Mechanical properties of amorphous and semi-crystalline semi-aromatic polyamides

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A B S T R A C T

We investigate the mechanical properties of amorphous and semi-crystalline semi-aromatic polyamides, polyphthalamides (PPA). Three relaxation processes have been identified by DMTA which is consistent with literature for polyamide. PPA exhibit a brittle-to-ductile transition from a low impact strength to a high impact strength. At room temperature, all the studied samples are brittle. During both tensile and compression experiments, a strain hardening behavior is observed for all the studied samples and is more pronounced in compression. The testing temperature has an influence on the strain hardening modulus, contrary to the crystallinity. Strain hardening gives properties of stability and resistance to damage.

1. Introduction

Polyamides are engineering thermoplastics which are useful for their high barrier properties. They are widely used in textile and automotive industries, where they compete with metals in a context of weight's reduction [1, 2, 3]. Polyamides are generally aliphatic and semi-crystalline. This is the case of PA 6, PA 66 or PA 6,10. Recently, polymers with different structures have been formulated to meet more technical applications. This is the case for example of semi-aromatic or fully-aromatic polyamides (MXDA, PA 6T/X, PA 10T/X, PA 10T [4]), and also amorphous polyamides [1], especially in order to improve the mechanical and thermal properties [5]. Polyphthalamides (PPA) are part of polyamide group. The main difference is the presence of aromatic rings in PPA's backbones, allowing them to have high mechanical and thermal resistance. PPA are synthesized by a reaction between aromatic acids (terephthalic acid or isophthalic acid) and aliphatic diamines (such as HMDA). If the PPA is mainly based on PA6T, the resulting PPA will be semi-crystalline [1]. PA6T is obtained by the reaction of terephthalic acid and HMDA. On the contrary, when the PPA is mainly based on PA6 (i.e. more than 55% of isophthalic acid), the resulting polymer will be amorphous [6]. This new class of polyamides has better properties compared to aliphatic polyamides (PA6 or PA66 [7] as an example), whether thermal (higher melting points and glass transition temperatures, better thermal stability), or chemical (better chemical resistance and lower water absorption). Few studies have been done for characterizing the properties of neat-PPA, such as thermal [8] or mechanical properties [9], but some studies exist on blends-based PPA or glass fiber reinforced PPA [10]. There is a need of more detailed data concerning mechanical properties. The study of the properties of this class of polymers is important, especially since their applications are different from aliphatic polyamides. PPA are used in several industries such as electronic devices, packaging or automotive industries. They can be used in composites for high temperature applications. PPA used in composites are mostly semi-crystalline because they maintain their properties at Tg, which is not the case of amorphous PPA. In this study, we will focus on the characterization of semi-crystalline and amorphous PPA. The ultimate mechanical properties and durability of polyphthalamides expected in applications such as automotive industry depend on the properties of strain hardening and impact strength [11]. Indeed, when dealing with ultimate mechanical properties the brittle-ductile transition Tbd is an essential notion to characterize, as well as the strain hardening regime. The strain hardening is generally interpreted as a result of a stress contribution of the orienting molecular network [11, 12, 13, 14, 15]. The objective of this paper is to study the ultimate mechanical properties of amorphous and semi-crystalline PA 61/6T, through the study of the strain hardening and the brittle-to-ductile transition temperature. We consider three PPA, PA 61/6T, with different proportions of PA61 or 6T, which gives the amorphous or semi-crystalline character of the polymer. The

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viscoelastic properties in the linear regime will be studied by Dynamical Mechanical Thermal Analysis (DMTA). The yield stress $\sigma_y$ and Young’s modulus $E$ measured by tensile tests, as well as the brittle-ductile transition temperature $T_{bd}$ measured by both tensile and Charpy impact tests are determined for the considered PPA samples. The strain hardening in compression is studied.

2. Experimental methods

2.1. Materials

Three semi-aromatic polyamides were considered. Figure 1 shows the structure of the copolymer PA6I/6T. Polymers are formed by copolymerization of the PA6T and PA6I in different proportions. Monomers are obtained by the condensation reaction of hexamethylenediamine (HMDA) with a diacid: isophthalic (terephthalic) acid for the PA6I (PA6T) monomer. The resulting PPA can be amorphous or semi-crystalline depending on the combination of the monomers [1]. Semi-crystalline PPA are mainly based on PA6T, while the resulting copolymer is amorphous if there is more PA6I [6]. Each PPA corresponds to a different fraction in PA6I or PA6T, indicated in Table 1.

The number-average and weight-average molecular weight $M_n$ and $M_w$ were determined by Size Exclusion Chromatography (SEC). $M_n$ is around 10000 g mol$^{-1}$ for Polyamide A and B and around 6000 g mol$^{-1}$ for Polyamide C whereas $M_w$ is around 30000 g mol$^{-1}$ for Polyamide A, B and C. $M_n$ and $M_w$ were used to calculate the polydispersity index $I_p$ (see Table 1). As explained by Martins et al [16], secondary reactions may occur during polymer synthesis. These secondary reactions lead to branched chains in small proportions and, possibly, may explain why the polydispersity index varies from 3.0 to 5.1 [16]. As observed in Table 1, the values of polydispersity are larger than 2, which is the value expected by Flory’s theory for linear polycondensation [16,17].

The glass transition temperature $T_g$ was determined by Differential Scanning Calorimetry (DSC). $T_g$ is similar and about 130 °C. Like all semi-aromatic PPA with more than 55% of PA6I [6], Polyamide A is amorphous. Polyamide B and C are both semi-crystalline, with a crystallinity ratio of 4.3% and 16.4%, respectively. Crystalline fractions were calculated using the following formula (Equation 1):

$$\chi = \frac{\Delta H_{\text{melted}}}{\Delta H_{\text{100%}}}$$  \hspace{1cm} (1)

where $\Delta H_{\text{100%}}$ is the enthalpy of melting of a 100% crystalline polymer.

It can be found in literature for PA6,6 (188 J g$^{-1}$ [18]) and PA6,10 (207 J g$^{-1}$ [18]), but not for the crystalline PA6T fraction of Polyamide C. As a consequence, an average value of 200 ± 20 J g$^{-1}$ is commonly used [19]. To provide a better estimation of the crystalline fraction, $\Delta H_{\text{100%}}$ value for the PA6T was determined by WAXS (Wide-Angle X-ray Scattering) experiments. The peaks obtained in WAXS were deconvoluted and the amorphous halo was subtracted from the crystalline peaks. The crystalline fraction $\chi_{\text{XAXS}}$ was calculated using Eq. (2):

$$\chi_{\text{XAXS}} = \frac{A_C}{A_C + A_A} \times 100$$  \hspace{1cm} (2)

with $A_C$ and $A_A$ the areas of crystalline and amorphous parts, respectively.

Then the enthalpy of melting of a 100% crystalline PA6T is calculated as follow (Equation 3):

$$\Delta H_{\text{100%}} = \frac{\Delta H_{\text{DSC}}}{\chi_{\text{XAXS}}}$$  \hspace{1cm} (3)

For a 100% crystalline PA6T, the enthalpy of melting is 196 J g$^{-1}$. An Oxford Xcalibur Mova diffractometer was used in transmission mode in order to record WAXS data. Measurements were performed at the Henri Longchamton Diffraction Center of University of Lyon.

2.2. Injection molding

Polymers were injection-molded into tensile and impact strength specimens with a Billion select 100T injection press. Prior to molding, water content has been controlled by Karl Fischer in order to avoid hydrolysis or post-condensation reaction. Higher water content leads to hydrolysis and the molecular weight decreases. If the moisture content is lower than that of the chemical equilibrium, a post-condensation reaction with water formation and an increase of the molecular weight of the resulting polyamide may occur. Pellets were dried 24 h at 110 °C under vacuum before processing. Mold temperature was kept at 30 °C. After molding, the samples were stored in sealed bags to maintain them dry. Tensile and impact strength specimens dimensions were 150 mm x 4 mm and 80 x 10 x 4 mm$^3$ respectively (ISO-527 and ISO-157 norms) (see Figure 2-1 for tensile geometry and Figure 2-2 for impact strength geometry). In Table 2, we gather the processing conditions of our samples.

The injection process has an influence on mechanical properties of polymers, in particular on the skin-core effect due to flow during injection [20]. This effect is present in the industrial process, due to a temperature gradient between the mold and the polymer melt (at higher temperature) during the injection process. A skin-core effect was observed for Polyamide C by cross-polarized optical microscopy. Indeed, a birefringent character was observed between the skin and the core of the polymer. Samples of Polyamide C were injection-molded with different mold temperatures (30, 60, 80 and 100 °C). The storage modulus $E'$ determined by DMTA shows no difference regardless of the mold temperature ($E' = 3.1$ GPa at 25 °C for the four mold temperatures).

The temperature of the mold during the injection has no impact on the modulus $E$. The degree of crystallinity remains low and is homogeneous over the thickness for the two semi-crystalline PPA (Polyamide B and Polyamide C), and was verified by DSC experiments. The skin-core effect observed for Polyamide C only is related to shearing during the injection process and not to a difference in crystallinity within the material. The choice of setting the mold temperature at 30 °C corresponds to an internal injection process and has no impact on our results.
Table 1. List of studied semi-aromatic polyamides and corresponding molecular weight distribution (number-average Mₙ and weight-average Mₘ, polydispersity index (Iₚ = Mₘ/Mₙ) determined by Size Exclusion Chromatography (SEC) in PMMA equivalents), glass transition T_g and melting temperatures T_m determined by Differential Scanning Calorimetry (DSC), crystallinity ratio determined by Wide Angle X-Ray Scattering (WAXS). All the samples were dried as molded (d.a.m.).

| Polyamide | Mₙ (g mol⁻¹) (±5%) | Mₘ (g mol⁻¹) (±2.5%) | Iₚ = Mₘ/Mₙ | Crystallinity (%) (d.a.m.) | T_g (°C) | T_m (°C) |
|-----------|--------------------|----------------------|------------|---------------------------|----------|---------|
| Polyamide A | 9356 | 29963 | 3.0 | 0 | 129.2 | / |
| Polyamide B | 10424 | 32917 | 3.2 | 4.3 | 129.3 | 265 |
| Polyamide C | 6450 | 32779 | 5.1 | 16.4 | 132.4 | 319 |

Table 2. Injection conditions for ISO-527 (Tensile) and ISO-157 (Choc) geometries.

| Screw | Temptures (°C) | Molding cycle time (s) |
|-------|----------------|------------------------|
|       | Choc specimens | Tensile specimens | Choc specimens | Tensile specimens |
| Polyamide A | 280 | 280 | 36.43 | 45.26 |
| Polyamide B | 290 | 290 | 41.32 | 47.24 |
| Polyamide C | 330 | 330 | 33.36 | 33.18 |

Figure 2. Tensile geometry of the specimens (1) and impact strength geometry of the specimens (2).
true strain and the true stress during the test, in a representative volume element. The representative volume element can be defined by several dot markers placed in the middle of the tensile specimen. The development of localization phenomena like necking is taken into account in the measured behavior [24]. In the studied samples, the necking area is reproducible. The dot markers are placed in order to study this area. Samples were dried as molded (d.a.m.) and were strained at a constant strain rate $\dot{\varepsilon} = 1.10^{-3} \text{s}^{-1}$ at different temperatures (between -40 °C to 160 °C). The lower temperature of chamber is -40 °C. Each sample was conditioned 20 min in the temperature chamber before being tested. For each temperature, five samples were tested.

The nominal strain $\varepsilon_n$ is given by Eq. (4):

$$\varepsilon_n = \frac{\Delta l}{l_0} = \frac{l - l_0}{l_0}$$

with $l$ the length at each time $t$ and $l_0$ the initial length of the specimen.

The nominal stress $\sigma_n$ can be expressed as:

$$\sigma_n = \frac{F}{S_0}$$

with $F$ the force acting on the specimen and $S_0$, the initial cross sectional area.

At large deformations, amorphous polymers have a high ductility. During the tensile test, the sample cross sectional area is not constant. The instantaneous cross sectional area $S(t)$ should be used instead of $S_0$. The videoextensometer gives access to the elastoviscoplastic response of polymers under uniaxial tension. Local measurements of true strains are possible to determine the barycenter of each marker drawn on the specimen and calculate their relative displacements (Figure 3). Thus, the system calculate simultaneously in-plane and out-of-plane deformations.

2.3.5. Compression

Compression tests were performed on a Zwick/Roell Z050 universal testing machine equipped with a 50 kN load cell, a thermally controlled chamber and a non-contact extensometer (VideoTraction®) [23]. The geometry of the sample is an important limitation of this test. Cubes of dimensions $10 \times 10 \times 4 \text{ mm}^3$ were cut in the ISO-527 tensile specimens. It is necessary to avoid the barreling or buckling of the sample [26]. The friction has been reduced by lubrication of the plate to prevent the buckling of the sample. Thanks to VideoTraction®, we could check that there is no barrel nor buckling. It allows us to consider the friction as negligible in the test and then the compression field homogeneous all over the specimen.

Specimens were compressed at a constant strain rate $\dot{\varepsilon} = 1.10^{-3} \text{s}^{-1}$ between two parallel flat steel plates. Tests were performed at different temperatures, from -20 °C to 120 °C. Each sample was conditioned 20 min in the temperature chamber before being tested. For each temperature, five samples were tested.

For the analysis of the strain hardening response, the compression curves were plotted versus the Green-Lagrange strain [27]:

$$g(\lambda) = \lambda^2 - \lambda^{-1}$$

(9)

Thanks to the two cameras, the VideoTraction system makes it possible to determine the barycenter of each marker drawn on the specimen and calculate their relative displacements (Figure 3). Thus, the system calculate simultaneously in-plane and out-of-plane deformations.

![Figure 3. Representation of the VideoTraction® system (1) and the markers on the middle of the tensile specimen with the two cameras (2). Adapted from [23] with permission from Elsevier.](image)

![Figure 4. Temperature dependences of the storage modulus $E'$, the loss modulus $E''$ and the damping factor $\tan \delta$, as determined at 1 Hz for the different PPA by DMTA measurements. The different relaxation processes are indicated on the tan$\delta$ curves.](image)
The strain hardening modulus, $E_{SH}$, was determined from the slope of the curves in the strain range $1.75 \geq \gamma(\lambda) \geq 1.25$.

3. Results and discussion

3.1. Thermo-mechanical properties

Temperature sweep measurements were performed at frequencies of 0.1, 1, 10, 50 and 75 Hz. The temperature of each relaxation was determined as the maximum of the relaxation peak observed in the loss modulus $E''$ plot. To determine correctly the characteristic temperature of each relaxation process, a Gaussian function was used to fit each peak, and therefore determined the peak maximum. At 23 °C and 1 Hz, the storage modulus $E'$ is high and is 2.92 GPa for Polyamide A, 3.01 GPa for Polyamide B and 2.96 GPa for Polyamide C, which is comparable with the elastic moduli of 2.5 GPa for poly(phenylene oxide) PPO and 3 GPa for poly(phenylene sulfide) PS) [12]. PA66, which is an aliphatic polymer, has an elastic modulus of 2.8 GPa, measured at 23 °C at 1 Hz, which is comparable to the elastic modulus of our samples [28,29]. The differences observed in the elastic moduli are not significant. Indeed, the two semi-crystalline PPA have the same behavior as the amorphous PPA, with a module of 3 GPa. The crystallinity has no influence in our case.

The temperature dependences of the storage modulus $E'$ and the damping factor $\tan\delta$, as determined at 1 Hz for the different PPA, are listed in Table 3. As shown by the data displayed in Table 3, the increase in PA6T content induces a slight increase of the $\alpha$-relaxation temperature of 6 °C, which is also observed in literature for other polyamides [30,37]. A weak and wide shoulder is also observed in our measurements around 70 °C and can be associated with the departure of water [31,33]. As measured by Karl Fischer, our polymers contain about 700 ppm of water. A departure of water contained in the polymer causes a shift of the relaxation towards high temperatures.

### Table 3. Temperatures of the different relaxations, $\alpha$, $\beta$ and $\gamma$ for each polymer determined at 1 Hz.

| Copolyamides | $T_\alpha$ (°C) | $T_\beta$ (°C) | $T_\gamma$ (°C) |
|--------------|----------------|----------------|----------------|
| Polyamide A  | 128.2          | -51.7          | -140.6         |
| Polyamide B  | 129.3          | -46.7          | -139.6         |
| Polyamide C  | 134.3          | -48.6          | -137.6         |

At the lowest temperature, the $\gamma$-relaxation is generally assigned to local motions of short aliphatic sequences -(CH$_2$)$_n$-internal to the monomer for aliphatic polyamides [30,36]. This relaxation is observed around -140 °C at 1 Hz, which is comparable to the $\gamma$-relaxation observed by Varlet et al [36] for PA 12. The $\beta$-relaxation is associated to the rotation of amide groups (-NHCO-) along the polyamide chain, and is observed around -50 °C at 1 Hz. The $\alpha$-relaxation corresponds to segmental movements (several monomers). This main relaxation is observed at high temperature and is close to the glass transition temperature measured by DSC. The temperatures $T_{\alpha}$, $T_{\beta}$ and $T_{\gamma}$ determined by DMTA at 1 Hz for the three PPA, are listed in Table 3. As shown by the data displayed in Table 3, the increase in PA6T content induces a slight increase of the $\alpha$-relaxation temperature of 6 °C, which is also observed in literature for other polyamides [30,37]. A weak and wide shoulder is also observed in our measurements around 70 °C and can be associated with the departure of water [31,33]. As measured by Karl Fischer, our polymers contain about 700 ppm of water. A departure of water contained in the polymer causes a shift of the relaxation towards high temperatures.

#### 3.1.1. Time/temperature dependence of relaxations

From the DMTA curves obtained at different frequencies (0.1, 1, 10, 50 and 75 Hz), we plot the time/temperature dependence of the loss modulus and therefore determined the peak maximum. At 23 °C and 1 Hz, the storage modulus $E'$ is high and is 2.92 GPa for Polyamide A, 3.01 GPa for Polyamide B and 2.96 GPa for Polyamide C, which is comparable with the elastic moduli of 2.5 GPa for poly(phenylene oxide) PPO and 3 GPa for poly(phenylene sulfide) PS) [12]. PA66, which is an aliphatic polymer, has an elastic modulus of 2.8 GPa, measured at 23 °C at 1 Hz, which is comparable to the elastic modulus of our samples [28,29]. The differences observed in the elastic moduli are not significant. Indeed, the two semi-crystalline PPA have the same behavior as the amorphous PPA, with a module of 3 GPa. The crystallinity has no influence in our case.

The temperature dependences of the storage modulus $E'$ and the damping factor $\tan\delta$, as determined at 1 Hz for the different PPA, are shown in Figure 4.

Starting from low temperature, the storage modulus $E'$ reduces slowly and decreases strongly at the glass transition temperature $T_g$.

In addition to the final relaxation process ($\alpha$) we observe two peaks on $\tan\delta$ for each polymer, denoted $\gamma$ and $\beta$. Indeed, three relaxations processes have been identified in other semi-aromatic and aliphatic polyamides [30,31,32,33] by DMTA and by broadband dielectric spectroscopy (BDS) [34,35].

#### Figure 5. Time/temperature dependence of relaxations for the three PPA. From left to right, the different relaxations are shown: $\alpha$, $\beta$ and $\gamma$, as well as the $T_g$ determined by DSC.

#### Figure 6. Brittle-ductile transition curves of all the PPA samples obtained from Charpy impact measurements. Evolution of the energy dissipated by the material with the temperature and the brittle-ductile transition temperature $T_{bd}$. The stars represent the unbroken samples above the $T_{bd}$.
characteristic time $\tau_0$, the entropy $-T_0\Delta S$ and the free energy $\Delta G$ of the $\gamma$ and $\beta$ relaxations for each PPA.

### 3.1.2. Secondary relaxations

For the $\gamma$ relaxation, the activation energy $E_A$ is in the range of 40 kJ mol$^{-1}$ (from 41 to 46 kJ mol$^{-1}$). This range of activation energy was reported in literature by several authors for aliphatic polyamides or semi-aromatic copolymers based on PA 6I [31,33,40]. The expected value for the prefactor $\tau_0$ is $10^{-12}$ s, which is the Debye time ($\tau_{\text{Debye}} = 10^{-12}$ s [41]) if there is no contribution to the free energy barrier. This is not the case here, since the prefactor $\tau_0$ is smaller than this value. Very small relaxations time values are an indication of an entropic contribution. Note that Laurati et al and Laredo et al have observed in the presence of water smaller values of $\tau_0$, close to the values determined for our polyamers (see Table 4) [31,33].

The value of $\Delta G$ (about 17 kJ mol$^{-1}$) for polyamides A and B are identical to the value corresponding to the rotational barrier for the C–C torsion motion [42,43].

In the case of the $\beta$-relaxation, for the amorphous PPA, Polyamide A, the free energy $\Delta G$ is 45.4 kJ mol$^{-1}$. This value is in good agreement with the value determined by Bocahut et al for the free energy barrier associated to the rotation of amides groups ($\Delta G = 40 \pm 5$ kJ mol$^{-1}$) [44].

Note that the entropy $\Delta S$ of Polyamide C is twice the entropy of polyamides A and B. Small values of $\Delta S$ for polyamides A and B indicate that the motions responsible for the $\beta$-relaxation are very localized modes [30,37]. On the contrary, the entropy $\Delta S$ is twice for Polyamide C, based mainly on terephthalic acid, which is an indication that the motional cooperativity is higher [30].

### 3.1.3. Main relaxation $\alpha$

The $\alpha$-relaxation can be fitted using the WLF equation mentioned above (Equation 10). The WLF constants $C_1$ and $C_2$ were respectively 7.54 and 32.33 K, for the three PPA. Because of the dependency in frequency and temperature of $E'$, a time-temperature superposition curve ($t_{TS}$) can be established for Polyamide A. The shift factor $\alpha_T$ can be fitted with the WLF equation. $C_1$ and $C_2$ WLF constants are respectively 17.62 and 71.98 K [39,45]. $C_1$ and $C_2$ WLF constants are reported to $T_g$ with Eqs. (12) and (13) [46]:

$$C_1^f = \frac{C_1C_2}{C_2 + T_g - T_{ref}}$$  \hspace{1cm} (12)

$$C_2^f = C_2 + T_g - T_{ref}$$  \hspace{1cm} (13)

Where $C_1$ and $C_2$ are the WLF constants, $T_g$ is the glass transition temperature determined by DSC for each polymer and $T_{ref}$ is the arbitrary chosen reference temperature defined as 300 K.

The WLF constants $C_1^f$ and $C_2^f$ are reported in Table 5. No significant difference was observed in the WLF constants.

### Table 4. Activation energy $E_A$, characteristic time $\tau_0$, entropy $-T_0\Delta S$ and free energy $\Delta G$ of the $\gamma$ and $\beta$ relaxations for each PPA.

| Polymer     | $\gamma$-relaxation | $\beta$-relaxation |
|-------------|----------------------|---------------------|
|             | $E_A$ (kJ mol$^{-1}$) | $\tau_0$ (s)       | $-T_0\Delta S$ (kJ mol$^{-1}$) | $\Delta G$ (kJ mol$^{-1}$) |
| Polyamide A | 41.16                | $10^{-16.1}$        | 10.35                           | 17.75                       |
| Polyamide B | 43.37                | $10^{-16.7}$        | 12.05                           | 16.3                        |
| Polyamide C | 46.66                | $10^{-18}$          | 15.48                           | 12.4                        |

### Table 5. WLF fitting parameters for the $\alpha$-relaxation.

| Copolyamides | $C_1^f$ | $C_2^f$ (K) |
|--------------|---------|-------------|
| Polyamide A  | 1.81    | 134.68      |
| Polyamide B  | 1.81    | 134.78      |
| Polyamide C  | 1.77    | 137.88      |

Figure 7. Uniaxial tensile true stress-true strain curves determined for Polyamide A (1), Polyamide B (2) and Polyamide C (3) at several temperatures and a strain rate of $1.10^{-3}$ s$^{-1}$. 

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temperatures, the specimens do not break and present a ductile behavior. Failure with an impact strength varying from 3 to 11 kJ m\(^{-2}\) at high temperature, the studied samples. At low temperatures, all samples show a brittle behavior. A well-defined transition from brittle to ductile behavior is observed for all polymers. A large region of plastic deformation close to the tip of the tail is observed. Specimens evolve from a fragile elastic behavior to a ductile plastic behavior. A brittle-ductile transition can be determined for the three PPA (Figure 6).

### 3.2. Characterization of the brittle-ductile transition \(T_{bd}\)

#### 3.2.1. Charpy impact strength

The transition from brittle to ductile, denoted \(T_{bd}\), may be characterized by Charpy impact test or in uniaxial tensile experiments. Charpy impact test is a dynamic test at a frequency of \(10^3\) Hz. Impact strength tests are conducted on all the studied samples as described in the experimental section. Figure 6 shows the energy dissipated during impact as a function of temperature (brittle-to-ductile transition curves) for all the studied samples. At low temperatures, all samples show a brittle failure with an impact strength varying from 3 to 11 kJ m\(^{-2}\). At high temperatures, the specimens do not break and present a ductile behavior. A well-defined transition from brittle to ductile behavior is observed for all polymers. A large region of plastic deformation close to the tip of the tail is observed. Specimens evolve from a fragile elastic behavior to a ductile plastic behavior. A brittle-ductile transition can be determined for the three PPA (Figure 6).

For the amorphous polymer, Polyamide A, the \(T_{bd}\) is equal to 140 °C. For the low semi-crystalline PPA, Polyamide B, the \(T_{bd}\) is close, 135 °C. For these two polymers, we can see that this transition \(T_{bd}\) is very close to the glass transition \(T_g\) determined by DSC (see Table 1). We observe that the brittle-ductile transition temperature is higher for the PPA with the largest crystalline fraction, Polyamide C (192 °C).

The same behavior is observed for different PA6,6 with a well-defined brittle-ductile transition with a resilience at low temperature of order 2–5

\[
\text{kJ m}^{-2}
\]

order 60 kJ m\(^{-2}\), which is lower than for the studied PPA. The brittle-ductile transition temperature of PA6,6 is of order 20 °C, which is very low compared to the studied PPA.

The energy dissipated during impact in the ductile regime at 150 °C is high (from 130 to 160 kJ m\(^{-2}\)). The brittle-ductile transition temperature is also very high for the three PPA.

#### 3.2.2. Influence of frequency on \(T_{bd}\)

The brittle-ductile transition temperature \(T_{bd}\) at lower frequency is observed in uniaxial tensile experiments as the temperature at which failure occurs at the yield stress \(\sigma_y\) [25]. The true stress-true strain curves obtained from tensile experiments at different temperatures are presented in Figure 7 for the three polyamides. When the temperature decreases, the rigidity of the polymer increases. A transition from ductile to brittle behavior can be observed in Figure 7. Below 110 °C, Polyamide C is brittle, the sample breaks before reaching the yield stress \(\sigma_y\). When the temperature increases, the mobility of the chains is accelerated and a yield point can be determined, as observed for Polyamide A and B, and above 110 °C for polyamide C (Figure 7-3). As explained above (see 3.2.1), the behavior goes from brittle to ductile. The temperature \(T_{bd}\) is defined for Polyamide A and Polyamide B below -40 °C. For Polyamide C, \(T_{bd}\) is clearly visible and is determined at 110 °C. Because of the limitation of the temperature of the temperature chamber, we cannot perform tensile tests below -40 °C. Contrary to the Charpy impact strength described in the previous paragraph, the tensile test is a quasi-static test at a frequency of \(10^{-3}\) Hz. We can emphasize the influence of the frequency on this temperature: the higher the frequency, the higher the temperature \(T_{bd}\). As for the Charpy impact test, the brittle-ductile transition temperature is strongly influenced by the crystallinity and is higher for the most semi-crystalline PPA, Polyamide C (192 °C).

#### 3.3. Tensile behavior

Figure 7 represents the true stress-true strain curves obtained from tensile experiments for the three polyamides. The behavior of all samples is essentially the same. Beyond the yield point, a strain softening regime is observed. It corresponds to a stress decrease with increasing deformation [50]. The strain softening is followed by a strain hardening regime.

The strain hardening behavior is also observed in other amorphous polymers such as cellulose acetate, PC, PMMA or PVC [12, 51, 52, 53]. It can be defined as a stress increase at large strains. The strain hardening modulus \(E_{sh}\) is defined as the slope at large strains. The three PPA studied have a very ductile behavior. Beyond the brittle-ductile transition \(T_{bd}\), the failure takes place at a deformation larger than the deformation accessible within the testing machine, which is a limitation for the study of strain hardening.

The equations mentioned so far apply when a polymer exhibits uniform deformation (see Equations (4),(5),(6),(7) and (8)). Beyond the plasticity threshold, several polymers (such as PC, PE, PVC, PP or PA) [25, 54, 55, 56] show deformation heterogeneities called necking. This phenomenon is related to a local stress concentration (due to a variation of section) which makes the deformation field non-uniform within the sample. The appearance of this phenomenon is a consequence of a mechanical instability due to a strain softening. Strain softening is stabilized by strain hardening. In tensile test, further studies shown that the strain hardening regime is influenced by the temperature, the polymer chains orientation and the geometry of the sample [51, 57]. The study of strain hardening will be detailed in the case of the compression test. The strain softening amplitude is larger at low temperatures than at high temperatures.
temperatures, which is similar to the behavior observed for PMMA or PC [54,58].

3.3.1. Evolution of the young modulus $E$ and the yield stress $\sigma_y$

The Young modulus $E$ is calculated from the tangent line in the elastic domain (between 0.05 and 0.25% of true strain) and the yield stress $\sigma_y$ is defined as the observed maximum stress.

Figure 8 shows the evolution of the young modulus (Figure 8-1) and the yield stress (Figure 8-2) as a function of $T_g$ - $T$. This representation makes it possible to compare the 3 PPA at a given state of molecular mobility. Young modulus $E$ and yield stress $\sigma_y$ values are reported for temperatures below the glass transition temperature $T_g$. No particular relation appears for the Young Modulus $E$ when plotted as a function of $T_g$ - $T$, whereas the yield stress $\sigma_y$ fall on a linear master curve. The Young Modulus $E$ of the studied PPA is much higher than that of a PA66, which is an aliphatic polyamide. Indeed, the PA66 has a Young Modulus $E$ of the order of 1100 MPa (at room temperature and 10 mm min$^{-1}$) [48].

3.4. Compression behavior

The true stress-true strain curves obtained in tensile tests present a necking phenomenon. We performed uniaxial compression tests to avoid localization phenomena at large deformation. We plot the true strain as $(\lambda^2 - \lambda^{-1})$, which is a standard representation for the study of the strain hardening and often used in literature [12,27].

Figure 9 shows the results plotted as true stress versus $(\lambda^2 - \lambda^{-1})$ for the three polyamides at several temperatures. A moderate strain softening followed by a strain hardening results in a macroscopic ductile behavior [59]. The strain softening is more pronounced for the amorphous PPA. Indeed, the strain softening is an amorphous property [60] and increasing the crystallinity seems to result in a decrease in strain softening.

Figure 10 shows the evolution of the strain hardening modulus $E_{SH}$ determined from the true stress – $(\lambda^2 - \lambda^{-1})$ curves with the temperature for each polymer. Values of hardening modulus are shown in Table 6. The strain hardening modulus is similar for the three PPA. The strain hardening modulus of the semi-crystalline PPA is found to be equal to that of the amorphous PPA and is clearly not related to the degree of crystallinity. This was observed in literature by Schrauwen et al with different semi-crystalline polymers (polyethylene, polypropylene and poly(ethylene terephthalate)) [61]. At room temperature, the strain hardening modulus $E_{SH}$ for the three PPA is about 18 MPa. It is larger than the strain hardening modulus of PS (13 MPa) [12] but smaller than other amorphous polymers (at room temperature, $E_{SH}$ of PC, PPO and PMMA are 29 MPa [12], 75 MPa [12] and 25 MPa [27,62,63], respectively. The strain hardening modulus decreases linearly with the temperature for Polyamide B and Polyamide C, which is observed in literature by Engels and Van Melick with other polymers such as polycarbonate [12,59]. For Polyamide A, the strain hardening modulus seems no affected by temperature: there is no dependence to temperature.
4. Conclusions

In this paper, the mechanical properties of polyphthalamides samples processed by injection molding have been investigated. The thermo-mechanical properties have been studied through DMTA experiments. All the studied PPA exhibit a characteristic dynamic mechanical response for a thermoplastic material. Three relaxations processes have been identified, denoted γ, β and α from the lower to the higher temperature. The impact properties were studied on a broad temperature range, using an instrumented Charpy impact test. The three PPA samples showed a brittle-ductile transition varying from a low energy dissipated during impact test to a high energy dissipated during impact of the order 130–160 kJ m⁻². At room temperature, the three PPA studied are brittle. They should be used for a composite application and thus improve their Tbd. The tensile and the compression behavior of three PPA with different degree of crystallinity have been studied. In tensile test, the PPA with the largest crystallinity is brittle at room temperature (Polyamide C), while the polyamide A and polyamide B are ductile. In both tests, we observed a strain hardening behavior, which is more pronounced in compression. The strain hardening regime in tensile test is influenced by the temperature as well as the amorphous or semi-crystalline character of the studied PPA. The measured strain hardening moduli in compression are around 18 MPa for the three PPA at 23 °C. The values of the ES1 modulus are relatively low compared to the PPO (75 MPa [12]). The strain hardening modulus is shown not to depend on crystallinity. Indeed, the strain hardening modulus ES1 of the semi-crystalline PPA, Polyamide C and Polyamide B, is found to be equal to the hardening modulus of the amorphous. Only the temperature has an influence on the strain hardening modulus ES1: the strain hardening modulus decreases with increasing temperature. Stress hardening is a key feature for resistance to damage [11,64].

Declarations

Author contribution statement

Stéphanie Djukić, Anthony Bocahut, Jérôme Bikard, Didier R. Long: Conceived and designed the experiments; Performed the experiments; Analyzed and interpreted the data; Contributed reagents, materials, analysis tools or data; Wrote the paper.

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Additional information

The raw/processed data required to reproduce these findings cannot be shared at this time as the data also forms part of an ongoing study.

References

[1] M.I. Kohan, Nylon Plastics Handbook, Hanser Publishers, 1995. https://books.google.fr/books?id=-oZbOpqACAAJ.
[2] C. Duval, Plastiques et automobile - D'hier à aujourd'hui, Techniques de l’Ingénieur 1 (2007). AM 3590.
[3] C. Duval, Plastiques et automobile - D'hier à aujourd'hui, Techniques de l’Ingénieur 1 (2007). AM 3591.
[4] M. Li, J. Blijleveld, T. Dingemann, Synthesis and properties of semi-crystalline poly(decamethylene terephthalamide) thermosets from reactive side-group copolyamides, Eur. Polym. J. 98 (2017).
[5] A.J. Uddin, Y. Okoshi, Y. Gotoh, M. Nagura, R. Endo, T. Hara, Melt spinning and laser-heated drawing of a new semiaromatic polyamide, PA9-F fiber, J. Polym. Sci. B Polym. Phys. 42 (2004) 433–444.
[6] T.F. Novinsky, C.A. Lange, L.J. Mathias, S. Osborn, R. Ayotte, S. Manning, Extrinsic melting behavior of polyamide 10T-co-6T and 12T-co-6T copolyterephthalamides, Polymer 51 (2010) 2417–2425.
[7] C. Leboeuf, D.A. Harbourne, Synthesis of Semi-crystalline Polyphthalamides through Reactive Extrusion of Hexamethylene Terephthalamide Oligomer with Lower-Melting, Semi-crystalline or Amorphous Polyamides, WO1999061509A1, 1999. https://patents.google.com/patent/WO1999061509A1. (Accessed 1 April 2019).
[8] T. Cousin, J. Gay, J. Dupuy, Molecular modelling of polyphthalamides thermal properties: comparison between modelling and experimental results, Polymer 53 (2012) 3262–3210.
[9] G.P. Desio, Characterization and properties of polyphthalamide/polycryl blends and polyphthalamide/polycryl blends of polyethylene, J. Vinyl. Additive Technol. 2 (1996) 229–234.
[10] J.S. Lyons, Time and temperature effects on the mechanical properties of glass-filled amide-based thermoplastics, Polym. Test. 17 (1998) 237–245.
[11] L.E. Govaert, T.A.P. Engels, M. Wendlandt, T.A. Tervoort, U.W. Suter, Does the microstructure influence on the origin of strain hardening in glassy polymers, Polymer 44 (2003) 2493–2502.
[12] E.M. Arruda, M.C. Boyce, Evolution of plastic anisotropy in amorphous polymers during finite straining, Int. J. Plast. 9 (1993) 697–720.
[13] R.N. Haward, The application of a Gauss-Eyring model to predict the behavior of thermoplastics in tensile experiments, J. Polym. Sci. B Polym. Phys. 33 (1995) 1481–1494.
[14] T.A. Tervoort, L.E. Govaert, Strain hardening behavior of polycarbonate in the glassy state, J. Rheol. 44 (2000) 1263–1277.
[15] A.R. Martins, A. Bocahut, M.-L. Michon, P. Sotta, Effect of intermolecular interactions on the viscoelastic behavior of entangled polyamide melts, J. Rheol. 63 (2019) 377–389.
[16] P.J. Flory, Principles of Polymer Chemistry, Cornell University Press, 1953. https://books.google.fr/books?id=CQ0EbE8TSRQC.
[17] J. Brandrup, E.H. Immergut, E.A. Gruilk, Polymer Handbook, fourth ed., Wiley, 2003. https://books.google.fr/books?id=VssV5ggAAQAAJ.
[18] M. Pareda, PhD Thesis, Dynamics of Polyamide in the Solid State in Presence of Solvents and in the Molten State, 1, Université Lyon, 2016.
[19] T.B. van Eer, L.E. Govaert, G.W.M. Peters, Mechanical performance of injection-molded poly(propylene): characterization and modeling, Macromol. Mater. Eng. 298 (2013) 348–358.
[20] C. Miliot, Multi-scale Characterization of Deformation Mechanisms of Bulk Polyamide 6 under Tensile Stretching below and above the Glass Transition, PhD Thesis, INSA de Lyon, 2016.
[21] C. Millot, Multi-scale Characterization of Deformation Mechanisms of Bulk Polyamide 6 under Tensile Stretching below and above the Glass Transition, PhD Thesis, INSA de Lyon, 2016.
[22] A.A. Griffith, The phenomena of rupture and flow in solids, Philos. Trans. R. Soc. Lond. – Ser. A: Contain. Pap. a Math. or Phys. Character 221 (1921) 163–198.
[23] C. G’sell, J.M. Hiver, A. Dahoun, Experimental characterization of deformation damage in solid polymers under tension, and its interrelation with necking, Int. J. Solids Struct. 39 (2002) 3857–3872.
[24] M. Poncelet, F. Addiego, A. Dahoun, True intrinsic mechanical behaviour of semi-crystalline and amorphous polymers: influences of volume deformation and cavities shape, Int. J. Plast. 40 (2013) 126–139.
[25] J.L. Halary, F. Laupétre, L. Monnerie, Mécanique des matériaux polymères, 2008. Belin.
[26] A.H. Committee, ASM Handbook: Mechanical Testing and Evaluation, ASM International, 2000. https://books.google.fr/books?id=weZLAQAIAAJ.
[27] L.E. Govaert, T.A.P. Engels, M. Wendlandt, T.A. Tervoort, U.W. Suter, Does the strain hardening modulus of glassy polymers scale with the flow stress? J. Polym. Sci. B Polym. Phys. 46 (2008) 2475–2481.
