



Thermal ageing of PTFE in the melted state: Influence of interdiffusion on the physicochemical structure

Victor Henri, Eric Dantras, Colette Lacabanne, Anca Goleanu Dieudonne,
Flavien Koliatene

► To cite this version:

Victor Henri, Eric Dantras, Colette Lacabanne, Anca Goleanu Dieudonne, Flavien Koliatene. Thermal ageing of PTFE in the melted state: Influence of interdiffusion on the physicochemical structure. *Polymer Degradation and Stability*, 2020, 171, pp.1-8. 10.1016/j.polymdegradstab.2019.109053 . hal-02436683

HAL Id: hal-02436683

<https://hal.science/hal-02436683>

Submitted on 13 Jan 2020

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.






Open Archive Toulouse Archive Ouverte (OATAO)

OATAO is an open access repository that collects the work of Toulouse researchers and makes it freely available over the web where possible

This is an author's version published in: <http://oatao.univ-toulouse.fr/25261>

Official URL: <https://doi.org/10.1016/j.polymdegradstab.2019.109053>

To cite this version:

Henri, Victor  and Dantras, Eric  and Lacabanne, Colette  and Dieudonne, Anca Goleanu and Koliatene, Flavien *Thermal ageing of PTFE in the melted state: Influence of interdiffusion on the physicochemical structure.* (2020) Polymer Degradation and Stability, 171. 1-8. ISSN 0141-3910

Any correspondence concerning this service should be sent
to the repository administrator: tech-oatao@listes-diff.inp-toulouse.fr

Thermal ageing of PTFE in the melted state: Influence of interdiffusion on the physicochemical structure

V. Henri ^{a, b}, E. Dantras ^{a, *}, C. Lacabanne ^a, A. Dieudonne ^b, F. Koliatene ^b

^a CIRMAT, Université Toulouse III Paul Sabatier, Physique des Polymères, 118 Route de Narbonne, 31062, Toulouse, France

^b Safran Electrical & Power - DTI EWISE, Parc d'activité d'Andromède, 1 Rue Louis Blériot, CS80049, 31702, Blagnac, France

ARTICLE INFO

Keywords:

PTFE
Interdiffusion
Thermal ageing
Dynamic mechanical analysis
Thermal analysis
Physico-chemical structure

ABSTRACT

PTFE is one of the most used polymer for electrical insulation. For future aircraft, PTFE will be exposed to thermal constraints above its melting temperature. Its high melt viscosity allows PTFE to be operable but it will be subjected to thermal oxidative ageing. PTFE presents two initial states, associated with its thermal history corresponding to the interdiffusion phenomenon. In the case of thermo oxidative ageing in the melt, interdiffusion impairs the thermal stability by shifting the thermal degradation towards lower temperature. While interdiffusion reduces the thermal stability for long time ageing, strong physical interactions reduce the impact of degradation on the mechanical behaviour for short time ageing. Chemical ageing induced by degradation promotes recrystallisation of PTFE shorter chains; this crystalline phase modifies the β anelastic relaxation mode. The $\tan \delta$ thermograms allows us to identify the β_1 and β_2 components of the anelastic effects of respectively the triclinic/hexagonal and hexagonal/pseudo hexagonal transitions observed by X Rays Diffraction. Upon chemical ageing, the evolution of the β mode is mainly governed by the decrease in the β_2 component corresponding to the pseudo hexagonal phase.

1. Introduction

The PolyTetraFluoroEthylene (PTFE) is a semi crystalline thermoplastic polymer that was synthesised in 1938 by DuPont de Nemours. PTFE is one of the most used polymer for electrical insulation due as well to its excellent dielectric strength (between 172 and 36 kV.mm⁻¹ according to authors) as its thermal stability (operating temperature up to 260 °C) [1–3]. Such properties are explained by its chemical structure and the C–F chemical bonds strength ($E_a \approx 500$ kJ.mol⁻¹) [4]. PTFE presents a helical conformation due to the repulsion between fluorine atoms which gives it a global apolar character despite its polar bonds.

Used in aeronautics as an electrical insulator, this polymer is exposed to both thermal and electrical constraints which can affect its physicochemical structure. Nowadays, it is used in a wide range of temperature (from 50 °C to 316 °C). For future generations of airships, insulation materials will have to reach temperature higher than PTFE melting temperature. In this case, it will be subjected to thermal oxidative ageing in the melted state [4–6], which may

impact its dielectric properties and be responsible for failures aboard aircrafts.

PTFE can be used above its melting temperature because it maintains its mechanical strength in the melted state. This specific behaviour is associated with the electrostatic interactions of fluorine atoms and its high molecular weight ($\approx 10^6$ g.mol⁻¹). Due to its high melt viscosity (10^{10} – 10^{12} Pa.s) [1,7] it is not processed as classical thermoplastic polymers. The method to produce PTFE tape is derived from ceramic process. PTFE tapes are obtained from the compaction of a highly crystallised fine powder (about 98%) [1] and then extruded in the solid state. At this step, the PTFE presents a structure composed by particles linked by fibrils, caused by shear stress during the extrusion [8–10]. Finally PTFE tapes is brought above its melting temperature, it leads to a dense material [1,3]. This final step, borrowed from ceramic process, is improperly called PTFE sintering. The mechanism involved is specific to polymers and should be called interdiffusion. With a sufficient molecular mobility brought by heat, the entanglement resulting from the macromolecule diffusion of two polymers induce the formation of a new interphase. It is widely used for welding or materials assembly [11]. In the case of PTFE, the interdiffusion occurs in the melted state, PTFE macromolecules interpenetrate in order to lead to a dense

* Corresponding author.

E-mail address: eric.dantras@univ-tlse3.fr (E. Dantras).

material. Due to the strong electrostatic interactions, the crystal organisation of PTFE is irreversibly modified. It results in a decrease in the crystallinity ratio and in an increase in the mechanical properties.

Studies have been carried out in order to follow the evolution during various ageing of extruded or raw PTFE [12–14]. As far as we know, this study is the first one to determine the influence of the interdiffusion phenomenon on chemical and physical structures associated with thermal ageing above the PTFE melting temperature.

2. Materials and methods

2.1. Materials

For this study, PTFE was used in the form of high crystallinity tape with a thickness of about 100 μm . Samples were in two initial states. The first initial state, called PTFE before interdiffusion, was the as received PTFE tape previous any melting. The second initial state, called PTFE after interdiffusion, is the same material after melting at 360 $^{\circ}\text{C}$ during 5 min. Interdiffusion was performed in a hot press between two aluminium plates.

A PTFE plate with a thickness of about 1 mm provide by Goodfellow was used in order to perform Dynamic Mechanical Analysis in shear mode. The as received plate has already been melted.

2.2. Thermal ageing protocol

The samples were cut in pieces of 150 \times 51 mm and placed on an aluminium plate where extremities were maintained to avoid overlaying during ageing. They were heated above the melting temperature at 450 $^{\circ}\text{C}$ in an oven and maintained at this temperature during 170 min–680 min. Each sample was weighed before and after ageing with a microbalance of 10^{-5} g resolution in order to quantify the ageing progress by the mass loss labelled Δw .

$$\Delta w = \frac{w - w_0}{w_0} \times 100 \quad (1)$$

2.3. ThermoGravimetric analysis (TGA)

In order to investigate evolution upon polymer degradation and thermal stability, ThermoGravimetric Analyses (TGA) were performed on a Q50 thermobalance from TA instrument. Samples were placed in two different atmospheres, oxidising atmosphere (synthetic air) or inert atmosphere (nitrogen), heated from room temperature to 1000 $^{\circ}\text{C}$ at a heating rate of 15 $^{\circ}\text{C} \cdot \text{min}^{-1}$ and under a flow rate of 10 $\text{mL} \cdot \text{min}^{-1}$.

2.4. Differential Scanning Calorimetry (DSC)

For the physical structure study, Differential Scanning Calorimetry (DSC) thermograms were performed on a PerkinElmer DSC 7. Measurements were carried out on aged samples with a mass between 5 and 20 mg. Analyses involved three successive heating and cooling runs between 50 $^{\circ}\text{C}$ and 400 $^{\circ}\text{C}$. Each run was performed at a heating rate of 10 $^{\circ}\text{C} \cdot \text{min}^{-1}$ under nitrogen flow.

The temperature of first order transitions was taken at the maximum of the peak. Crystallinity ratio of samples was calculated from melting enthalpy by using equation (2)

$$\chi_c = \frac{\Delta H_m}{\Delta H_{\infty}} \times 100 \quad (2)$$

where ΔH_m is the sample melt enthalpy ($\text{J} \cdot \text{g}^{-1}$) and ΔH_{∞} is the theoretical melt enthalpy of a 100% crystalline sample. For PTFE, ΔH_{∞} value is 82 $\text{J} \cdot \text{g}^{-1}$ [15–17].

2.5. Fourier Transform Infrared Spectroscopy (FTIR)

FTIR spectra were acquired with a Nicolet 5700 FT IR spectrometer. Due to samples thickness and opacity the spectrometer is using in ATR mode with a diamond crystal window. Each spectrum is the average of 32 consecutive spectra presented in the 400 to 4000 cm^{-1} range with 1 cm^{-1} in resolution. Spectral bands identification is reported in Table 1 [18–20].

2.6. Dynamic Mechanical Analysis (DMA)

Dynamic Mechanical Analyses (DMA) were realised on the ARES G2 strain controlled rheometer from TA Instruments. Sample dimensions are 35 mm \times 12.5 mm. Due to their thickness, PTFE films were analysed in tensile geometry mode in order to extract both storage $E'(T)$ and loss $E''(T)$ moduli. For each samples, heating runs were performed from 135 $^{\circ}\text{C}$ to 360 $^{\circ}\text{C}$ at a heating rate of 3 $^{\circ}\text{C} \cdot \text{min}^{-1}$. Strain and frequency were respectively fixed at 0.07% and 1 Hz.

PTFE plate aged samples were analysed in shear mode in order to extract storage $G'(T)$ and loss $G''(T)$ moduli. Sample dimensions are 40 mm \times 11 mm. Heating runs were performed from 135 $^{\circ}\text{C}$ to 360 $^{\circ}\text{C}$ at a heating rate of 3 $^{\circ}\text{C} \cdot \text{min}^{-1}$. Strain and frequency were respectively fixed at 0.1% and 1 Hz.

3. Results and discussion

3.1. Impact of the interdiffusion on the thermal stability

Fig. 1a and 1b shows the thermogravimetric analysis thermograms obtained respectively under air and nitrogen for samples before and after interdiffusion. The normalised weight w/w_0 and its derivative are plotted for each sample.

Before interdiffusion, PTFE presents, under inert atmosphere, a degradation mechanism in two distinct steps. According to the literature, the first step at 574.2 $^{\circ}\text{C}$ is associated with a first order kinetic mechanism that produces free radicals at chain ends, while the second step at 608.4 $^{\circ}\text{C}$ is associated with the reaction between free radicals and macromolecules that produces volatile tetra fluoroethylene C_2F_4 [4,5,21–25]. This last mechanism results in the complete degradation of the polymer. Isothermal degradation experiments were also carried out. They show that PTFE degradation starts for the isotherm 400 $^{\circ}\text{C}$ and presents significant weight loss as function of time for the isotherm 450 $^{\circ}\text{C}$. This last isotherm is chosen as ageing temperature. ATR FTIR analyses presented in Fig. 2 illustrate the decrease in intensity of the PTFE characteristic bands due to thermal degradation process. For purpose of clarity and due to the lack of any band above 1350 cm^{-1} , it was chosen to show

Table 1
Spectral bands identification and assignation of the bonds motions.

IR bands (cm^{-1})	Assignment
1200 1147	CF_2 symmetrical stretching
638	CF deformation
553	CF_2 rocking
501	CF_2 wagging

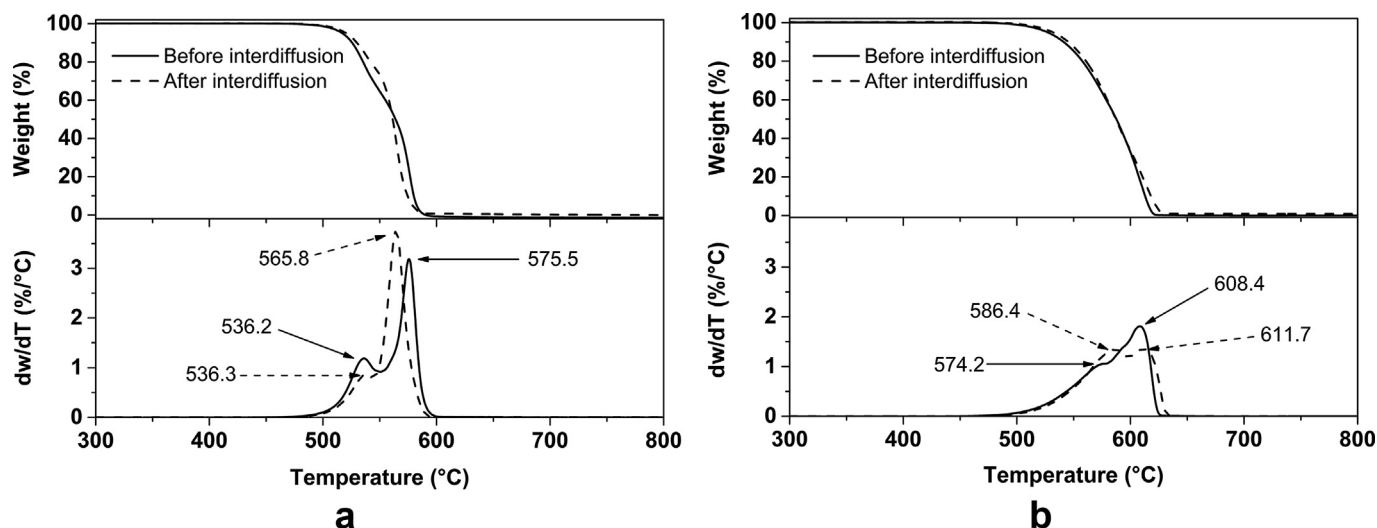


Fig. 1. Thermogravimetric analysis thermograms under b) inert atmosphere (nitrogen) and a) oxidising atmosphere (synthetic air) of PTFE before interdiffusion () and after interdiffusion ().

spectra between 400 and 1350 cm^{-1} . The production of monomers from the degradation of PTFE results in a depolymerisation mechanism [26].

Under oxidising atmosphere, PTFE presents also a two step degradation mechanism. The maximum of degradation for both steps is shifted to lower temperatures, $536.2\text{ }^{\circ}\text{C}$ and $575.5\text{ }^{\circ}\text{C}$ for the first and the second step respectively. The oxidising atmosphere has a weak influence on the degradation kinetics. For the first step, the value of the derivative increases from $1.0\%.\text{ }^{\circ}\text{C}^{-1}$ to $1.2\%.\text{ }^{\circ}\text{C}^{-1}$; the second step is strongly accelerated by the presence of oxygen, and the value of the derivative increases from $1.8\%.\text{ }^{\circ}\text{C}^{-1}$ to $3.1\%.\text{ }^{\circ}\text{C}^{-1}$. The presence of oxygen changes the depolymerisation mechanism in a chain scission mechanism. The random chain scission rate and reactions between radicals and macromolecules increases and produces volatile oxides like CO , CO_2 and COF_2 [5,27]. After interdiffusion under inert atmosphere, we observe a small shift of both degradation steps towards higher temperatures. The degradation kinetics evolution shows an increase in the free radicals creation and a decrease in random chain scissions. Under inert atmosphere PTFE after interdiffusion looks to be more stable than

before interdiffusion. Under oxidising atmosphere, the second degradation magnitude is stronger and the peak is shifted towards lower temperatures. For the first degradation, only the peak magnitude is modified: it is less intense. This evolution implies a decrease in the kinetic free radicals production. Since they are more reactive with oxygen, a more important chains degradation is observed.

The interdiffusion modifies the PTFE thermal stability. There is an opposite behaviour as a function of the atmosphere: Under inert atmosphere, the interdiffusion slightly improves the stability of the material by shifting the two degradations towards higher temperatures and decreases degradation kinetics; contrarily, under oxidising atmosphere, the interdiffusion reduces the thermal stability by increasing the reactivity of free radicals with macromolecules.

3.2. Effect of interdiffusion on thermal transitions

Fig. 3 presents the differential scanning calorimetry thermograms, before and after PTFE interdiffusion. For each sample, melting temperature and activation enthalpy as well as crystallinity ratio are reported in Table 2.

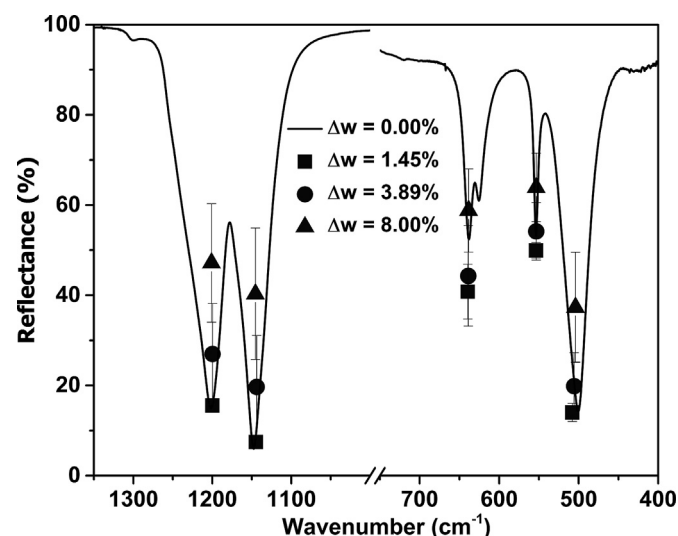


Fig. 2. ATR FTIR spectra of raw PTFE () and bands maxima after ageing (■ ● ▲).

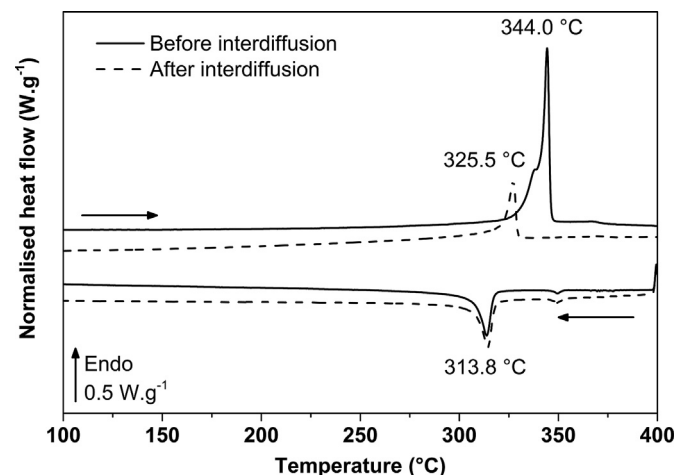


Fig. 3. DSC thermograms of PTFE before interdiffusion () and after interdiffusion ().

Table 2

Average values of melting and crystallisation temperatures, melting enthalpy and crystallinity ratio for aged PTFE before interdiffusion and after interdiffusion.

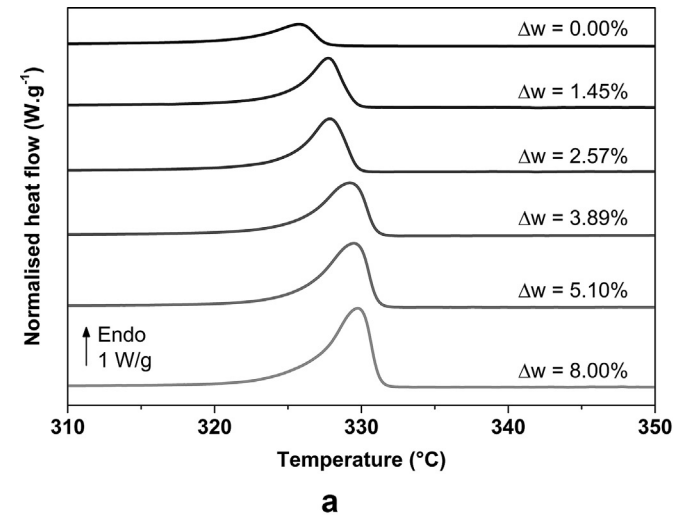
	T_m (°C)	ΔH_m (J.g ⁻¹)	χ_c (%)
Before interdiffusion			
Δw 0.00%	325.6 ± 0.1	23 ± 3	27 ± 3
Δw 1.45%	327.2 ± 0.4	31.4 ± 0.5	38 ± 1
Δw 2.57%	327.0 ± 0.8	33.5 ± 0.1	40 ± 1
Δw 3.89%	328.2 ± 0.8	39 ± 3	47 ± 4
Δw 5.10%	327.7 ± 0.1	42.4 ± 0.2	51 ± 1
Δw 8.00%	328.6 ± 0.4	50.3 ± 0.7	61 ± 1
After interdiffusion			
Δw 0.00%	325.6 ± 0.1	22 ± 3	27 ± 3
Δw 1.01%	328.0 ± 0.6	31.2 ± 0.9	38 ± 2
Δw 2.38%	327.3 ± 0.9	33.3 ± 0.5	41 ± 1
Δw 3.99%	328.0 ± 0.5	40.8 ± 0.3	50 ± 1
Δw 4.89%	328.6 ± 0.8	48 ± 1	58 ± 2
Δw 6.89%	328.7 ± 0.8	49.5 ± 0.7	60 ± 1

Before interdiffusion, PTFE exhibits an important endothermic peak at 344.0 °C corresponding to the melting of the crystalline phase; the crystallinity ratio is 77%. This peak presents a shoulder on the low temperature side indicating the existence of two crystalline phases: PTFE particles and fibrils. These last were formed under shear stress during extrusion [1]. During cooling, the temperature of the crystallisation peak is independent from the cooling rate. Strong electrostatic interactions in the molten state allow a very fast reorganisation during crystallisation which cannot be modified with usual cooling rates [28].

After interdiffusion, the melting enthalpy is divided by 3 and the melting temperature is shifted towards lower temperatures. The peak does not exhibit a shoulder anymore; PTFE presents a unique crystalline phase with a crystallinity ratio of 27%. Structural modifications associated with the interdiffusion phenomenon are irreversible.

PTFE thermograms do not exhibit glass transition. Due to the chain rigidity inherent to strong electrostatic interactions, the heat capacity step at the glass transition cannot be detected by calorimetric methods.

For the purpose of clarity, only the melting will be presented on the following DSC thermograms, crystallisation enthalpy values are reported in Table 2. In order to erase the thermal history after ageing, a first DSC cycle, heating and cooling scans, was performed between 50 and 400 °C at 10 °C/min.



Figs. 4a and 5a present the DSC thermograms (second run) of aged PTFE samples before and after interdiffusion respectively. Figs. 4b and 5b present the evolution of crystallinity ratio and melting temperature as a function of the chemical ageing associated with the Δw weight loss.

After ageing, an irreversible modification of the crystalline structure of all samples is observed. The melting temperatures are shifted towards higher temperatures and the melting enthalpy increases. The chemical ageing due to thermal stress modifies the chemical structure by reducing chain length (depolymerisation mechanism); shorter chains exhibit an easier crystallisation, forming larger crystallites with a higher melting temperature.

Suwa et al. proposed an empirical method to determine the number average molecular weight value [28,29]. By linking the well known number average molecular weight of several samples with their crystallisation enthalpy, and knowing that the crystallisation enthalpy is independent from the cooling rate, equation (3) is obtained.

$$\overline{M}_n = 2.1 \times 10^{10} \Delta H_c^{-5.16} \quad (3)$$

where \overline{M}_n is the number average molecular weight expressed in 10⁶ g.mol⁻¹, ΔH_c the crystallisation enthalpy expressed in cal.g⁻¹. When ΔH_c is in J.g⁻¹, the equation can be rewrite as follows:

$$\overline{M}_n = 2.1 \times 10^{10} (4.184 \times \Delta H_c)^{-5.16} \quad (4)$$

This equation, initially introduced for non aged sample, can give an idea of the molecular weight evolution. By using equation (4), we can calculate an approached value of the number average molecular weight for each aged sample in order to quantify the impact of the chemical ageing on the PTFE chain length. The calculated values of \overline{M}_n and the experimental values of ΔH_c are reported in Table 3.

Fig. 6 represents the evolution of the number average molecular weight as a function of the ageing time.

The number average molecular weight calculation confirms the chain shortening under chemical ageing. For short time ageing, both materials follow the same behaviour. The effect of the interdiffusion is significant for long times ageing. Polymer after interdiffusion appears more impacted.

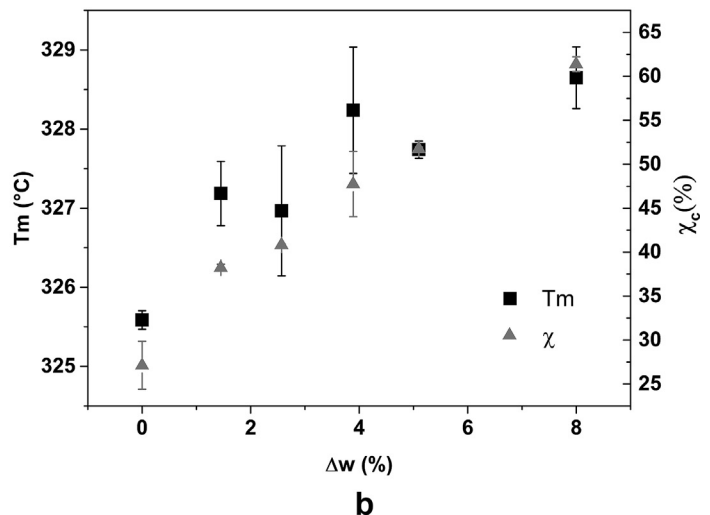


Fig. 4. a) Second DSC scans of aged PTFE after interdiffusion. b) Melting temperature and crystallinity ratio as a function of weight loss.

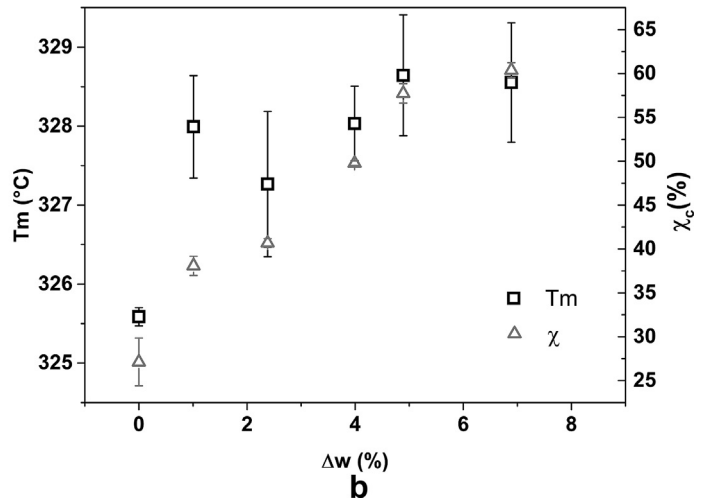
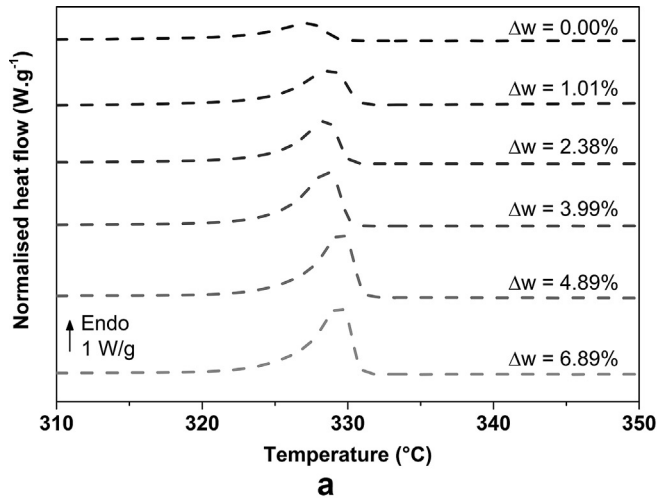


Fig. 5. a) Second DSC scans of aged PTFE before interdiffusion. b) Melting temperature and crystallinity ratio as a function of weight loss.

Table 3

Ageing time, crystallisation temperature, crystallisation enthalpy and calculated number-average molecular weight for aged PTFE before interdiffusion and after interdiffusion.

Ageing time (min)		ΔH_c (J.g ⁻¹)	\overline{Mn}_{calc} (g.mol ⁻¹)
Before interdiffusion			
Δw 1.45%	170	35.1 ± 0.3	(1.4 ± 0.1).10 ⁵
Δw 2.57%	255	36 ± 2	(1.3 ± 0.2).10 ⁵
Δw 3.89%	340	40 ± 2	(7 ± 1).10 ⁴
Δw 5.10%	510	46.2 ± 0.1	(3.4 ± 0.1).10 ⁴
Δw 8.00%	680	53.5 ± 0.4	(1.6 ± 0.1).10 ⁴
After interdiffusion			
Δw 1.01%	170	35 ± 2	(1.4 ± 0.2).10 ⁵
Δw 2.38%	255	36.4 ± 0.2	(1.2 ± 0.1).10 ⁵
Δw 3.99%	340	43.6 ± 0.2	(4.5 ± 0.1).10 ⁴
Δw 4.89%	420	50.3 ± 0.2	(2.2 ± 0.1).10 ⁴
Δw 6.89%	510	52.9 ± 0.2	(1.7 ± 0.1).10 ⁴

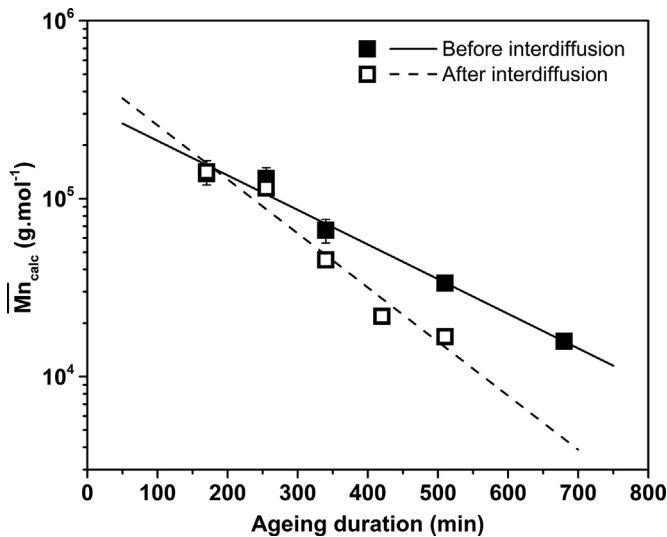


Fig. 6. Evolution of calculated number-average molecular weight as a function of ageing time for PTFE before interdiffusion and after interdiffusion.

3.3. Effect of interdiffusion on dynamic mechanical properties

Fig. 7 shows the Dynamical Mechanical Analysis thermograms, in elongation mode for PTFE before and after interdiffusion. Mechanical relaxations are shown on the E' storage modulus and the E'' loss modulus.

Between 0 and 30 °C, the β mechanical relaxation is associated with two successive crystal-crystal transitions whose temperatures are close to each other [30–33]. These transitions correspond to a drop of storage modulus due to a change of crystalline structure at atmospheric pressure, from a triclinic crystal under 0 °C to a hexagonal crystal until 30 °C and finally to a pseudo hexagonal crystal above 30 °C [34–36]. At 100 °C, the viscoelastic relaxation called the γ mode liberates the molecular mobility of the amorphous phase allowing the crystal/crystal transitions. At 120 °C the weak mechanical event designated as the α relaxation has been associated to the amorphous phase located between crystalline entities [37–39]. Since this phase is under stress, it corresponds to the rigid amorphous phase by opposing to the mobile amorphous phase corresponding to the classical glass transition. This relaxation cannot be observed before interdiffusion due to the high crystallinity ratio. The concept of Mobile Amorphous Phase (MAF) and Rigid Amorphous Phase (RAF) in PTFE has been proposed by Dlubeck et al. [12] and used later on by Calleja et al. [26]. At higher temperature, the last mechanical event has been associated with the melting. Even in the melted state, PTFE maintains a mechanical modulus of about 5 MPa.

After interdiffusion, the crystallinity ratio decrease is responsible for significant modifications of the mechanical behaviour. The increase in the γ peak magnitude is related to an increase in the mobile amorphous phase. The loss modulus decrease in β mechanical manifestation is explained by the crystallinity decrease. After interdiffusion, PTFE presents over the entire temperature range, a higher storage modulus. This storage modulus increase, even with a significant decrease in crystallinity, is related to the electrostatic interactions that strongly modify the mechanical behaviour. This behaviour is consistent with previous results on fluorine polymers as PVDF copolymers [40,41].

Fig. 8 presents the DMA thermograms of PTFE aged samples before and after interdiffusion. At low temperature, from 135 °C to 30 °C, samples have the same mechanical behaviour. After ageing, the vitreous storage modulus in the low temperature range

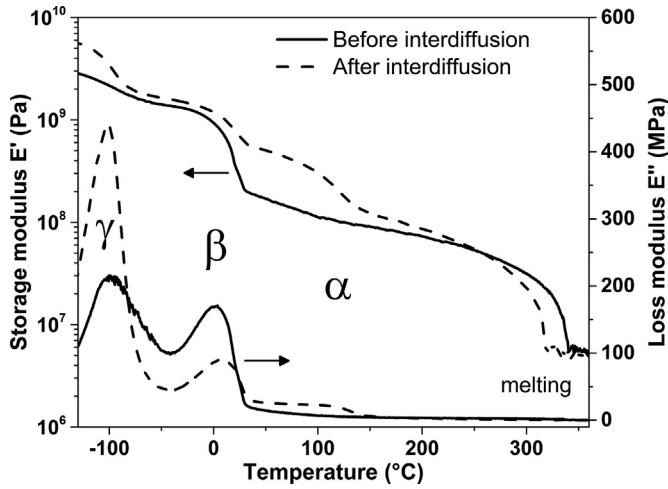


Fig. 7. DMA thermograms of PTFE before interdiffusion () and after interdiffusion ().

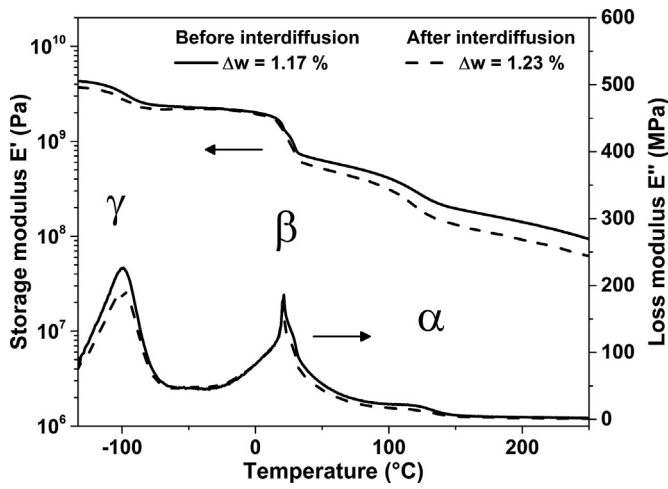


Fig. 8. DMA thermograms of aged PTFE before interdiffusion () and after interdiffusion ().

decreases from 5.56 GPa to 4.30 GPa. The magnitude of the γ relaxation decreases with the percentage of amorphous phase. The β transition is shifted towards higher temperatures and the loss peak is sharper than before ageing. It can be explained by the new morphology of crystallite formed during the cooling. We assume that the formation of a smaller quantity of large crystallites make the transition from one crystal structure to another more difficult. The two transitions overlap at higher temperature. From 30 °C to 250 °C for the sample aged after interdiffusion, there is no modification of the storage modulus after ageing. We notice a small decrease in the loss modulus at T_{α} . For the sample aged before interdiffusion, there is an important increase in the storage modulus from 30 °C on vitreous and rubbery plateau. The formation of new strong physical bonds by interdiffusion limits the influence of short time ageing on the mechanical behaviour.

Figs. 9 and 10 show respectively the loss modulus and the $\tan \delta$ temperature dependence, in the shear mode for samples aged after interdiffusion from 1.77% to 27.00% of weight loss.

Upon ageing, the evolutions of the magnitude of the γ and α modes are coupled: the percentage of mobile amorphous phase and rigid amorphous phase is modified in favour of the first one. The modification of the crystalline phase might explain this behaviour.

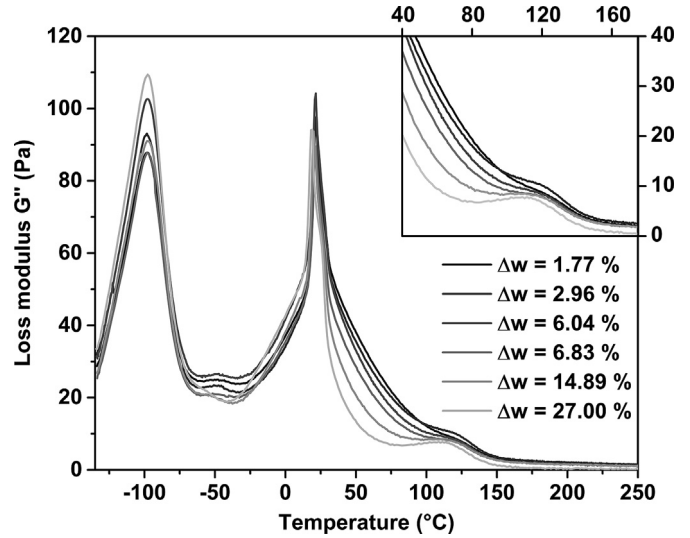


Fig. 9. DMA thermograms of G'' loss modulus for aged PTFE after interdiffusion. The framed detail represents the magnification of the α mode.

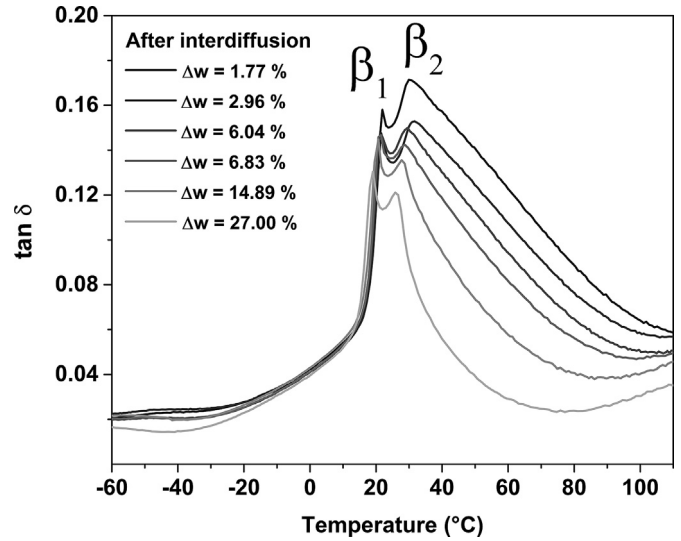


Fig. 10. DMA thermograms of $\tan \delta$ for aged PTFE after interdiffusion in the vicinity of crystal-crystal transitions.

The β relaxation is more impaired than the other modes. The $\tan \delta$ versus temperature representation allows us to distinguish two components designated as β_1 and β_2 in the order of increasing temperature. The two crystal crystal transitions – triclinic/hexagonal and hexagonal/pseudo hexagonal – observed by X rays diffraction [28] generate distinct anelastic effects. Upon ageing, the evolution is mainly governed by the decrease in the β_2 component. This result indicates that the hexagonal phase is favoured upon ageing so that the pseudo hexagonal phase decreases significantly.

4. Conclusion

The effect of interdiffusion on the thermal and mechanical behaviour of PTFE during a thermal ageing in the melted state is studied. Thermal ageing was carried out at 450 °C on raw PTFE and PTFE after interdiffusion. Ageing was always performed in an oven under oxidising atmosphere.

TGA coupled with FTIR spectroscopy reveals a degradation mechanism by depolymerisation. Under oxidising atmosphere, interdiffusion impairs the PTFE thermal stability by increasing the reactivity of the free radicals.

DSC analyses show an irreversible modification of transitions after chemical ageing under thermal stress. The melting temperature is shifted towards higher temperature and the melting enthalpy increases. The depolymerisation mechanism reduces chain length so that larger crystallites, which melt at higher temperature, are formed. By using empirical equation, we deduce from crystallisation enthalpy the number average molecular weight. Interdiffusion improves the stability of PTFE for short time ageing; it is the contrary for long time ageing.

DMA provides complementary data due to the analyses of storage modulus, loss modulus and $\tan \delta$. At 100 °C, the γ visco elastic relaxation liberates the molecular mobility of the mobile amorphous phase. It corresponds to the classical glass transition. At 120 °C, the weak α relaxation has been associated to the amorphous phase located between crystalline entities: i.e. the rigid amorphous phase.

After interdiffusion, the decrease in crystallinity is responsible for significant modifications of the mechanical behaviour. The concomitant increase in the γ peak reflects the evolution of the mobile amorphous phase.

The $\tan \delta$ thermograms allows us to identify the β_1 and β_2 components of the anelastic effects of respectively the triclinic/hexagonal and hexagonal/pseudo hexagonal transitions observed by X rays diffraction. Upon chemical ageing, the evolution of the β mode is mainly governed by the decrease in the β_2 component corresponding to the pseudo hexagonal phase.

Author contribution statement

V. Henri: Conceptualization, Methodology, Validation, Investigation; Writing Review & Editing. E. Dantras: Conceptualization, Methodology, Validation, Investigation, Supervision, Writing Review & Editing. C. Lacabanne: Conceptualization, Methodology, Validation, Investigation, Supervision, Writing Review & Editing. A. Dieudonne: Conceptualization, Methodology, Validation, Investigation, Supervision, Writing Review & Editing. F. Koliatene: Conceptualization, Methodology, Validation, Investigation, Supervision, Writing Review & Editing.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Acknowledgements

The authors would like to thank SAFRAN Electrical and Power, NEXANS and the ANRT for the financial support in this project.

References

- [1] S. Ebnesajjad, *Expanded PTFE Applications Handbook*, Elsevier, 2017.
- [2] J. Bonnet, *Polymères Fluorés*, 2004. Tech. l'ingénieur, no. AM3390 V1.
- [3] F. Barbas, *Le Polytetrafluoroéthylène: Origines, Dérivés, Fabrication, Composés: Ses Multiples Applications*, Caliop, 1962.
- [4] J.A. Conesa, R. Font, *Polytetrafluoroethylene decomposition in air and nitrogen*, *Polym. Eng. Sci.* 41 (12) (2001) 2137–2147.
- [5] L.A. Wall, J.D. Michaelsen, *Thermal decomposition of polytetrafluoroethylene in various gaseous atmosphere*, *J. Res. Natl. Bur. Stand.* 56 (1) (1956) 1934.
- [6] C.M. Simon, W. Kaminsky, *Chemical recycling of polytetrafluoroethylene by pyrolysis*, *Polym. Degrad. Stab.* 62 (1) (1998) 1–7.
- [7] A. Frick, D. Sich, G. Heinrich, C. Stern, M. Gossi, T.A. Tervoort, *Relationship*

- between structure and mechanical properties of melt processable PTFE: influence of molecular weight and comonomer content, *Macromol. Mater. Eng.* 298 (9) (2013) 954–966.
- [8] S.G. Hatzikiriakos, A.B. Ariawan, S. Ebnesajjad, *Paste extrusion of polytetrafluoroethylene (PTFE) fine powder resins*, *Can. J. Chem. Eng.* 80 (6) (2002) 1153–1165.
- [9] D. Vavlekas, et al., "Role of PTFE paste fibrillation on Poisson's ratio, *Polym. Test.* 61 (2017) 65–73.
- [10] H.A. Ardakani, E. Mitsoulis, S.G. Hatzikiriakos, *A simple improved mathematical model for polytetrafluoroethylene (PTFE) paste extrusion*, *Chem. Eng. Sci.* 89 (2013) 216–222.
- [11] S.S. Voyutskii, V.L. Vakula, *The role of diffusion phenomena in polymer-to-polymer adhesion*, *J. Appl. Polym. Sci.* 131 (3) (1963) 475–491.
- [12] X.L. Huang, J. Martinez-Vega, D. Malec, *Morphological evolution of polytetrafluoroethylene in extreme temperature conditions for aerospace applications*, *J. Appl. Polym. Sci.* 131 (3) (2014) 39841.
- [13] T. Wang, J. Wang, P. Yan, J. Ran, *Influence of temperature on electrical aging characteristics of polytetrafluoroethylene under nanosecond pulses*, *IEEE Trans. Dielectr. Electr. Insul.* 22 (2) (2015) 1171–1175.
- [14] K. Schierholz, U. Lappan, K. Lunkwitz, *Electron beam irradiation of polytetrafluoroethylene in air: investigations on the thermal behaviour*, *Nucl. Instrum. Methods Phys. Res. Sect. B Beam Interact. Mater. Atoms* 151 (1–4) (1999) 232–237.
- [15] G. Dlubek, et al., *Glass transition and free volume in the mobile (MAF) and rigid (RAF) amorphous fractions of semicrystalline PTFE: a positron lifetime and PVT study*, *Polymer* 46 (16) (2005) 6075–6089.
- [16] H.W. Starkweather, *Melting and crystalline transitions in normal perfluoroalkanes and poly(tetrafluoroethylene)*, *Macromolecules* 19 (4) (1986) 1131–1134.
- [17] H.W. Starkweather, *The effect of heating rate on the melting of polytetrafluoroethylene*, *J. Polym. Sci. Polym. Phys. Ed* 23 (6) (1985) 1177–1185.
- [18] S. Fai Lau, H. Suzuki, B. Wunderlich, *The thermodynamic properties of polytetrafluoroethylene*, *J. Polym. Sci. Polym. Phys. Ed* 22 (3) (1984) 379–405.
- [19] H.W. Starkweather, R.C. Ferguson, D.B. Chase, J.M. Minor, *Infrared spectra of amorphous and crystalline poly(tetrafluoroethylene)*, *Macromolecules* 18 (9) (1985) 1684–1686.
- [20] J. Mihály, et al., *FTIR and FT-Raman spectroscopic study on polymer based high pressure digestion vessels*, *Croat. Chem. Acta* 79 (3) (2006) 497–501.
- [21] S.L. Madorsky, V.E. Hart, S. Straus, V.A. Sedlak, *Thermal degradation of tetrafluoroethylene and hydrofluoroethylene polymers in a vacuum*, *J. Res. Natl. Bur. Stand.* 51 (6) (1953) 327, 1934.
- [22] B. Atkinson, V.A. Atkinson, *The thermal decomposition of tetrafluoroethylene*, *J. Chem. Soc.* (1957) 2086.
- [23] J.C. Siegle, L.T. Muus, T.-P. Lin, H.A. Larsen, *The molecular structure of perfluorocarbon polymers. II. Pyrolysis of polytetrafluoroethylene*, *J. Polym. Sci. - Part A Gen. Pap.* 2 (1) (1964) 391–404.
- [24] R.E. Florin, L.A. Wall, D.W. Brown, L.A. Hymo, D. Michaelsen, *Factors affecting the thermal stability of polytetrafluoroethylene*, *J. Res. Natl. Bur. Stand.* 53 (2) (1954) 121–130, 1934.
- [25] A. Donato, M. Lenzi, A. Mele, *Thermal decomposition of polytetrafluoroethylene oxide*, *J. Macromol. Sci. Part A - Chem.* 1 (3) (1967) 429–438.
- [26] K. Pielichowski, J. Njuguna, *Thermal Degradation of Polymeric Materials*, Smithers Rapra Press, 2008.
- [27] L. Odochian, C. Moldoveanu, D. Maftai, "TG FTIR study on thermal degradation mechanism of PTFE under nitrogen atmosphere and in air. Influence of the grain size, *Thermochim. Acta* 598 (2014) 28–35.
- [28] T. Suwa, M. Takehisa, S. Machi, *Melting and crystallization behavior of poly(tetrafluoroethylene). New method for molecular weight measurement of poly(tetrafluoroethylene) using a differential scanning calorimeter*, *J. Appl. Polym. Sci.* 17 (11) (1973) 3253–3257.
- [29] T. Suwa, T. Seguchi, M. Takehisa, S. Machi, *Effect of molecular weight on the crystalline structure of polytetrafluoroethylene as-polymerized*, *J. Polym. Sci. Polym. Phys. Ed* 13 (11) (1975) 2183–2194.
- [30] R.K. Eby, E.S. Clark, B.L. Farmer, G.J. Piermarini, S. Block, *Crystal structure of poly(tetrafluoroethylene) homo- and copolymers in the high pressure phase*, *Polymer* 31 (12) (1990) 2227–2237.
- [31] E.S. Clark, *The molecular conformations of polytetrafluoroethylene: forms II and IV*, *Polymer* 40 (16) (1999) 4659–4665.
- [32] P.J. Rae, D.M. Dattelbaum, *The properties of poly(tetrafluoroethylene) (PTFE) in compression*, *Polymer* 45 (22) (2004) 7615–7625.
- [33] H.W. Starkweather, *A dynamic mechanical study of the β -relaxation in poly(tetrafluoroethylene)*, *Macromolecules* 19 (10) (1986) 2541–2544.
- [34] E.N. Brown, D.M. Dattelbaum, *The role of crystalline phase on fracture and microstructure evolution of polytetrafluoroethylene (PTFE)*, *Polymer* 46 (9) (2005) 3056–3068.
- [35] E.N. Brown, P.J. Rae, E. Bruce Orler, G.T. Gray, D.M. Dattelbaum, *The effect of crystallinity on the fracture of polytetrafluoroethylene (PTFE)*, *Mater. Sci. Eng. C* 26 (8) (2006) 1338–1343.
- [36] E.N. Brown, D.M. Dattelbaum, D.W. Brown, P.J. Rae, B. Clausen, *A new strain path to inducing phase transitions in semi-crystalline polymers*, *Polymer* 48 (9) (2007) 2531–2536.
- [37] N.G. McCrum, *An internal friction study of polytetrafluoroethylene*, *J. Polym. Sci.* 34 (127) (1959) 355–369.
- [38] G. Calleja, A. Jourdan, B. Ameduri, J.P. Habas, *Where is the glass transition temperature of poly(tetrafluoroethylene)? A new approach by dynamic*

- rheometry and mechanical tests, *Eur. Polym. J.* 49 (8) (2013) 2214–2222.
- [39] Y. Ohzawa, Y. Wada, Mechanical relaxations and transitions in polytetrafluoroethylene, *Jpn. J. Appl. Phys.* 3 (8) (1964) 436–447.
- [40] A. Roggero, E. Dantras, C. Lacabanne, Poling influence on the mechanical properties and molecular mobility of highly piezoelectric P(VDF-TrFE) copolymer, *J. Polym. Sci., Part B: Polym. Phys.* 55 (18) (2017) 1414–1422.
- [41] B. Ameduri, From vinylidene fluoride (VDF) to the applications of VDF-containing polymers and copolymers: recent developments and future trends, *Chem. Rev.* 109 (12) (2009) 6632–6686.