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

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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 δ 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 ther moplastic 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 17.2 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 ($E_a \approx 500 \text{ kJ.mol}^{-1}$) [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 fluo rine atoms and its high molecular weight ($\approx 10^6$ g.mol⁻¹). Due to its high melt viscosity (10¹⁰-10¹² 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 macromol ecule 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

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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 $\mu m.$ 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 °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 150×51 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 °C in an oven and maintained at this temper ature 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 .

$$\Delta w = \frac{w - w_0}{w_0} \times 100 \tag{1}$$

2.3. ThermoGravimetric analysis (TGA)

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

2.4. Differential Scanning Calorimetry (DSC)

For the physical structure study, Differential Scanning Calorim etry (DSC) thermograms were performed on a PerkinElmer DSC 7. Measurements were carried out on aged samples with a mass be tween 5 and 20 mg. Analyses involved three successive heating and cooling runs between 50 °C and 400 °C. Each run was performed at a heating rate of 10 °C.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)

$$\chi_c = \frac{\Delta H_m}{\Delta H_\infty} \times 100 \tag{2}$$

where ΔH_m is the sample melt enthalpy (J.g $^{-1}$) and ΔH_{∞} is the theoretical melt enthalpy of a 100% crystalline sample. For PTFE, ΔH_{∞} value is 82 J.g $^{-1}$ [15 $^{-1}$ 7].

2.5. Fourier Transform Infrared Spectroscopy (FTIR)

FTIR spectra were acquired with a Nicolet 5700 FT IR spec trometer. 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 iden tification 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 di mensions 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 °C to 360 °C at a heating rate of 3 °C.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 °C to 360 °C at a heating rate of 3 °C.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 °C is associated with a first order kinetic mechanism that produces free radicals at chain ends, while the second step at 608.4 °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 ex periments were also carried out. They show that PTFE degradation starts for the isotherm 400 °C and presents significant weight loss as function of time for the isotherm 450 °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 1Spectral 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	

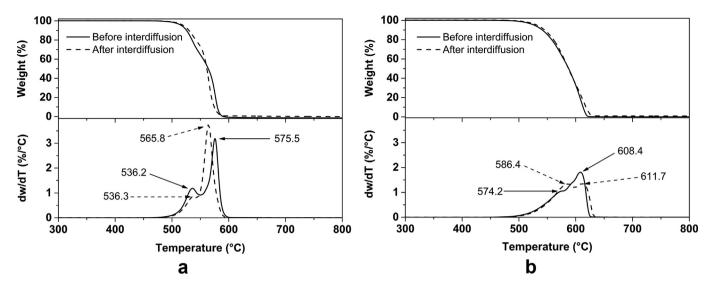


Fig. 1. Thermogravimetric analysis thermograms under b) inert atmosphere (nitrogen) and a) oxidising atmosphere (synthetic air) of PTFE before interdiffusion () and after interdiffusion ().

spectra between 400 and 1350 cm⁻¹. The production of monomers from the degradation of PTFE results in a depolymerisation mech anism [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 °C and 575.5 °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%. $^{\circ}$ C⁻¹ to 1.2%. $^{\circ}$ C⁻¹; the second step is strongly accelerated by the presence of oxygen, and the value of the derivative increases from 1.8%. C^{-1} to 3.1%. $^{\circ}C^{-1}$. The presence of oxygen changes the depolymerisation mechanism in a chain scission mechanism. The random chain scission rate and re actions between radicals and macromolecules increases and pro duces volatile oxides like CO, CO₂ and COF₂ [5,27]. After interdiffusion under inert atmosphere, we observe a small shift of both degradation steps towards higher temperatures. The degra dation 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 temper atures and decreases degradation kinetics; contrarily, under oxi dising 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 thermo grams, before and after PTFE interdiffusion. For each sample, melting temperature and activation enthalpy as well as crystallinity ratio are reported in Table 2.

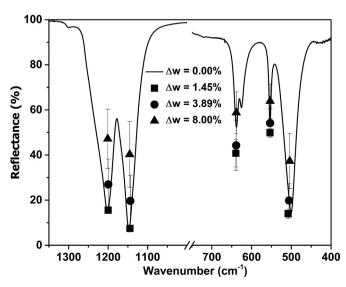


Fig. 2. ATR FTIR spectra of raw PTFE () and bands maxima after ageing (■ ● ▲).

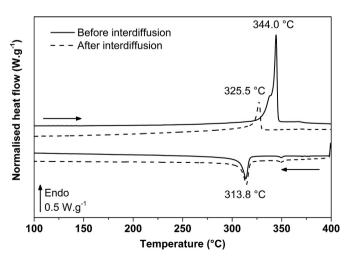


Fig. 3. DSC thermograms of PTFE before interdiffusion () and after interdiffusion ().

Table 2Average 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 (%)			
Befo	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 crys talline phases: PTFE particles and fibrils. These last were formed under shear stress during extrusion [1]. During cooling, the tem perature 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 mod ifications 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 calori metric 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 $^{\circ}\text{C}$ at 10 $^{\circ}\text{C/min}.$

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 associ ated 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 know number average molecular weight of several samples with their crystallisation enthalpy, and knowing that the crystal lisation enthalpy is independent from the cooling rate, equation (3) is obtained.

$$\overline{M_n}$$
 2.1 × 10¹⁰ $\Delta H_c^{-5.16}$ (3)

where \overline{Mn} is the number average molecular weight expressed in 10^6 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 × 10¹⁰ (4.184 × ΔH_c)^{-5.16} (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 mo lecular 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{Mn} 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 inter diffusion is significant for long times ageing. Polymer after inter diffusion appears more impacted.

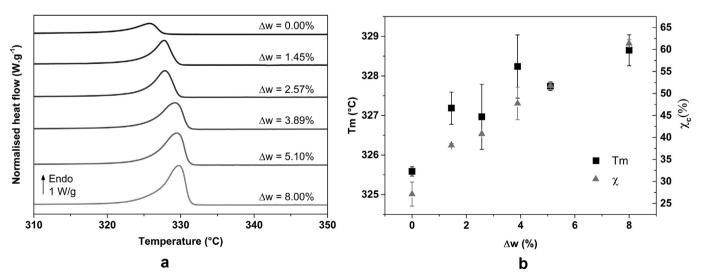


Fig. 4. a) Second DSC scans of aged PTFE after interdiffusion. b) Melting temperature and crystallinity ratio as a function of weight loss.

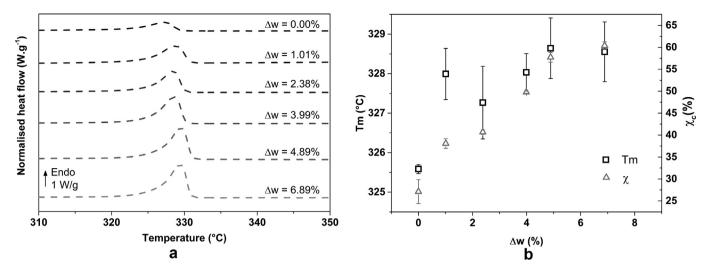


Fig. 5. a) Second DSC scans of aged PTFE before interdiffusion. b) Melting temperature and crystallinity ratio as a function of weight loss.

Table 3Ageing 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)	$\overline{\textit{Mn}}_{\textit{calc}}(\text{g.mol}^{-1})$		
Before interdiffusion						
Δw	1.45%	170	35.1 ± 0.3	$(1.4 \pm 0.1).10^5$		
Δw	2.57%	255	36 ± 2	$(1.3 \pm 0.2).10^5$		
Δw	3.89%	340	40 ± 2	$(7 \pm 1).10^4$		
Δw	5.10%	510	46.2 ± 0.1	$(3.4 \pm 0.1).10^4$		
Δw	8.00%	680	53.5 ± 0.4	$(1.6 \pm 0.1).10^4$		
After interdiffusion						
Δw	1.01%	170	35 ± 2	$(1.4 \pm 0.2).10^5$		
Δw	2.38%	255	36.4 ± 0.2	$(1.2 \pm 0.1).10^5$		
Δw	3.99%	340	43.6 ± 0.2	$(4.5 \pm 0.1).10^4$		
Δw	4.89%	420	50.3 ± 0.2	$(2.2 \pm 0.1).10^4$		
Δw	6.89%	510	52.9 ± 0.2	$(1.7 \pm 0.1).10^4$		

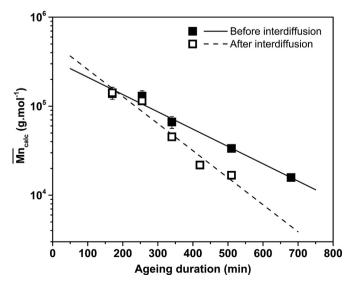


Fig. 6. Evolution of calculated number-average molecular weight as a function of ageing time for PTFE before interdiffusion and after interdiffusion.

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. Me chanical 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 an hexagonal crystal until 30 °C and finally to a pseudo hexagonal crystal above 30 °C [34-36]. At 100 °C, the viscoelastic relaxa tion 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 crystal linity ratio. The concept of Mobile Amorphous Phase (MAF) and Rigid Amorphous Phase (RAF) in PTFE has been proposed by Dlu beck 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 maintain a mechanical modulus of about 5 MPa.

After interdiffusion, the crystallinity ratio decrease is respon sible 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 me chanical 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

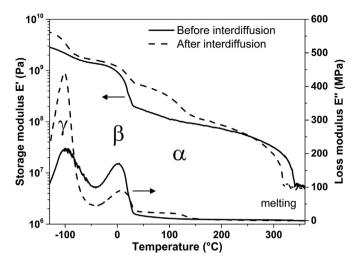


Fig. 7. DMA thermograms of PTFE before interdiffusion () and after interdiffusion ().

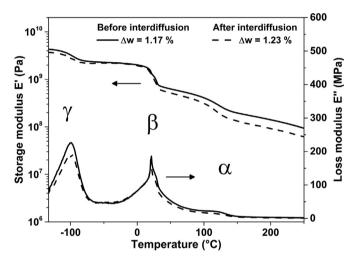


Fig. 8. DMA thermograms of aged PTFE before interdiffusion () and after interdiffusion ().

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 sharpener than before ageing. It can be explained by the new morphology of crystallite formed during the cooling. We as sume 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 in fluence of short time ageing on the mechanical behaviour.

Figs. 9 and 10 show respectively the loss modulus and the tan δ 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.

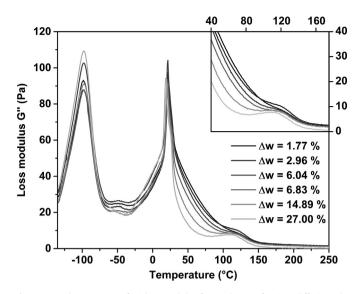


Fig. 9. DMA thermograms of G'' loss modulus for aged PTFE after interdiffusion. The framed detail represents the magnification of the α mode.

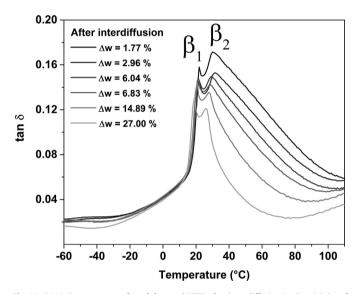


Fig. 10. DMA thermograms of tan δ for aged PTFE after interdiffusion in the vicinity of crystal-crystal transitions.

The β relaxation is more impaired than the other modes. The tan δ 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/hexag onal 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 $^{\circ}$ 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 tempera ture is shifted towards higher temperature and the melting enthalpy increases. The depolymerisation mechanism reduces chain length so that larger crystallites, which melt at higher tem perature, 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 δ . 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 δ 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.

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