users may download and print one copy of any publication from the public portal for the purpose of private study or research.
• You may not further distribute the material or use it for any profit-making activity or commercial gain
• You may freely distribute the URL identifying the publication in the public portal.

If the publication is distributed under the terms of Article 25fa of the Dutch Copyright Act, indicated by the ”Taverne” license above, please follow below link for the End User Agreement:
www.tue.nl/taverne

Take down policy
If you believe that this document breaches copyright please contact us at:
openaccess@tue.nl
providing details and we will investigate your claim.
Glass transition temperature versus structure of polyamide 6: A flash-DSC study

E. Parodi⁎, L.E. Govaert, G.W.M. Peters

⁎ Corresponding author.
E-mail address: g.w.m.peters@tue.nl (G.W.M. Peters).

ABSTRACT

The glass transition temperature (Tg) is a crucial parameter for understanding the mechanical behavior of polyamide 6. It depends mainly on two aspects: hydration level and processing, i.e. the thermal history and the flow conditions. In this work, the effect of the thermal history on Tg was investigated by means of fast scanning calorimetry (flash-DSC). Two different solidification procedures were studied; isothermal crystallization and continuous cooling were performed at different temperatures and rates respectively. The procedures have led to two contradictory trends of glass transition evolutions when related to their crystallinity fraction. The concept of rigid amorphous phase is used. This is considered as a part of the amorphous phase with a lower mobility, present at the inter-phase between crystals and bulk amorphous (mobile amorphous fraction). The analysis leads to the conclusion that the thermal history affects the ratio between rigid and mobile amorphous phases and it is this ratio that determines the glass transition temperature of dry polyamide 6.

1. Introduction

Polyamide 6 (PA6) is an engineering polymer, commonly known as “Nylon 6”, which is used in the field of load-bearing applications where mechanical performance and lifetime are keywords. Applications such as under-the-hood components and sport items are often exposed to demanding conditions like high load, challenging temperature regimes and elevated relative humidities. However, the performance of PA6 (and also most other polymers) depends strongly on micro-structural details (such as crystallinity, lamellar thickness and phase content) that, to a great extent, are determined during processing. Therefore, it is obvious that an investigation of the influence of processing on properties is required to predict and improve the performance.

PA6 belongs to the family of aliphatic polyamides. Its monomer has two polar groups: the amide and carbonyl groups. These polarities can form hydrogen bonds between chains, leading to high strength [1]. However, this polar character causes a crucial characteristic of polyamide 6; hygroscopicity [2]. Indeed, if exposed to a humid environment, PA6 absorbs water till reaching a saturation level which is dependent on temperature and relative humidity [3]. If this occurs, part of the hydrogen bonds are broken and new H bonds are formed with the water molecules [4]. This phenomenon is called plasticization and results in a depression of the glass transition temperature [5]. The plasticization causes a considerable deterioration of the mechanical properties, as shown by a number of authors in literature [6–9]. Therefore, it is clear that the glass transition temperature is an important parameter for PA6 properties.

However, the glass transition temperature of PA6 not only depends on the hydration level; it also changes with crystallinity [10,11], amorphous orientation [11,12] and, as more recently reported, with the rigid amorphous phase content (RAF) [13,14]. An illustrative example of the influence of processing on the glass transition is given in Fig. 1, where the storage modulus (E′) is displayed as a function of temperature for three samples produced with three different thermal histories. The drop in the modulus due to the glass transition is different for the three samples, and also the value of Tg changes. In order to understand how processing affects the glass transition, we will use a model that describes a semi-crystalline polymer as a system composed by three phases: the crystalline phase, the rigid amorphous (RAF) and the mobile amorphous phase (MAF). The main difference is in the molecular mobility, the highest mobility belongs to the mobile amorphous phase, the lowest to the crystalline domains and the rigid amorphous phase has an intermediate mobility [14–16]. The rigid amorphous phase, as assumed in this model, is a sort of inter-phase between the crystalline and the mobile amorphous phase. This concept was employed also to other systems [17–19]. Many experimental techniques are used, but the most common one is the traditional differential scanning calorimetry (DSC), focusing on the change of specific heat capacity due to the glass
transition. From this it is possible to estimate the amount of amorphous phase that did not transform to the rubbery state during the glass transition. This excess of amorphous phase is defined as the rigid amorphous phase. Fast scanning calorimetry (flash-DSC) allows us to investigate a wide range of cooling rates and cooling procedures that are not achievable by traditional DSC. This gives the possibility to a) get completely amorphous samples, b) perform real isothermal crystallization and c) suppress cold crystallization upon heating.

The difference in Fig. 1 are typically caused by processing-induced differences in structure. An important characteristic of PA6 is its polymorphism; there are two important crystal forms with respect to melting: the most stable α-phase (monoclinic cell) for low under-cooling or high isothermal crystallization temperature, and the less stable γ-mesophase (pseudo-hexagonal cell) for high under-cooling or medium to low isothermal crystallization temperatures. In case of very fast cooling also a completely amorphous sample can be obtained [20]. Mileva et al. [21], have shown that melt-crystallization at low under-cooling or high isothermal crystallization temperature, and the δ mesophase, while high under-cooling leads to γ-mesophase with a nodular morphology for which no lamella can be observed. The aim of this work is to investigate the structure formation in PA6 for a wide range of cooling procedures and conditions mainly by means of fast scanning calorimetry, in order to determine the relation of the glass transition temperature with the structure, i.e. the amount of crystalline phase, MAF and RAF. This will form the basis for future works on transition temperature with the structure, i.e. the amount of crystalline phase that did not transform to the rubbery state during the glass transition. This excess of amorphous phase is defined as the rigid amorphous phase. Fast scanning calorimetry (flash-DSC) allows us to investigate a wide range of cooling rates and cooling procedures that are not achievable by traditional DSC. This gives the possibility to a) get completely amorphous samples, b) perform real isothermal crystallization and c) suppress cold crystallization upon heating.

The difference in Fig. 1 are typically caused by processing-induced differences in structure. An important characteristic of PA6 is its polymorphism; there are two important crystal forms with respect to melting: the most stable α-phase (monoclinic cell) for low under-cooling or high isothermal crystallization temperature, and the less stable γ-mesophase (pseudo-hexagonal cell) for high under-cooling or medium to low isothermal crystallization temperatures. In case of very fast cooling also a completely amorphous sample can be obtained [20]. Mileva et al. [21], have shown that melt-crystallization at low under-cooling is connected with the formation of lamella, also for the γ-mesophase, while high under-cooling leads to γ-mesophase with a nodular morphology for which no lamella can be observed. The aim of this work is to investigate the structure formation in PA6 for a wide range of cooling procedures and conditions mainly by means of fast scanning calorimetry, in order to determine the relation of the glass transition temperature with the structure, i.e. the amount of crystalline phase, MAF and RAF. This will form the basis for future works on transition temperature with the structure, i.e. the amount of crystalline phase that did not transform to the rubbery state during the glass transition. This excess of amorphous phase is defined as the rigid amorphous phase. Fast scanning calorimetry (flash-DSC) allows us to investigate a wide range of cooling rates and cooling procedures that are not achievable by traditional DSC. This gives the possibility to a) get completely amorphous samples, b) perform real isothermal crystallization and c) suppress cold crystallization upon heating.

The difference in Fig. 1 are typically caused by processing-induced differences in structure. An important characteristic of PA6 is its polymorphism; there are two important crystal forms with respect to melting: the most stable α-phase (monoclinic cell) for low under-cooling or high isothermal crystallization temperature, and the less stable γ-mesophase (pseudo-hexagonal cell) for high under-cooling or medium to low isothermal crystallization temperatures. In case of very fast cooling also a completely amorphous sample can be obtained [20]. Mileva et al. [21], have shown that melt-crystallization at low under-cooling is connected with the formation of lamella, also for the γ-mesophase, while high under-cooling leads to γ-mesophase with a nodular morphology for which no lamella can be observed. The aim of this work is to investigate the structure formation in PA6 for a wide range of cooling procedures and conditions mainly by means of fast scanning calorimetry, in order to determine the relation of the glass transition temperature with the structure, i.e. the amount of crystalline phase, MAF and RAF. This will form the basis for future works on transition temperature with the structure, i.e. the amount of crystalline phase that did not transform to the rubbery state during the glass transition. This excess of amorphous phase is defined as the rigid amorphous phase. Fast scanning calorimetry (flash-DSC) allows us to investigate a wide range of cooling rates and cooling procedures that are not achievable by traditional DSC. This gives the possibility to a) get completely amorphous samples, b) perform real isothermal crystallization and c) suppress cold crystallization upon heating.

The difference in Fig. 1 are typically caused by processing-induced differences in structure. An important characteristic of PA6 is its polymorphism; there are two important crystal forms with respect to melting: the most stable α-phase (monoclinic cell) for low under-cooling or high isothermal crystallization temperature, and the less stable γ-mesophase (pseudo-hexagonal cell) for high under-cooling or medium to low isothermal crystallization temperatures. In case of very fast cooling also a completely amorphous sample can be obtained [20]. Mileva et al. [21], have shown that melt-crystallization at low under-cooling is connected with the formation of lamella, also for the γ-mesophase, while high under-cooling leads to γ-mesophase with a nodular morphology for which no lamella can be observed. The aim of this work is to investigate the structure formation in PA6 for a wide range of cooling procedures and conditions mainly by means of fast scanning calorimetry, in order to determine the relation of the glass transition temperature with the structure, i.e. the amount of crystalline phase, MAF and RAF. This will form the basis for future works on transition temperature with the structure, i.e. the amount of crystalline phase that did not transform to the rubbery state during the glass transition. This excess of amorphous phase is defined as the rigid amorphous phase. Fast scanning calorimetry (flash-DSC) allows us to investigate a wide range of cooling rates and cooling procedures that are not achievable by traditional DSC. This gives the possibility to a) get completely amorphous samples, b) perform real isothermal crystallization and c) suppress cold crystallization upon heating.
crystallization process. Completion of the crystallization process means that the full volume of the sample has been converted in a semi-crystalline state, i.e. a mixture of ordered (lamella) and amorphous material. The amount of crystal material is called the degree of crystallinity ($X_c$). The fraction of semi-crystalline material is called the space filling ($\xi$), completion means $\xi = 1$. The crystallinity for a specific space filling $\xi$ is given by:

$$ X_c = \xi \cdot X_{C=\infty} $$  \hspace{1cm} (2)

where $X_{C=\infty}$ is the maximum crystallinity at the completion of space filling. For high enough temperatures, this maximum crystallinity can increase by perfection of the crystals (secondary crystallization), i.e. $X_{C=\infty}(T, t)$. Space filling and (final) crystallinity depend both on cooling rate (continuous cooling) and on the crystallization time and temperature (isothermal crystallization). For example, fast cooling and short crystallization times will cause incomplete space filling, a low crystallinity temperature with sufficient time will lead to lower crystallinity levels $X_{C=} \text{ while space filling } \xi = 1$. After crystallization, the sample is cooled down to $-50 \degree C$ at $1000 \degree C/s$. Finally, heating up to $300 \degree C$ at $1000 \degree C/s$ is performed. The final heating run is used to retrieve the characteristics, such as glass transition temperature, crystallinity and heat capacity.

In order to study the case of isothermal crystallization with space filling lower than 1, isothermal crystallization were performed at 90 and 180 °C varying the duration of the isothermal segment.

2.2.4. Analysis

The glass transition temperature was determined by estimating the midpoint in proximity of the change in specific heat ($\Delta C_p$). Lines tangential to the $C_{p, \text{solid}} / C_{p, \text{liquid}}$ and the transient in between were drawn, see Fig. 3a. The intersections between $C_{p, \text{solid}} / C_{p, \text{liquid}}$ and transient are defined as $T_g$ onset and $T_g$ end-set respectively. The midpoint of the segment between $T_g$ onset and $T_g$ end-set was defined as the glass transition temperature, as shown in Fig. 3a.

The crystallinity degree was calculated by:

$$ X_c = \frac{\Delta H_m}{\Delta H_f^\gamma} $$  \hspace{1cm} (3)

where $\Delta H_f^\gamma$ is the thermodynamic fusion enthalpy (241 J/g for the $\alpha$-phase [22] and 58 J/g for the $\gamma$-mesophase [23]) and $\Delta H_m$ is the integral of the observed melting peak, as shown in Fig. 3b.

Unfortunately, estimating the crystallinity is not always possible. In fact, despite high heating rate (1000 °C/s), starting from $\gamma$-mesophase in the solid state, partial melting and re-organization in the more stable $\alpha$-phase will take place. Thus, the measured melting area would not be related to only the pre-existing crystallinity but also to the heat necessary to melt the transformed fraction of crystals. This fraction cannot be estimated from the DSC measurements. Therefore, also in situ wide angle X-ray diffraction (WAXD) experiments were carried out on samples on the flash-DSC sensor for several solidification procedures. The crystallinity ($X_c$) obtained by WAXD was subsequently used for the structural analysis (details about this procedure are explained in Section 2.3 and Appendix C. The estimation of the mobile amorphous fraction (MAF) is based on the ratio:

$$ \text{MAF} = \frac{\Delta C_p}{\Delta C_{p, \text{am}}} $$  \hspace{1cm} (4)

where $\Delta C_p$ is the measured variation of heat capacity during glass transition and $\Delta C_{p, \text{am}}$ is related to a completely amorphous sample as already proposed by [24–26]. Therefore, imposing the following statement:

$$ 1 = \text{RAF} + \text{MAF} + X_c $$  \hspace{1cm} (5)

the rigid amorphous fraction can be calculated by:

$$ \text{RAF} = 1 - (\text{MAF} + X_c) $$  \hspace{1cm} (6)

Notice that we do not study the evolution of the structural parameters but we focus on the resulting values for a wide variety of thermal histories. Such an in-depth study is beyond the scope of this work. Examples of such studies can be found in [27,28].

2.3. X-ray diffraction

Wide angle X-ray diffraction (WAXD) experiments were carried out in situ on the samples on the sensors during fast-scanning calorimetry experiments. The choice of an in situ technique was crucial because of the hydrophilic nature of PA6, as explained in Section 1. With ex situ experiments, the sample would uptake water, decrease its $T_g$ (even below room temperature) and therefore, crystallization at room temperature may occur. It is important to point out that the saturation time scales inversely with the sample size; thus, a sample size in the order of hundreds micron lead to saturation in a matter of minutes. These experiments were performed at the European Synchrotron Radiation Facility (ESRF) of Grenoble in France, at the Dutch-Belgian beamline 26 (DUBBLE). An innovative setup able to allow fast-scanning calorimetry with in situ X-ray was used, this setup is extensively described in [29]. In this work, the samples were not irradiated with X-ray during the whole thermal protocol. Only at the end of each solidification procedure (at room temperature) patterns were taken with an exposition time of 15 s. After normalization, the crystallinity was estimated by subtracting the amorphous halo (experimentally obtained). Finally, the degree of crystallinity is calculated by:

$$ X_c = \frac{T - A}{T} $$  \hspace{1cm} (7)

where $T$ is the total scattered intensity and $A$ is the scattering from the amorphous halo.

Also small angle X-ray scattering was performed on flash-DSC sensor (ex situ). Lorentz [30] and thermal density fluctuation [31] correction were applied to the pattern. Thus, the peak position of the SAXS pattern ($d'$) is used to define the long period ($\xi_b$):

$$ \xi_b = \frac{2 \pi}{d'} $$  \hspace{1cm} (8)

Fig. 3. Example of a) glass transition temperature definition and $\Delta C_p$ determination and b) crystallinity estimation.
which is used to estimate the average lamellar thickness:

\[ l_b = \frac{l_c}{X_c} \]  

where \( l_b \) is the long period and \( X_c \) is the crystallinity. Ex situ experiments were performed only in the case of isothermal crystallization, where full space filling was reached and therefore the influence of hydration on structure development is minor.

3. Results and discussion

Two illustrative results of this study are given in Fig. 4. The solidification procedures are compared; in Fig. 4a the two step continuous cooling and in Fig. 4b isothermal crystallization. Both show a clear influence of solidification parameters on the glass transition temperature. In Fig. 4a two heating curves, related to samples cooled with different cooling rates, show two main differences: a) melting occurs only for the slow cooled samples and b) the glass transition temperatures are different. Fig. 4b shows the results for samples that are crystallized isothermally. Again a clear difference in melting behavior is observed. This is related to crystallization of different crystalline phases as demonstrated by, for example, van Drongelen et al. [32]. Again, differences in glass transition temperatures are found.

The crystallinity values are derived from the patterns shown in Fig. 5 applying the X-ray analysis explained in Appendix C and Section 2.3. The WAXD analysis also gives information about the crystallographic phase obtained by several solidification procedures. As far as the two step continuous cooling is concerned, a completely amorphous sample was obtained by very fast cooling at 200 °C/s; at 75 °C/s a weak \( \gamma \)-form characteristic reflection was found; with a cooling rate of 5 and 2.5 °C/s a predominance of the \( \gamma \)-form reflection with \( \alpha \)-phase shoulders was observed; for very slow cooling (0.1 °C/s), only \( \alpha \)-phase reflections were observed, see Fig. 5a. In the case of isothermal crystallization, at low temperature (90 °C) only the \( \gamma \)-form reflection was found, for temperatures between 120 and 170 °C the \( \gamma \)-characteristic reflection is predominant and rather weak \( \alpha \)-phase shoulders were observed; at 180 °C only the \( \alpha \)-phase characteristic reflections were found, see Fig. 5b.

First the influence of cooling rate and isothermal temperature on

\[ l_b = \frac{l_c}{X_c} \]  

(a) crystallinity (Fig. 6) and b) glass transition temperature (Fig. 7) will be presented. In Fig. 6a, the overall crystallinity obtained by two step continuous cooling is reported as a function of the initially applied cooling rate. As expected, cooling rates higher than \( \approx 100 \) °C/s lead to a completely amorphous sample while for cooling rates lower than 100 °C/s, a rapid increase of crystallinity is observed up to a maximum value of about 37% (a clear plateau in crystallinity was not reached because of the impossibility to perform experiments with cooling rate slower than \( \approx 0.1 \) °C/s). Upon isothermal crystallization for temperatures between 90 °C and 180 °C, a rather slight increase in crystallinity is found from about 30% at the lowest \( T_{iso} \) of 90 °C up to 36% at the highest \( T_{iso} \) of 180 °C, see Fig. 6b.

Plotting the glass transition temperature as a function of applied cooling rate a minimum (\( \approx 66 \) °C) is found for the higher cooling rates where the samples are completely amorphous, and a maximum (\( \approx 77 \) °C) for the lower cooling rates where crystallinity is the highest. Similar to crystallinity, \( T_g \) also increases with the decreasing cooling rate. In the case of isothermal crystallization (Fig. 7b), the glass transition shows a monotonic decrease.

Next, the correlation between structural parameters and \( T_g \) is investigated. In Fig. 8 the glass transition is plotted as a function of crystallinity. In the case of continuous cooling, the highest \( T_g \) corresponds to the highest crystallinity and the increase of glass transition is close to proportional with crystallinity. In contrast, the isothermal crystallization displays a totally different scenario; the glass transition temperatures measured in the case of isothermal crystallization is opposite to what is observed from continuous cooling. This is the first clear sign that crystallinity is not a determining parameter for the glass transition temperature, in contrast to what previously proposed by [10,11]. In the following we will present a concept that explains these results and, moreover, a rather simple model that can capture them and predict the \( T_g \) as a function of structural parameters that, again, are determined by the thermal history.

Next, a phase composition analysis was performed in order to investigate the influence of the solidification procedure on the RAF, MAF and crystallinity content. In Fig. 9a the fraction of rigid amorphous phase, mobile amorphous phase and crystallinity are presented as a function of applied cooling rate. When completely amorphous samples
are obtained, the rigid amorphous fraction (RAF) and crystallinity \( (X_c) \) are both zero while the mobile amorphous fraction (MAF) is stable at 1. For cooling rates between about 10 and 90 °C/s, both crystallinity and RAF increase rapidly, while MAF decreases. For even lower cooling rates, the rigid amorphous fraction appears to be rather stationary while the mobile amorphous fraction keeps on decreasing slightly. Fig. 9b shows the case of isothermal crystallization. In this case, only temperatures leading to complete space filling were selected. In fact, the maximum MAF estimated is about 0.5 for crystallization at 180 °C where the crystallinity is the highest and RAF the lowest. Moving towards lower isothermal temperatures, crystallinity slowly decrease and, at the same time, the mobile amorphous fraction decreases and the rigid amorphous increases till a maximum at 90 °C.

By comparing Figs. 7 and 9, it is observed that the glass transition follows a similar trend as the rigid amorphous fraction; opposite to the one observed for the mobile amorphous fraction. This observation is made for both, continuous cooling and isothermal crystallization. Fig. 10a shows the glass transition temperature as a function of mobile amorphous fraction for samples solidified by continuous cooling and by isothermal crystallization while in Fig. 10b the glass transition temperature is plotted as a function of the rigid amorphous fraction. These two figures demonstrate that, although not perfectly, both solidification procedures give a similar trend for \( T_g \) if plotted as a function of RAF or MAF. This is, an indication that structural investigation are crucial to understand the glass transition in PA6.

In order to understand the role of crystallinity for a given crystallization temperature \( (T_{iso}) \), isothermal crystallization at 90 and 180 °C were performed varying the isothermal segment duration \( (t_{iso}) \). In Fig. 11, the glass transition of samples crystallized at different \( T_{iso} \)
and $T_{iso}$ is plotted as a function of crystallinity. Remarkably a lower $T_{iso}$ leads to a higher $T_g$ for the same fraction of crystallinity. Therefore, a phase composition analysis was performed and shown in Fig. 12. The fractions of RAF, MAF and crystallinity are plotted as functions of crystallization time, for the crystallization temperature at 90 and 180 °C.

From Fig. 12a and b, it becomes clear that these differences can be rationalized in terms of the RAF content. At lower crystallization temperature the resulting RAF content is higher.

In Fig. 13a and b, comparisons between $T_{iso}$ 90 °C and 180 °C are given. In this case, MAF and RAF are plotted as functions of crystallinity level, for isothermal crystallization at 90 °C (indicated with lines) and one for 180 °C.

### 3.1. Relations between phase contents

Some rather straightforward arguments are presented to capture the coupling between the different phases in a semi-quantitative way. This will help to understand and interpret the experimental results presented before. Starting point is the idea that RAF is a layer of changing mobility adjacent to the crystalline lamella, i.e. the amount of RAF is proportional to the face areas of the lamella, see Fig. 14.

With the space filling given by $0 < \xi < 1$ and crystallinity level in the space filled by $X_{\infty}$ it follows that the crystallinity $X_c$ and the fraction of RAF in a volume $V_0$ are given by:

$$X_c = \xi X_{\infty} = \frac{\xi A_c l_c}{V_0} \quad (10)$$

$$RAF = \frac{2\xi A_c l_R}{V_0} \quad (11)$$

in which $A_c$ is the total lamellar face area in a volume $V_0$, $l_c$ the lamellar thickness and $l_R$ the thickness of the RAF layer. For now, the thickness of the RAF layer is considered to be (approximately) constant. It easily follows that:

$$MAF = 1 - X_c \left(1 + \frac{2l_R}{l_c}\right) = 1 - \xi X_{\infty} \left(1 + \frac{2l_R}{l_c}\right) \quad (13)$$

First, we will discuss some direct consequences and trends resulting from this model. For a constant crystallinity $X_c$, the fraction of RAF goes up and for MAF goes down with decreasing lamellar thickness $l_c$. Moreover, this increase (decrease) is stronger for higher $X_c$-values. For isothermal crystallization the lamellar thickness $l_c$ is directly related with the crystallization temperature, i.e. a higher crystallization temperature leads to higher MAF values at equal $X_c$-values. In the same way, using the expression for the RAF content, it is found that, for isothermal crystallization, the RAF content is higher for lower crystallization temperatures at equal $X_c$-values. For isothermal crystallization with completed space filling, see Fig. 9b, the final crystallinity $X_{\infty}$ varies with crystallization temperature; a higher $T_{iso}$ ($T_c$) means more mobility and thus more perfect crystals and a higher crystallinity. From Eqs. (12 and 13) it follows, when considering crystallinity only, that MAF and RAF should decrease and increase, respectively. However, the
opposite is observed. This is due the dominant role of the varying lamellar thickness.

It is clear that knowledge of the lamellar thickness is crucial and, therefore, this was separately measured for the case of isothermal crystallization only by means of ex situ SAXS. Results are shown in Fig. 15a. For the non-isothermal experiments the crystallization-peak was defined as the (average) crystallization temperature, see Fig. 15b. Using interpolation of the isothermal results for $l_c$ versus $T_c$, the $l_c$-values for the non-isothermal experiments were estimated; see again Fig. 15a. As mentioned in Section 1, crystallization of γ-mesophase at high undercooling leads to a non-lamellar morphology; thus, $l_c$ values obtained at temperatures below 130 °C should be interpreted as crystal thickness rather than lamellar thickness [21].

With a full model for the crystallization kinetics, including secondary crystallization, and the relation between crystallization temperature(s) and lamellar thickness it would be possible to predict the MAF and RAF content for a given thermal history. However, the formulation and experimental validation of such a model is outside the scope of this paper. Instead we will use the experimentally measured space filling and the estimates for the final crystallinity levels to give predictions for the MAF and RAF contents for the whole range of experimental conditions.

The results from isothermal crystallization for two crystallization temperatures (90 and 180 °C, see Figs. 12 and 13) and different crystallization times are discussed first. Values given below are estimates from these figures. Three regimes can be observed: regime I) for too short times no observable crystallinity is found ($t_{iso} < 8$ s for $T_{iso} \approx 90$ °C, $t_{iso} < 20$ s for $T_{iso} \approx 180$ °C), regime II) crystallization with growing space filling and RAF-fraction ($1$ s < $t_{iso} < 8$ s for $T_{iso} \approx 90$ °C, $20$ s < $t_{iso} < 120$ s for $T_{iso} \approx 180$ °C). The crystallinity $X_\infty$ at space filling $\xi = 1$ estimated to be $\approx 0.15$ and $\approx 0.3$ for $T_{iso} = 90$ and 180 °C, respectively. Finally, regime III) crystallinity increases further while the RAF becomes approximately constant, i.e. $X_\infty$ increases to its maximum that is in the order of $\pm 0.3$. The average lamellar thickness for these two crystallization temperatures is $\approx 1.8$ and 3.4 nm, respectively (see Fig. 15a). Using the numbers at the end of regime II) in Eq. (12) it follows that the thickness of the RAF layer is about $1$–$1.15$ nm where the higher value is found for the lower temperature. This small difference in RAF layer thickness could be related to the freezing of lower mobility at a lower crystallization temperature. More important is the observation of a much higher RAF content for $T_{iso} = 90$ °C compared to the results for $T_{iso} = 180$ °C, while the crystallinity values $X_c$ show the opposite. This is rationalized by Eq. (12): the large difference in the lamellar thickness over-compensates the difference in crystallinity. Moreover, in regime III crystallinity can still grow via crystal perfectioning, i.e. lamellar thickening, while RAF does not hardly change since $X_\infty$ and $l_c$ are proportional, see Eq. (10). This is
most clear for \( T_{\text{iso}} = 180 \degree C \) while for \( T_{\text{iso}} = 90 \degree C \), where less perfect crystals are grown, also some new lamella could be created and thus some new surface for RAF. However, this effect is small.

Using the estimated value \( l_R = 1.1 \, \text{nm} \), interpolated values for the measured crystallinity \( \chi_{\text{ic}} \) (see Fig. 6b) for isothermal crystallization for 180 s for which the space filling \( \xi = 1 \) and the lamellar thickness given in Fig. 15a, the MAF and RAF fractions are calculated over the whole range of temperatures by applying Eqs. (12) and (13). The results are presented in Fig. 16 and they show a clear match between the experimental and the model results (the line for \( X_c \) is the interpolation line). Notice that in Figs. 9b and 16 the trend for the crystallinity is smooth while the MAF and RAF show a slight change in the slope at \( T_{\text{iso}} = 145 \degree C. \) This could be related to the presence of a fraction of \( \alpha \)-phase that increases with crystallization temperature (see also Fig. 5) and, therefore, indicate that polymorphism might play a role. However, these results are not strong and convincing enough to include such a more detailed concept in our model. For varying isothermal crystallization times for the case of isothermal crystallization, space filling \( \xi \) varies from 0 to 1. The range where \( \xi = 0 \) or \( \xi = 1 \) correspond to \( X_c = 0 \) and \( X_c = X_\infty \), respectively. The transition between these two regions is captured by a descriptive auxiliary function:

\[
\hat{\xi} = (c_1 - c_2)(1 + (\xi - c_3)^2)^{(h_1 - 1) + c_2}/c_2
\]  

(14)

in which the parameters have no physical meaning, the values are chosen such that the desired smooth transition is obtained and \( x \) is the time.

The lamellar thickness was assumed to be constant, at \( l_c = 1.7 \, \text{nm} \) for 90 \( \degree C \) and \( l_c = 3.4 \, \text{nm} \) for 180 \( \degree C. \) Fig. 17a and b give the results for \( l_R = 1.1 \, \text{nm} \). Clearly the trends are captured quite well but the final levels of the MAF and RAF fractions are off. By adjusting the RAF-layer thickness \( l_R = 0.8 \, \text{nm} \) the results look much better, see Fig. 18a and b. However, for the longer crystallization times \( (t_{\text{iso}} > 180 \, \text{s}) \) the same \( l_R \) as for the isothermal experiments with varying \( T_{\text{iso}} \) and \( t_{\text{iso}} = 180 \, \text{s} \) should be used.

Next, continuous cooling results are analyzed. These non-isothermal crystallization cases are rather complex. Crystalline structures are formed in a range of temperatures leading to a more broad distribution of lamellar thickness, new nuclei may occur during the cooling history and the spherulite growth rate varies. Moreover, similar to the varying isothermal crystallization time experiments, a range of cooling rates did not lead to complete space filling. Therefore, we use the auxiliary function (Eq. (14)) again, but now with the cooling rate as the argument. As mentioned before, the enthalpy-peak during crystallization was defined as average crystallization temperature, see Fig. 15a. This is only possible for a limited number of intermediate cooling rates. The corresponding lamellar thickness are plotted in Fig. 15a. Clearly, full space filling, i.e. \( \xi = 1 \), is obtained at a crystallinity higher than 0.2, from where on the RAF fraction is constant. The \( X_\infty \) was chosen equal to the maximum crystallinity reached at the lowest cooling rate, \( X_\infty = 0.36 \), from which the crystallinity is obtained with Eq. (2). As already discussed, the lamellar thickness could not be estimated along the full range of cooling rates; hence, the \( l_R \) values were obtained by interpolation over the full range of cooling rates, see Fig. 19b. Also in this case, the RAF thickness \( (l_R) \) is fixed at 1.1 \( \text{nm} \).

Fig. 19a gives the MAF and RAF fractions as a function of the crystallinity for all continuous cooling rates. The results for which a crystallization temperature could be defined are indicated by solid symbols.

The results shown in Fig. 20 are quite reasonable; again, the trends are captured well but the final levels of the MAF and RAF fractions can be improved by varying one of the parameters. The RAF-layer thickness is not measured directly and the lamellar thickness is an estimated average value. The results improve by varying of \( l_R \) from 1.1 nm to 1.25 nm, see Fig. 21a, or decreasing of \( l_R \) by multiplying with a factor 0.85 and keeping \( l_R = 1.1 \, \text{nm} \), see Fig. 21b.

These results show the potential of this model. However, the model could be improved by a further investigation of the non-isothermal crystallization case. In particular, the lamellar thickness distribution, which is expected to be broader in non-isothermal conditions; in fact, the low thickness part of the population would contribute to a higher RAF. Another aspect to investigate further is the RAF thickness \( (l_R) \). This effect is mimicked by decreasing \( l_R \), see Fig. 21b. It seems reasonable to think that \( l_R \) is not really a constant but varies with the temperature. However, these parameters are not easily achievable, in particular in the case of flash-DSC samples.

### 3.2. Relation between \( T_g \) and the RAF and MAF content

A relation between the glass transition temperatures \( T_g \) and the RAF and MAF content is proposed and compared with the experimental results for a range of crystallization conditions. Please note that a relation between the glass transition temperature and the RAF content was already reported in the literature for isotactic Polypropylene [33].
The starting point is the idea that, in the case of pure RAF or pure MAF the material has a corresponding $T_g$, i.e. the $T_{g,RAF}$ or $T_{g,MAF}$, respectively. Note that pure RAF (or MAF) means that 100% of the amorphous phase is RAF (or MAF). For any crystallinity value $X_c$, it is the ratio between RAF and MAF that determines the $T_g$. The simplest relation one can think of is a linear function between the two $T_g$’s. For a given $X_c$ the MAF varies between 0 and 1 $- X_c$ (RAF between 1 $- X_c$ and 0) while $T_g$ is between $T_{g,RAF}$ and $T_{g,MAF}$. It easily follows that:

$$T_g = T_{g,MAF} + \frac{1}{1 + \text{MAF/RAF}} (T_{g,RAF} - T_{g,MAF})$$  \hspace{1cm} (15)

The value for $T_{g,MAF}$ is obtained from the experimental results (66.3 °C) while the $T_{g,RAF}$ is used as the only fitting parameter, which correspond to 91 °C. Note that this is not necessarily the actual $T_{g,RAF}$ whatever that might be, since RAF is not really a phase but rather represents a layer with a gradient in the reduced mobility. Fig. 22a-c show the results; the model captures the experimental $T_g$ results quite well. The standard deviation is 1.15 °C.

Note that a model for the crystallization kinetics that includes the evolution of the distribution of the lamellar thickness is available, see for example Caelers et al. [34]. Connecting such a model with the one presented in this study, will create the possibility of making a prediction of the $T_g$ and this result can be used as input for deformation kinetics modeling that is used for lifetime predictions.

4. Conclusions

In this work, the influence of thermal history on glass transition was investigated. The glass transition temperature was found to be not directly dependent on crystallinity whilst a clear relation with structures was established. In fact, the content of crystallinity, rigid and mobile amorphous phase for different cooling procedure were measured. A marked relation between glass transition and RAF–MAF content was found. More in particular, $T_g$ is directly proportional to RAF and inversely proportional to MAF. This founding is also in agreement with the mobility scenario; indeed glass transition is a physical parameter strictly related to mobility, thus an high content of low mobility amorphous phase (RAF) would lead to high $T_g$. In the opposite case, a full mobile amorphous sample can only have a minimum value of glass transition temperature. The structural investigation led to deny any strict correlation between RAF–MAF content and the crystalline unit cell (as shown in 5a and b), as supported by X-ray experiments. Moreover, a model able to predict the structure development (RAF and MAF content) was proposed. Finally an equation able to predict the glass transition temperature as function of RAF–MAF content was presented.

Acknowledgements

This work is part of the Research Program of the Dutch Polymer Institute DPI, Eindhoven, the Netherlands, project number #786. The authors thank: Dr. D. Baeten (KU/Leuven) for the use of the fast-scan ning calorimetry with in situ X-ray setup; the Dutch-Belgian beamline (DUBBLE) at the ESRF facility in Grenoble (ESRF), in particular Dr. D. Hermida-Merino; Dr. M. van Drongelen (UT) for helping with the ex situ small angle X-ray experiments on flash-DSC sensors.
Appendix A

As mentioned in Section 1, the typical continuous cooling from melt to solid was replaced by a so called two step continuous cooling. This is due to the kinetic response of the $\Delta C_p$, which is a crucial characteristic in order to define the RAF and MAF content. In fact, as already proposed by [26], the change in heat capacity at glass transition temperature ($\Delta C_p$) varies for different applied cooling rate even if the same amount of crystalline phase is obtained and the probing heating rate is consistent. By performing typical continuous cooling experiments (i.e. cooling continuously from the melt to the solid passing through the glass transition region) at different cooling rates, not only crystallinity is varied but also the amorphous state is affected. The influence of applied cooling rate on $\Delta C_p$ is attributed to a) change in crystallinity, b) variation of RAF–MAF content due to ageing and c) kinetic behavior. In Fig. 23a, a clear example of the applied cooling rate influence on amorphous state is given. In this case, two procedures are compared; two step continuous cooling (blue line) and continuous cooling (red line). In both the experiments, the cooling rate during crystallization is 1 °C/s. In the case of two step continuous cooling, at 100 °C the cooling rate is switched to 1000 °C/s. As visible in 23a, the two experiments differ

Fig. 21. Crystallinity, space filling, MAF and RAF as a function of applied cooling rate; dashed lines are the results of the model and the markers are experimental results. a) Parameters: $l_R = 1.25 \text{ nm}$, $X_\infty = 0.36$. b) Parameters: $l_R = 1.1 \text{ nm}$, $X_\infty = 0.36$ and $l_\xi = l_\xi \cdot 0.85$.

Fig. 22. Overall overview of glass transition as a function of RAF and MAF in a 3D plot. The plane is the result of Eq. (15). Three views are shown.
only in the change in $C_p$; the crystallinity is exactly the same.

Thus, by performing experiments with the same cooling rate before $T_{\text{switch}}$ (e.g. 1 °C/s) and varying the applied cooling rate after $T_{\text{switch}}$, we obtain substantial differences in change of heat capacity and glass transition, see Fig. 24a and b, respectively. In these experiments with fixed crystallinity, the variation of $\Delta C_p$ and $T_g$ might be attributed to the variation of RAF–MAF content due to ageing and kinetic behavior. Therefore, experiments on completely amorphous samples were performed. In this case, only the kinetic behavior plays a role because only mobile amorphous phase is present. A decrease of $\Delta C_p$ is observed for increasing applied cooling rate after $T_{\text{switch}}$, although smaller than the effect shown in Fig. 24a.

In this section, the use of “two step continuous cooling” rather than typical continuous cooling was explained and justified. Indeed, this work was meant to investigate the influence of structure formation on the glass transition temperature and, therefore, this procedure was chosen to avoid influence of ageing and kinetics (Fig. 25).

Appendix B

In this section, the conditioning procedure is described and justified. This procedure was applied for mainly two reasons: a) drying the sample and b) erase the thermal history. As explained in Section 1, PA6 has a strong hydrophilic character which leads to water absorption. Moreover, the absorbed water acts as plasticizer and lowers the glass transition. The conditioning procedure is performed prior to each experiments. The procedure consist of two times heating at 1000 °C/s followed by a short isothermal period at high temperature (300 °C for 1 s) and quenching at 1000 °C/s to −50 °C, see Fig. 26. By applying this procedure, the thermal history is erased and the sample is dried thanks to the high temperature reached and the inert ambient (nitrogen).
Appendix C

The estimation of the crystalline fraction is a crucial part of this study. Indeed, because of possible re-organization and (or) phase transformations during heating, the enthalpy of fusion obtained for samples containing a mixture of $\gamma$-mesophase and $\alpha$-phase can not be accurately deconvoluted to the pre-existing crystalline fraction. Unfortunately, this happens for most of the applied cooling rates and isothermal temperatures. Only in the extreme cases, where only $\gamma$-mesophase or $\alpha$-phase exists, crystallinity can be estimated from the thermograms, i.e. very low and very high isothermal temperatures (or cooling rates). Therefore, another technique must be used. Wide angle X-ray diffraction experiments were performed in situ for several solidification procedures. An estimation of crystallinity was made for samples cooled at different cooling rates. In Fig. 27a, the crystallinity estimated by WAXD is compared with the few interpretable results obtained by flash-DSC (i.e. the experiment with lowest cooling rate where only $\alpha$-phase was obtained, and the measurements leading to completely amorphous samples). As is observed, the crystallinity onset resulting from the values obtained by WAXD (green markers in Fig. 27a) takes place at cooling rate higher than the onset obtained with flash-DSC results (blue markers). In 27b four cooling thermograms are compared. The blue (dashed) and red (solid) lines are related to experiments carried out in in-house laboratories and at the synchrotron in Grenoble, respectively. For a set cooling rate, the experiment performed at the synchrotron show a higher crystallization temperature than in the case of in-house flash-DSC. The reason of these differences is related to the difference between the two experimental equipments. Therefore, a shift factor was applied on the cooling rate vector. To estimate this shift factor, the cooling curve obtained by the external flash-DSC at 50 °C/s was taken as a reference. Next, the cooling curve from the in-house flash-DSC that matches the reference curve was determined. As shown in Fig. 28a, a match between 50 °C/s and 20 °C/s was found, thus a factor 0.4 was applied to the cooling rates (see Fig. 27a). The results are shown in 27a (red markers).

Also for the case of isothermal crystallization, flash-DSC results were compared with those from WAXD. In this case two measurements obtained
by thermal analysis are taken as reference points i.e. the isothermal crystallization at 180 °C and 90 °C. In these cases, only one phase was crystallized, thus a deconvolution of the flash-DSC thermogram was possible; the melting of γ-phase and β-phase take place at different temperatures, therefore the melting peak area can be measured and the crystallinity can be estimated using Eq. (3). The crystallinity values estimated by X-ray are comparable with the one obtained by flash-DSC, see Fig. 28b, thus they are used in the analysis. In order to estimate the crystallinity at temperatures for which no WAXD was performed, an interpolation over the full range of temperature was performed, see Fig. 28b (red circles).

References