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Ageing of polyimide under thermal stress: Relaxational effects and charge transport

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ABSTRACT

Polyimide is one of the most used polymer for electrical insulation in severe environment. For future aircrafts, polymer electrical insulation will be exposed to thermal constraints that can affect its physicochemical structure. Effects of thermal ageing are studied through their impact on the relaxational behaviour. Thermal degradation impairs first the aromatic entities and lately the carbonyls. It is responsible for the strong acceleration of mobility observed for both localised β and γ relaxation modes. Both DMA and swelling test exhibit an acceleration of localized molecular mobility. However, as the local mobility is accelerated, the increase in heterogeneities visible through the evolution of the MWS polarisation brings up to light a change in the charge transport mechanism. The chain scission degradation mechanism, leads to a decrease of the density of deep traps. It explains the evolution of both the value of DC conductivity and its activation energy upon ageing.

1. Introduction

Aeronautic environment is characterised by several kinds of stresses applied in a wide range of temperature, pressure and electric field. For devices requiring electrical insulation, materials are exposed to combined thermal and electrical constraints. In fact, polymers used as electrical insulator have to operate at temperatures up to 260 °C [1] under high frequency electric fields.

The introduction of the Polyimide class of polymer as electrical insulator was the response to a need of high temperature operating materials for aeronautic applications. Polyimides possess many attributes that justify their use for high performance applications. Their photosensitive properties are required for microelectronic component fabrication; moreover, their high radiation tolerance and mechanical properties allows them to be used for applications in space environment. Despite the difficulty of manufacturing due to both insolubility and high-temperature transition, their excellent dielectric strength (from 118 to 300 kV/mm according to previous studies) and their high thermal stability (isothermal degradation is about 0.01 wt %·h⁻¹ at 300 °C) make polyimides suitable for aeronautic applications [2–6].

Polyimides are synthesised by a two-step method. First, it consists to use step polymerisation between a dianhydride and a diamine in order to synthesis the soluble precursor named poly(amic

acid). Second, the final polyimide is formed by the thermal conversion of this poly(amic acid). This allow a large variety of thermoplastic polyimides depending on the different precursors [7,8].

Polyimide Kapton HN is an amorphous high-performance thermoplastic polymer synthesised in 1960s by DuPont de Nemours. The presence of several aromatic cycles in the main chain explains the stiffness of macromolecules and the high thermal stability of this amorphous polymer [7]. In this work, polyimide will refer to polyimide Kapton [8].

Polyimide is used in aeronautics coupled with PTFE for electrical insulation under both thermal and electrical stresses that can modify its physicochemical structure [9]. The thermal properties of polyimide are remarkable with an onset of thermal degradation at 585 °C and a high thermal stability (isothermal degradation < 0.1%/h at 300 °C). Nowadays, it is used in a wide range of temperature (from -55 °C to 260 °C). Then, it will be subjected to thermal-oxidative ageing that can deteriorate dielectric properties and may be responsible for failures aboard aircrafts.

This last decade, studies were carried out in order to follow the ageing of various polyimides under different stresses [10–13]. Ortelli *et al.* [14] provided important information on the degradation mechanism. Moreover, evolutions of electrical properties with ageing were investigated by Sombel *et al.* [12] and reveal an improvement in electrical properties of PI with ageing. Mechanical properties were also well studied in order to determine the origin of mechanical relaxation by Bernier and Kline [15], later by Harris and Robeson [16] then Habas *et al.* [17]. However, as far as we know,

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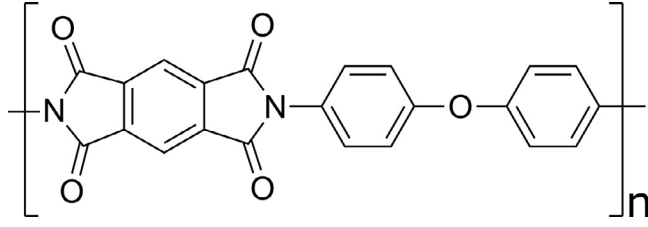


Fig. 1. Polyimide monomer unit.

none of these studies focused on the effect of chemical ageing on molecular mobility and the link with the evolutions of electrical properties. In order to predict lifetime of this material used in severe environment it is important to understand this relation. This paper aims to determine the evolution of the electrical properties of polyimide by studying the evolution of chemical structure and molecular mobility through various experimental techniques.

2. Materials and methods

2.1. Materials

For this study, Polyimide (PI, Kapton commercialised by Dupont/USA) was used in the form of a totally amorphous film with a thickness of about 50 μm .

2.2. Thermal ageing protocol

Two morphologies were used for this study. First, samples used for mechanical and absorption tests were rectangles $32 \times 12.5 \text{ mm}^2$ placed on an aluminium plate during ageing. Second, samples used for dielectric analysis were disk shaped 40 mm in diameter.

Both kind of samples were heated at about 450 $^{\circ}\text{C}$ under oxidising atmosphere, in an oven and maintained at this temperature during 60 min to 180 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 Δm .

$$\Delta m = \frac{m - m_0}{m_0} \times 100 \quad (1)$$

After ageing, all samples were conditioned under room atmosphere during several days in order to allow water intake. All further analyses were performed on hydrated samples ($\approx 0.5\%$ of water content).

The temperature of ageing was chosen in accordance with literature and thermogravimetric analysis. This temperature is well below the onset of thermal degradation (585 $^{\circ}\text{C}$) but at sufficiently high temperatures to allow a chemical ageing according to isothermal TGA ($\Delta m \approx 2\%$ at 400 $^{\circ}\text{C}$ and $\Delta m \approx 10\%$ at 450 $^{\circ}\text{C}$ during 180 min). According to literature, the accelerated ageing is performed assuming that the high temperature does not modify the ageing mechanism [18–22].

Table 1 show the ageing time and corresponding mass loss for each aged samples prepared for this study.

Table 1
Ageing time and corresponding mass loss for aged samples.

Ageing time (min)	Mass loss (%)
0	$\Delta m = 0.00$
60	$\Delta m = 0.73 \pm 0.01$
120	$\Delta m = 1.59 \pm 0.22$
180	$\Delta m = 2.78 \pm 0.11$

2.3. Broadband dielectric spectroscopy

Broadband Dielectric Spectroscopy (BDS) is a well-known technique used for the analysis of dielectric relaxations and charge transport in polymers [23]. Analyses were performed on a Novo-control BDS 4000 impedance analyser on disk shaped samples. A sinusoidal voltage of 1 V amplitude was applied isothermally in the frequency range $[10^{-2}; 10^6 \text{ Hz}]$ every 5 $^{\circ}\text{C}$ from -150 to 250 $^{\circ}\text{C}$. The complex impedance $Z^*(\omega)$ was measured in order to extract both complex permittivity and complex conductivity of the material by using the following equations.

$$\varepsilon^*(\omega) = \varepsilon'(\omega) - i\varepsilon''(\omega) = \frac{1}{i\omega C_0 Z^*(\omega)} \quad (2)$$

$$\sigma^*(\omega) = \sigma'(\omega) + i\sigma''(\omega) = \frac{e}{SZ^*} \quad (3)$$

Where $C_0 = \frac{\varepsilon_0 S}{e}$, S is the section of the sample, e is its thickness and ε_0 is the vacuum permittivity.

It is possible at low frequency, to extract from the real part of the complex conductivity the value of the conductivity associated with the free charge transport σ_{DC} by using the Eq. (4) [24].

$$\sigma'(\omega) = \sigma_{\text{DC}} + A\omega^S \quad (4)$$

Static conductivity σ_{DC} data were fitted according to Arrhenius equation.

$$\sigma_{\text{DC}} = \sigma_0 \exp\left(\frac{-\Delta H}{RT}\right) \quad (5)$$

Analyses of relaxation phenomenon were made according to the Havriliak-Negami parametric equation [25,26].

$$\varepsilon^* = \varepsilon_{\infty} + \frac{\varepsilon_s - \varepsilon_{\infty}}{(1 + (i\omega\tau_{\text{HN}})^{\alpha_{\text{HN}}})^{\beta_{\text{HN}}}} \quad (6)$$

Where ε_{∞} and ε_s are respectively the high and low frequency limits of relative permittivity. τ_{HN} is the average characteristic relaxation time of the distribution, α_{HN} and β_{HN} are two adjustable parameters for respectively the width and the asymmetry of the relaxation mode. τ_{HN} is the most pertinent relaxation time for describing experimental data.

The temperature dependence of relaxation modes was fitted by using the Arrhenius equation.

$$\tau(T) = \tau_0 \exp\left(\frac{\Delta H}{RT}\right) \quad (7)$$

where τ_0 is the pre-exponential factor, ΔH is the activation energy in J.mol^{-1} , and R are the ideal gas constants.

2.4. Dynamic mechanical analysis

Dynamic Mechanical Analyses (DMA) were realised on the ARES G2 strain-controlled rheometer from TA Instruments. Sample dimensions were 35 mm \times 12.5 mm. Samples thickness of 50 μm require an analysis in the tensile geometry mode in order to extract both storage $E'(T)$ and loss $E''(T)$ moduli. For each sample, heating runs were performed at a heating rate of 3 $^{\circ}\text{C.min}^{-1}$ from -135 $^{\circ}\text{C}$ to 300 $^{\circ}\text{C}$. Strain and frequency were respectively fixed at 0.05 % and 1 Hz.

2.5. Penetrant absorption tests

Penetrant absorption tests were performed on 400 mm² and 50 μm thick films. Samples were vacuum dried in a desiccator for one week to remove residual water and weighted before being immersed in ethanol. Samples were regularly weighted in order to measure the amount of absorbed ethanol.

It is possible to determine the diffusion coefficient of the penetrant in the material if the experimental data of the swelling test follows a Fick's diffusion law. According to Alfrey *et al.* [27], the following general equation allows us to determine the link between the weight gain and the time of immersion.

$$\frac{m_t}{m_\infty} = Kt^n \quad (8)$$

Where m_t is the weight gain and m_∞ is the equilibrium weight gain. K is a coefficient related to the diffusion coefficient D . Alfrey *et al.* distinguish three different absorption mechanisms according to the n parameter. For an n value of $1/2$ the absorption mechanism fits the Fick's law and in this case, the K parameter is directly proportional to the diffusion coefficient. If the n value equals 1, the mechanism is called a Case II diffusion. Then, the parameter K is associated to the penetrant front velocity. Finally, an n value between 0.5 and 1, refers to an anomalous diffusion, in that case, the K parameter is related to the absorption kinetic but its physical interpretation is complex. It is the case of polymer diffusion in the glassy state [27–30].

Indeed, below the glass transition, the relaxation time of macromolecules is higher than the characteristic time of diffusion; the diffusion is then limited by the mobility of the macromolecules and leads to an anomalous diffusion mechanism [30]. Contrarily, above the glass transition, due to the disruption of the network of physical bonds, the characteristic time of macromolecules becomes lower than the diffusion time. Then, the absorption is controlled by the diffusion of the penetrant and it can be fitted by a Fick's law.

3. Results and discussion

3.1. Evolution of mechanical properties with ageing

Fig. 2 shows the Dynamic Mechanical thermograms of the unaged polyimide film in the elongation mode. Relaxations are observed on both storage (E') and loss (E'') moduli.

Polyimide exhibits two relaxations particularly visible on the loss modulus. The first relaxation at -85°C designated as γ , is associated with the local mobility of polar groups hydrogen bonded to water molecules. This assumption is consistent with the decrease of the storage modulus in the range $-135^\circ\text{C}/200^\circ\text{C}$ and the absence of this anelastic relaxation from -135°C to 0°C during the second run, when sample is dry. Indeed, after the first run, the sample was cooled down at $10^\circ\text{C}/\text{min}$ in order to avoid water uptake before the second run.

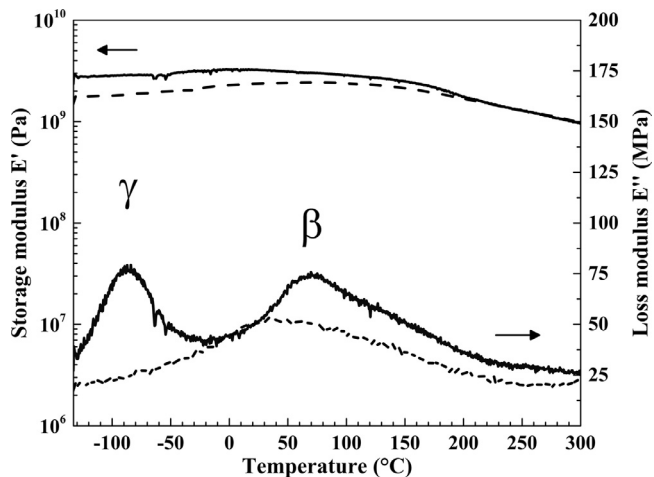


Fig. 2. DMA thermograms of unaged polyimide, first heat scan in full line and second in dashed line.

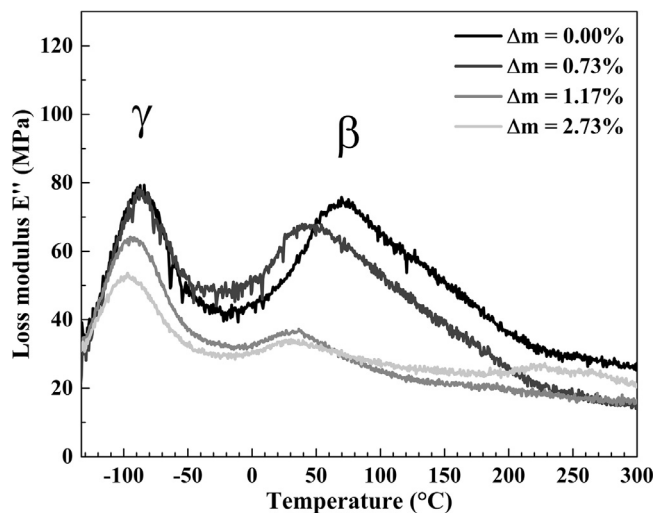


Fig. 3. DMA thermograms of E'' loss modulus for aged PI.

The second relaxation called β is located at 69°C . Many hypothesis are proposed for describing the molecular origin of this very broad relaxation [15,31]. First, it was attributed to the departure of water molecules from the material, and second to the slippage of crystalline structure or defects due to agglomerate of polymer chains [17]. According to Sun *et al.* [32], this relaxation might be associated with molecular oscillations of p-phenylene groups and the rigid structure around ether group acting like central “hinges”. A similar mobility can be seen in the Poly(Aryl Ether Ketones) family [16,33–37].

Fig.3 shows the evolution of the E'' loss modulus for aged PI samples from 0% to 2.73%.

After ageing at 0.73% of mass loss, there is first a weak decrease in the β relaxation magnitude and a shift to lower temperature (from 69°C to 40°C). There is no modification of the γ relaxation at this point. As ageing progresses, the amplitude of the β relaxation decreases significantly. From 1.17 % of mass loss, the low temperature relaxations are impacted by ageing and exhibit a progressive decrease in its amplitude also a slight shift towards lower temperatures. According to the degradation mechanism proposed by Ortelli *et al.* [14] under oxidising atmosphere, the early step of decomposition focuses on the aromatic entities located on either side of the ether group. This assumption explains the first decrease in the high temperature relaxation. The next step of decomposition is the decomposition of carbonyl groups, which can be responsible for the later decrease in γ mode amplitude [14,38,39].

Both relaxations are shifted to lower temperatures as ageing progresses; the β mode is shifted from 69°C to 30°C and the γ mode from -86°C to -98°C respectively. The gap between these values can be explained by an acceleration of molecular mobility due to the degradation of macromolecules. The early degradation of aromatic cycles reducing the local stiffness of the backbone causes the first strong acceleration of the mobility of the β mode. The reduction of the amplitude of the γ mode implies an advanced degradation of carbonyls, which leads to an even greater acceleration of their mobility.

3.2. Effect of thermal ageing on diffusion behaviour

Penetrant absorption tests have already proved their efficiency in the study and analysis of polymer ageing [18]. Fig. 4 shows the evolution of the weight gain of PI samples as a function of the immersion time in ethanol. The inset shows the absorption data for

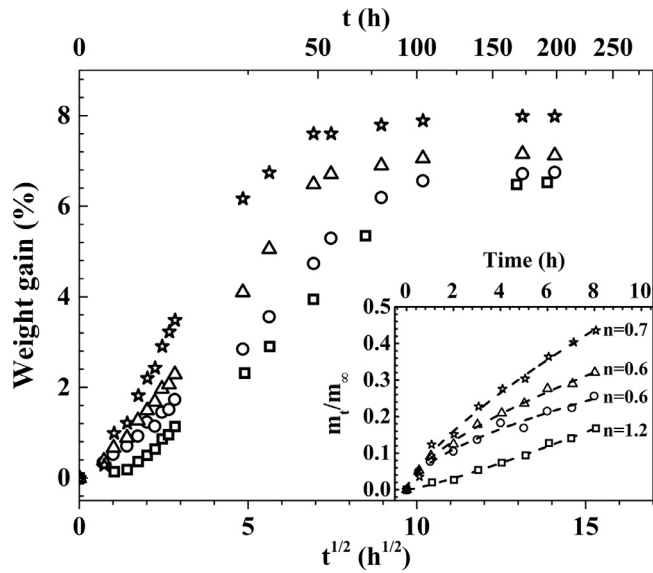


Fig. 4. Weight gain of PI samples immersed in ethanol. The inset represents weight gain normalised by m_∞ for short immersion times fitted with Eq. (7) (\square : $\Delta m = 0.00\%$; \circ : $\Delta m = 0.73\%$; \triangle : $\Delta m = 1.59\%$; \star : $\Delta m = 2.78\%$).

Table 2

Equilibrium weight gain, n and K values of the Eq. (7) for PI samples after penetrant absorption tests.

	m_∞ (%)	n	$K \text{ s}^{-n}$
Ageing			
$\Delta m = 0.00 \%$	6.5	1.2 ± 0.1	$(1.3 \pm 0.1) \times 10^{-2}$
$\Delta m = 0.73 \%$	6.7	0.6 ± 0.1	$(7.3 \pm 0.1) \times 10^{-2}$
$\Delta m = 1.59 \%$	7.1	0.6 ± 0.1	$(8.6 \pm 0.1) \times 10^{-2}$
$\Delta m = 2.78 \%$	8.0	0.7 ± 0.1	$(9.7 \pm 0.1) \times 10^{-2}$

short immersion times with a fit according to Eq. (7). Both values of K and n are extracted for each sample and reported in Table 2.

The swelling test allows us to make first some qualitative observations on the diffusion behaviour of the PI with ageing. Unaged PI presents a lower equilibrium weight gain m_∞ and a slower absorption kinetic. As the ageing progress, both absorption kinetics and m_∞ increases. Values of m_∞ are reported in Table 2.

Absorption curves plotted as a function of $t^{1/2}$ show an inflexion point. This specific shape, according to Berens and Hopfenberg [40], indicates a non-Fick diffusion mechanism; then, the determination of a diffusion coefficient D is not possible. For unaged PI sample the value of n is close to 1 ($n \sim 1.2$), this indicate a fast diffusion time compared with macromolecular relaxation time [41]. It is consistent with literature considering that the polymer is in the glassy state. After ageing the value of n decreases, closer to abnormal diffusion ($0.5 < n < 1$). The K parameter gives us information about the absorption kinetic for short times immersion. Its evolution from 1.3×10^{-2} to 9.7×10^{-2} shows an increase of absorption kinetic with ageing.

The evolution of n toward the lower values could be associated with the macromolecules characteristic relaxation time decrease i.e. DMA results point out a mobility acceleration with ageing. The diffusion in the material is easier as the mobility is faster.

Furthermore, the increase of m_∞ with ageing can be related to the chemical modifications due to thermal stress by a phenomenon of chain scission. The fact that the maximum amount of penetrant increases allows us to assume that the degradation caused by thermal stress leads to local heterogeneities (free volume and/or denser zone) probably due to recombination (intra-chains bonds).

Table 3

ΔH and τ_0 values extracted from Arrhenius diagram of aged PI samples.

Ageing	γ		MWS	
	ΔH (kJ.mol ⁻¹)	τ_0 (s)	ΔH (kJ.mol ⁻¹)	τ_0 (s)
0.00	104 ± 1	$(5 \pm 2) \times 10^{-14}$	473 ± 6	$(2 \pm 2) \times 10^{-23}$
0.73	107 ± 2	$(9 \pm 2) \times 10^{-16}$	411 ± 13	$(2 \pm 4) \times 10^{-18}$
1.53	109 ± 2	$(4 \pm 2) \times 10^{-14}$	267 ± 3	$(1 \pm 2) \times 10^{-11}$
2.93	89 ± 2	$(2 \pm 2) \times 10^{-14}$	\emptyset	\emptyset

3.3. Effect of thermal ageing on dielectric relaxations

In order to analyse the evolution of the molecular mobility, the evolution of the loss permittivity as a function of frequency and temperature was studied. The PI exhibit three dielectric phenomena. For the high temperature mode, the predominance of the conductivity over the permittivity requires the use of the Kramers-Kronig transform in order to highlight the dipolar process [42].

$$\varepsilon''_{KK}(\omega_0) = \frac{\sigma_{DC}}{\varepsilon_0 \omega_0} + \frac{2}{\pi} \int_0^\infty \varepsilon'(\omega) \frac{\omega_0}{\omega^2 - \omega_0^2} d\omega \quad (9)$$

Fig. 5 shows the evolution of the Kramers-Kronig loss permittivity (ε''_{KK}) as a function of temperature and frequency, the relaxation map has been filtered at low frequency due to a weak signal/noise ratio.

According to the increase of $\Delta \varepsilon'$ value (≈ 13) with frequency and to the high value of ε'' , this high temperature and low frequency mode has been attributed to a Maxwell-Wagner-Sillars (MWS) polarisation, associated with heterogeneities [23]. Localized γ and β relaxations have the same molecular origin than those presented in mechanical analysis [43–46].

The Arrhenius plot of Fig. 6 shows the evolution of $\tau_{HN}(T)$ for the γ mode and the MWS contribution as a function of ageing. The β mode cannot be analysed due to its weak signal.

Activation parameters are extracted from the Arrhenius diagram and reported in Table 3. Note that τ_0 has no physical meaning. According to Eyring's theory [47], the pre-exponential factor τ_0 is linked to the activation entropy ΔS of the relaxing entities by the following relationship:

$$\tau_0 = \frac{h}{k_B T} e^{\frac{-\Delta S}{R}} \quad (10)$$

Where h is the Planck constant and k_B is the Boltzmann constant.

The low values for the γ mode are consistent with the hypothesis of a localized molecular mobility; the high values of ΔS for the MWS mode indicates the delocalization of dipolar species around heterogeneities due to a high number of accessible sites.

The evolution of the γ relaxation towards lower temperature i.e. lower relaxation time (τ_{HN}) with no significant change in the enthalpy value (ΔH) confirms the acceleration of localised molecular mobility. However, the MWS mode is shifted towards higher temperatures after ageing; the increase in relaxation times can be associated with an evolution of the size of heterogeneities and consequently of the dynamic conductivity of the polymer.

3.4. Influences of thermal ageing on charge transport mechanism

The evolution of the MWS mode may indicate an evolution in polymer conductivity. As the relaxation time of the MWS mode scale inversely with the conductivity [23] an evolution in the MWS mode lead to a modification of the conductivity behaviour. The Fig. 7 shows the isothermal evolution of the real part of the conductivity as a function of the frequency in the temperature range [150 °C–250 °C].

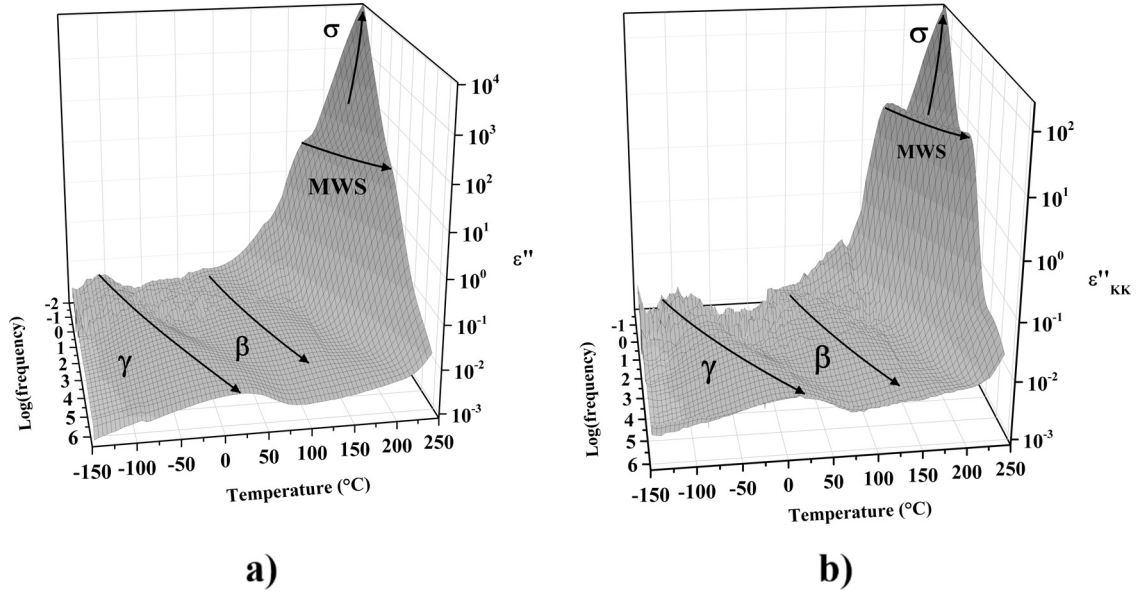


Fig. 5. Dielectric relaxation map of unaged PI (a) before and (b) after Kramers-Kronig transform.

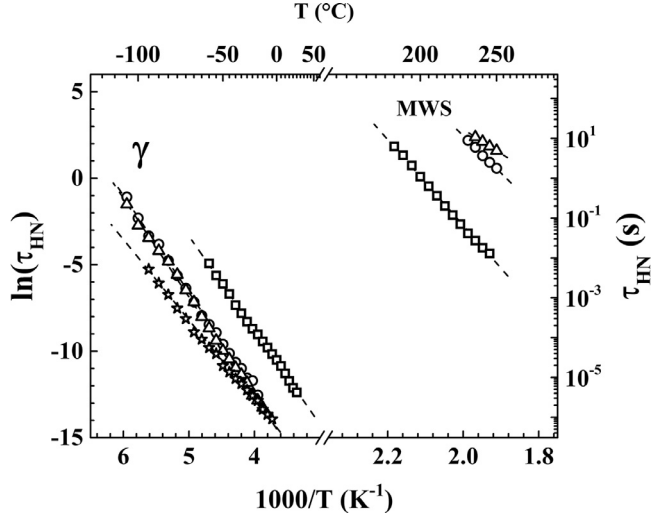


Fig. 6. Arrhenius plot of PI dielectric relaxations (\square : $\Delta m = 0.00\%$; \circ : $\Delta m = 0.73\%$; \triangle : $\Delta m = 1.53\%$; \star : $\Delta m = 2.93\%$). Dashed lines represent fitted data according to Arrhenius law.

Table 4
Conductivity activation parameters resulting from Arrhenius law fit.

Ageing Δm (%)	ΔH (kJ.mol ⁻¹)	σ_0 (S.m ⁻¹)
0.00	214 \pm 2	(8.1 \pm 2) $\times 10^{13}$
0.73	197 \pm 4	(5.6 \pm 3) $\times 10^9$
1.53	180 \pm 2	(3.5 \pm 2) $\times 10^7$
2.93	161 \pm 2	(1.5 \pm 2) $\times 10^5$

The real part of the dynamic conductivity follows Eq. (4). The universal dielectric response is slightly disturbed by the MWS contribution. We chose to define σ_{DC} values at the intercept of each conductivity plateau with the dotted straight line plotted on Fig. 7. This straight line is parallel to the $A\omega^s$ term of Jonscher's universal law [24]. Extracted σ_{DC} values are plotted on an Arrhenius diagram and reported on Fig. 8. Activation parameters are listed in Table 4.

PI presents high value of conductivity activation energy (from $\Delta H \sim 214$ kJ.mol⁻¹ to 161 kJ.mol⁻¹). ΔH values give us an in-

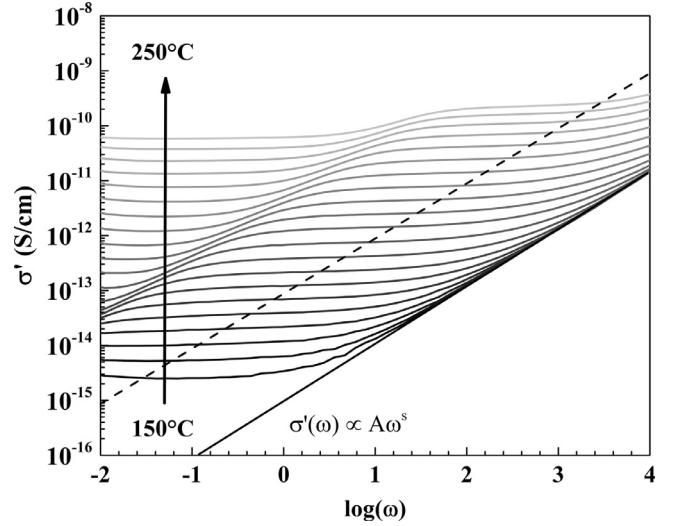


Fig. 7. Isothermal evolution of the conductivity as a function of the frequency for unaged PI sample from 150 °C to 250 °C.

formation on the nature of charge transport mechanism. High ΔH values indicate an ionic charge transport mechanism. The activation energy shows a linear decrease as a function of ageing time. This variation can be explained by an evolution of the charge carrier environment due to the degradation.

The chain scission and the formation of new intra-chains bonds may reduce the quantity of deeper traps in favour of more numerous shallow trap; this results in a lower average value of activation energy. In this case, charge carriers need less energy to be released.

The evolution of the MWS phenomenon and of the σ_{DC} conductivity are linked. For short time ageing, we notice a significant decrease of several decades for the σ_{DC} value. For long times ageing, the σ_{DC} decrease is less important but still present. It can be related to the increase of the size of heterogeneities that act like traps and limit the charge transport.

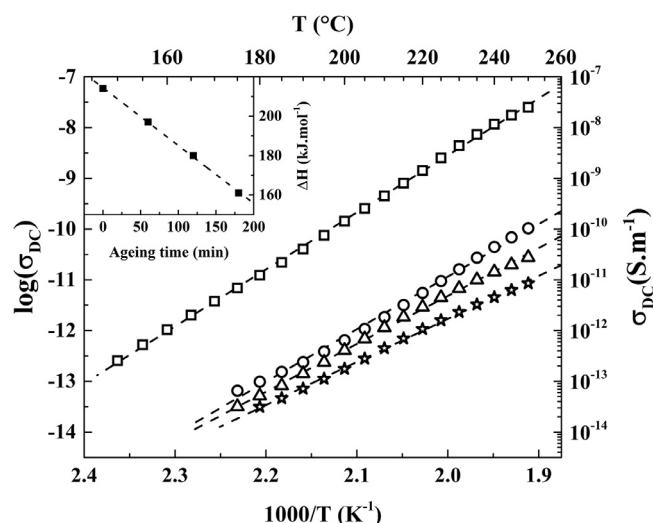


Fig. 8. Arrhenius plot of conductivity as a function of ageing (□: $\Delta m = 0.00\%$; ○: $\Delta m = 0.73\%$; △: $\Delta m = 1.53\%$; ☆: $\Delta m = 2.93\%$). Dashed lines represent fitted data according to Arrhenius law. The inset represents the evolution of activation energy as a function of ageing time.

4. Conclusion

The ageing under thermal stress significantly modify PI molecular mobility and consequently electrical properties. In this work, ageing was carried out at 450 °C in an oven under oxidising atmosphere. Mechanical analyses revealed two different relaxations γ and β associated with molecular mobility of polar groups in the vicinity of water molecules and molecular oscillation of p-phenylene groups respectively. The evolution of γ and β relaxations with ageing gave us information about the degradation mechanism. First, degradation causes a strong acceleration of the β relaxation mode that impairs aromatic cycles. At advanced ageing, degradation implies carbonyl groups resulting in a decrease in the γ relaxation amplitude and an acceleration of its mobility.

Swelling test results are consistent with the macromolecular dynamic behaviour: an evolution of both kinetics and m_{∞} values are pointed out. The diffusion kinetic increase has been attributed to an acceleration of the localized molecular mobility. The increase in m_{∞} can be related to chemical modifications: a chain scission mechanism which induces heterogeneities. The evolution of these heterogeneities as a function of ageing is confirmed by dielectric analyses of the Maxwell-Wagner-Sillars polarisation and by conductivity values.

We can conclude that the thermal degradation of polyimide led to an evolution of both macromolecular mobility and charge transport mechanism. Chain scission mechanism and the formation of new intra-chains bonds induce a modification of the environment of relaxing units, correlated with mobility acceleration. In the same time, the charge transport is limited by an increase of heterogeneities

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.

CRediT authorship 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. **F. Koliatene:** Conceptualization, Methodology, Validation, Investigation, Supervision, Writing - review & editing. **C. Trebosc:** Conceptualization, Methodology, Validation, Investigation, Supervision, Writing - review & editing.

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