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Dynamic molecular mobility of polyurethane by a broad range dielectric and mechanical analysis

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A B S T R A C T

The dynamic molecular mobility of poly(2-hydroxypropyl methacrylate) (PHPMA) base polyurethane (PU) was studied over a broad range of frequency and temperature by combining dynamic dielectric spectroscopy and dynamic mechanical analysis. Two hydrated levels were considered in this study: dry and room humidity states. In dry state, two secondary relaxations γ and β are identified. And in room humidity state, a β_{sw} mode is pointed out. These modes are well known in poly(hydroxylalkyl methacrylate)s. The main α relaxation is influenced by humidity and crosslinks. The Kramers-Kronig transform is used to reveal an ionic conductivity σ_{ionic} . Relaxation times extracted from dielectric and mechanical analyses are coherent for PU and PHPMA. This correlation allows us to propose an interpretation of relaxations at a molecular level.

1. Introduction

Poly(hydroxylalkyl methacrylate)s base polyurethane (PU) coatings are widely used in the coating industry [1,2]. The PU is classically obtained by the chemical reaction of polyol and isocyanate. A better understanding of relationships between its macromolecular dynamic and structure is necessary to improve these material properties for surface applications.

In previous works, spectroscopic studies have been devoted to the molecular mobility of poly(alkyl methacrylate)s below T_g [3–19]. Although the mechanical and dielectric behaviors of poly(2-hydroxyethyl methacrylate) (PHEMA) has been extensively studied [20–32], there is a paucity of academic data on the poly(2-hydroxypropyl methacrylate) (PHPMA). PHEMA has a primary alcohol while PHPMA has a secondary alcohol. The reaction with isocyanate is slowed down with a secondary alcohol located on an ester side chain [33]. This increase of reaction time with PHPMA permits to have an acceptable time to apply the coating.

The aim of this work is to study the molecular dynamics of PHPMA by dielectric and mechanical relaxation spectroscopy. The effects of hydration and crosslinking of PHPMA on the relaxation modes are shown and compared with the abundant literature on the water influence on the poly(hydroxylalkyl methacrylate)s relaxations by differential scanning calorimetry [33–40], dynamic dielectric spectroscopy [26,29,42–44] and dynamic mechanical analysis [45,46].

2. Experimental section

2.1. Materials

The PU coating is a two components system: PHPMA, MACRYNAL[®] VSM 6299w/42WA (Allnex, Belgium), in 40 wt% water; and Easaqua[™] X D 401 (Vencorex, France) composed of hexamethylene diisocyanate, isocyanurate (45 wt%) and 3-isocyanatomethyl-3,5,5-trimethylcyclohexyl isocyanate (30 wt%) in 15 wt% *n*-butyl acetate. The two parts are mixed at room temperature (ratio 3:1). The mixture is sprayed with a High Volume Low Pressure (HVL) spray gun. The curing process is 30 min at 80 °C. In the following sections, PU is referred to as cross-linked PHPMA with a degree of crosslinking of 75% determined by infrared transmission and PHPMA as the linear base.

3. Methods

3.1. Differential scanning calorimetry

Differential scanning calorimetry (DSC) experiments were carried out in a DSC 2920 apparatus (TA-Instrument, USA) under nitrogen gas at several heating rates from – 60 to 150 °C. The samples weight varied from 5 to 10 mg and they are sealed in aluminum pans. The equivalent frequency $f_{eq,DSC}$ [47] depends on the heating rate following the equation:

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$$f_{eq,DSC} = \frac{\nu}{2\pi a \delta T} \quad (1)$$

where ν is the heating rate, a is a constant ($a \sim 1$), δT is the mean temperature fluctuation.

The associated relaxation time can be determined:

$$\tau_{eq,DSC} = \frac{1}{2\pi f_{eq,DSC}} \quad (2)$$

3.2. Dynamic mechanical analysis

Dynamic mechanical analysis (DMA) was performed using an ARES G1 strain controlled rheometer (Rheometrics Scientific, USA). Experiments were carried out in rectangular torsion mode, over the temperature range from -145 to 150 °C at constant angular frequencies, with an heating rate of 3 °C/min. PU samples were sprayed on silicone mold with 45 mm length and 10 mm width. After the curing process, the sample thickness is approximately 500 μm .

3.3. Dynamic dielectric spectroscopy

A dynamic dielectric spectrometer (DDS) BDS 4000 (Novocontrol, Germany) was used in the frequency range from 10^{-2} to 10^{+6} Hz between -150 and 150 °C by 5 °C steps. The measurements were carried out in the parallel plates geometry using 35 mm aluminum circular electrodes. PU coatings were sprayed on the lower electrode. For the second run, the dielectric data were fitted with the Havriliak-Negami [48,49] parametric equation, which allowed us to extract the mean dipole relaxation time τ_{HN} :

$$\epsilon_T^*(\omega) = \epsilon_\infty + \frac{\epsilon_s - \epsilon_\infty}{[1 + (i\omega\tau_{HN})^{\alpha_{HN}}]^{\beta_{HN}}} \quad (3)$$

where ϵ_∞ is the high-frequency limit of the relative real permittivity, ϵ_s is the low-frequency limit of the relative real permittivity, ω is the angular frequency and α_{HN} and β_{HN} are the Havriliak-Negami fit parameters, respectively related to the width and symmetry of the distribution.

Dipolar relaxations are often hidden by dissipative losses due to ohmic conduction. The Kramers-Kronig [50] relations offer an analytical tool to calculate ϵ''_{KK} from the real permittivity $\epsilon'_T(\omega)$, thus virtually eliminating the contributions of purely dissipative phenomena.

$$\epsilon''_{KK}(\omega) = \frac{\sigma_0}{\epsilon_0\omega_0} + \frac{2}{\pi} \int_0^\infty \epsilon'_T(\omega') \frac{\omega_0}{\omega^2 - \omega_0^2} d\omega' \quad (4)$$

Molecular mobility is governed by the temperature dependence of $\tau(T)$. Two $\log \tau$ ($\frac{1}{T}$) behaviors are classically observed on an Arrhenius plot: a linear and a non-linear one. In the glassy state, the temperature dependence of relaxation times obeys the Arrhenius equation [5]:

$$\tau(T) = \tau_{0\alpha} \exp\left(\frac{\Delta H}{RT}\right) \quad (5)$$

where $\tau_{0\alpha}$ is the pre-exponential factor, ΔH is the activation enthalpy, R is the gas constant.

For molecular mobility governed by the free volume, the temperature dependency deviates from Arrhenius type behavior; it is then described by the Vogel-Fulcher-Tammann (VFT) equation [51]:

$$\tau(T) = \tau_{0v} \exp\left(\frac{1}{\alpha_f(T - T_\infty)}\right) \quad (6)$$

where τ_{0v} is the pre-exponential factor, α_f is the thermal expansion coefficient of the free volume and T_∞ is the ideal glass temperature below which there is no free volume.

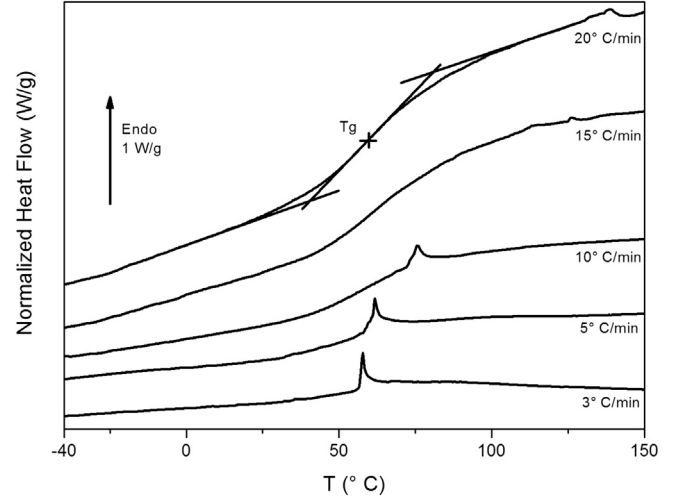


Fig. 1. DSC thermograms of PU for various heating rates (2nd heating). Lines correspond to the inflection point method.

4. Results and discussions

4.1. Physical structure

DSC analysis of PU was carried out with various heating rates (Fig. 1). The glass transition of PU, determined by the inflection point method (ASTM D3418), remains constant at 60 °C. An endothermic peak is pointed out: its intensity decreases and it is shifted toward higher temperatures with increasing heating rate. This endotherm is associated with the rupture of the hydrogen bonds forming a local order, as in segmented polyurethanes [52].

The extracted temperatures are reported in Table 1.

4.2. Mechanical relaxations

The storage modulus G' and the loss modulus G'' are reported in Fig. 2 for PU. In order to suppress the influence of water, the second thermograms are shown. The linear behavior of the mechanical response is checked from 1 to 100 rad/s. For the storage modulus G' , the glassy plateau is between 1 GPa at -145 °C and 0.6 GPa at 20 °C. At high temperature, the rubbery plateau is around 2 MPa. Between 30 °C and 110 °C, the modulus decrease associated with the mechanical manifestation of the glass transition, labelled α , is observed. This viscoelastic relaxation is shifted to higher temperatures with increasing angular frequencies.

At lower temperature, two secondary relaxations γ and β are observed. In order to resolve the lowest temperature mode, the angular frequency is increased toward 100 rad/s. The γ peak location is shifted toward higher temperatures as the angular frequency increases. The β mode amplitude becomes less intense and tends to merge with the α mode for 50 and 100 rad/s. T_α values are consistent with DSC results (Table 1). The relaxation modes temperatures as the function of the angular frequencies are reported in Table 2.

PU are sensitive to hydration, after 48 h at room humidity (RH), the

Table 1
Thermal parameters extracted from of DSC thermograms.

Heating rate (°C/min)	T_g (°C)	T_{endo} (°C)
3	–	58 ± 2
5	–	62 ± 2
10	58 ± 2	76 ± 2
15	60 ± 2	126 ± 3
20	60 ± 2	138 ± 3

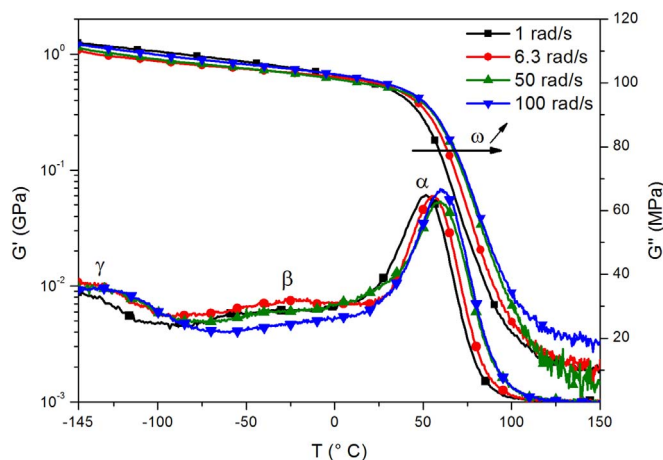


Fig. 2. Storage modulus G' and loss modulus G'' versus temperature for dry PU.

Table 2

Mechanical relaxation modes temperatures for PU at dry and room humidity state.

Mode	$T_{1 \text{ rad/s}}^{\text{AMD}}$ (°C)	$T_{6.3 \text{ rad/s}}^{\text{AMD}}$ (°C)	$T_{50 \text{ rad/s}}^{\text{AMD}}$ (°C)	$T_{100 \text{ rad/s}}^{\text{AMD}}$ (°C)
State	Dry			
γ	-	-	-140 ± 2	-135 ± 2
β	-30 ± 2	-25 ± 2	-	-
α	50 ± 2	55 ± 2	60 ± 2	61 ± 2
State	RH			
γ	-	-	-140 ± 2	-135 ± 2
β_{sw}	-98 ± 2	-89 ± 2	-78 ± 2	-75 ± 2
β	-	-	-	-
α	47 ± 2	52 ± 2	50 ± 2	52 ± 2

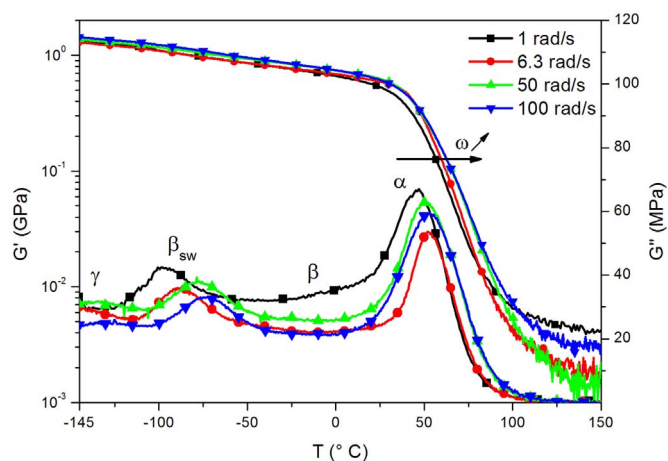


Fig. 3. Storage modulus G' and loss modulus G'' versus temperature for PU at RH state.

hydration level is near 1.3 ± 0.3 wt%. Their dynamic mechanical analyses are reported in Fig. 3.

At RH state, four mechanical relaxation modes are identified γ , β_{sw} , β and α . Their specific temperatures are reported in the Table 2 as a function of angular frequency. To resolve the lowest temperature mode, the angular frequency is increased toward 100 rad/s. The maximum of γ mode is visible above 50 rad/s. The associated temperatures T_γ are the same for the two hydrated states (dry and RH), suggesting that the γ mode is not influenced by the presence of humidity.

In the temperature range of -100 to -75 °C, a new mode, called β_{sw} , is observed. The index “sw” is defined as “swelling”. The molecular origin of this mode is explained later in this article. The β mode is hidden by the β_{sw} mode and the low temperature tail of α mode. Compared to the dry state, the viscoelastic relaxation mode is

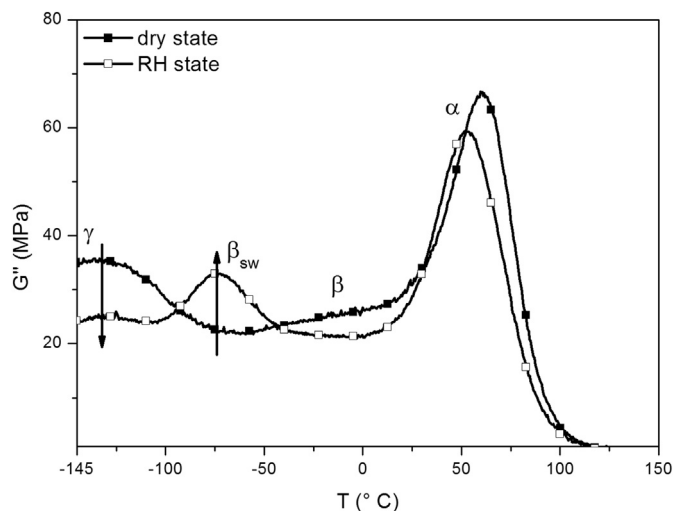


Fig. 4. Modulus loss G'' at 100 rad/s versus temperature for PU in dry and RH states.

shifted toward low temperatures; i.e. characteristic of a plasticization phenomenon.

Fig. 4 compares the dissipative modulus G'' for PU at 100 rad/s for dry and RH states. γ mode strength decreases strongly in the RH state, contrary to β_{sw} mode. The presence of humidity changes the amplitude of γ mode, but its temperature is unchanged.

4.3. Dielectric relaxations

Fig. 5 reports the dielectric loss surface of PU at RH state. Dielectric relaxation modes are consistent with mechanical results. In addition an ionic conductivity σ_{ionic} is observed at high temperatures and low frequencies. This dielectric contribution appears in the high frequency tail of the conductivity σ . This phenomenon has been associated with ions accumulation at electrode-sample interfaces, leading to a so-called “electrode polarization” effect [53] superimposed to the high-temperature conductivity in Fig. 5.

The dynamic conductivity σ' and permittivity ϵ' at 150 °C are reported in Fig. 6. For high frequency range, the conductivity is frequency dependent. It corresponds to ion mobility at short times [54,55]. At lower frequency, a nearly constant (σ_{dc}) plateau, associated with random ions hopping mobility, is observed. With decreasing frequency, the accumulation of ions near the electrodes leads to a

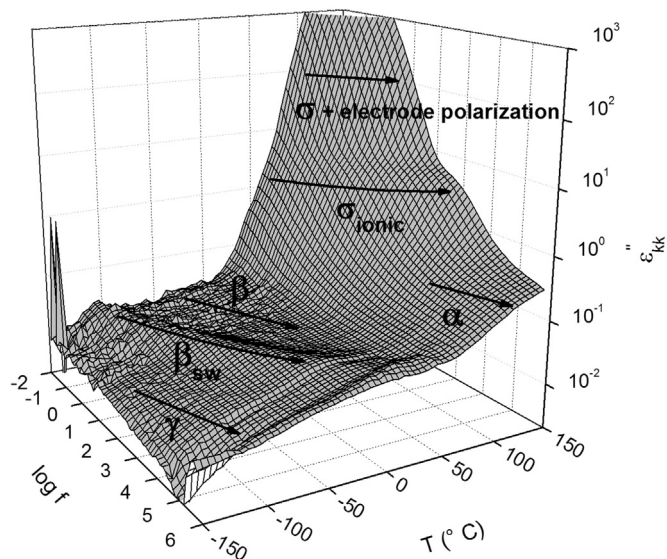


Fig. 5. Dielectric loss ϵ'' surface for PU at RH state.

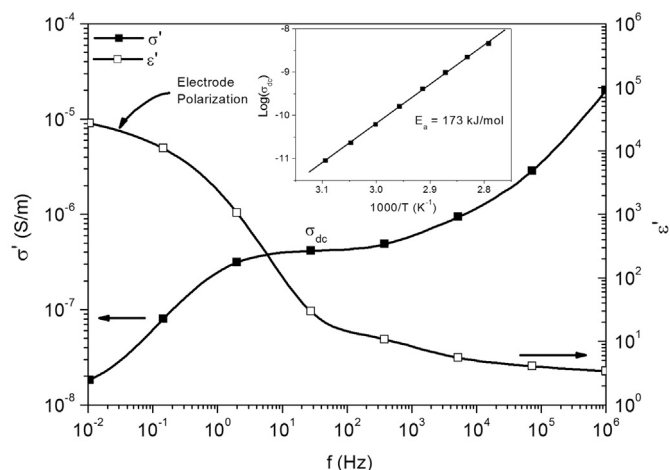


Fig. 6. Real part of the conductivity σ' and permittivity ϵ' versus frequency for PU at 150 °C. Inset: Arrhenius diagram of $\log \sigma_{dc}$.

decrease in the mobile ions density within the sample (σ' decreases). And additional polarization of the sample is induced by the ions stacked near the electrodes, resulting in an increase of ϵ' [53]. The inset in Fig. 6 shows that ionic conductivity is governed by an Arrhenius behavior with an activation energy greater than 100 kJ/mol. It confirms an ionic charge transport.

Fig. 7 shows the relaxation times behaviors on an Arrhenius diagram for PU in the dry and RH states. DDS and DMA relaxation times are reported. The temperature dependence of the γ , β_{sw} , β , α relaxations and σ_{ionic} are shown. Secondary relaxations and σ_{ionic} follow the Arrhenius behavior law described by Eq. (5). The extracted parameters are indexed in Table 3.

For the γ mode, we observe a discrepancy between dielectric and mechanical relaxation times at low temperature. It has been already reported in the literature [20,22,32,56]. The dielectric response under electric field is strongly dependent on the dipole moment, whereas the mechanical relaxation is directly linked with molecular mobility and Van der Waals binding forces. Aligning the dipole moment of $-OH$ group in the electric field is easier than overcoming the Van der Waals interactions.

At RH conditions, the β mode cannot be fitted due to β_{sw} relaxation. Mechanical and dielectric relaxation times are in agreement for β_{sw} and β modes, contrary to Gates et al. [22] results. They observe a β_{sw}

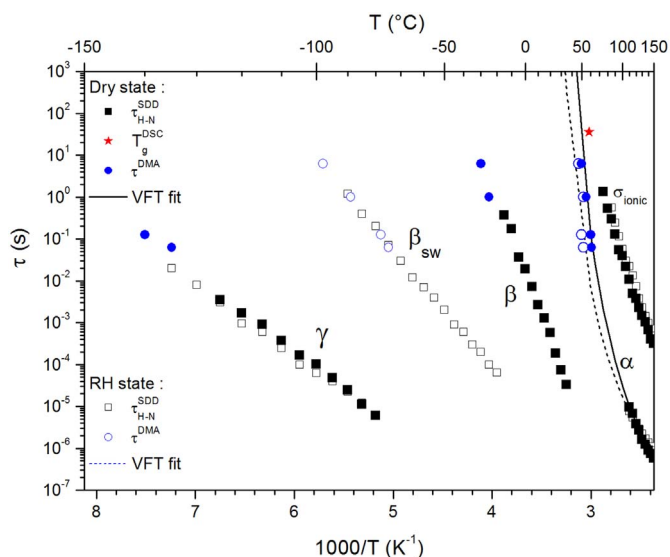


Fig. 7. Arrhenius diagram of dielectric and mechanical relaxations times of PU at dry and RH states. Lines correspond to VFT fit.

Table 3

Arrhenius fit parameters for secondary relaxations and σ_{ionic} in PU at dry and RH states.

Mode	Dry		RH	
	τ_0 (s)	E_a (kJ/mol)	τ_0 (s)	E_a (kJ/mol)
γ	5.10^{-15}	34 ± 1	1.10^{-14}	32 ± 1
β_{sw}	–	–	5.10^{-16}	54 ± 1
β	6.10^{-26}	123 ± 2	–	–
σ_{ionic}	4.10^{-21}	136 ± 3	4.10^{-21}	136 ± 2

Table 4

VFT fit parameters of α relaxation in PU at dry and RH states.

Mode	State	τ_0 (s)	T_{∞} (°C)	α_f (°C $^{-1}$)
α	Dry	2.10^{-10}	2 ± 1	8.10^{-4}
	RH	3.10^{-9}	1 ± 1	1.10^{-3}

peak slightly lower for dielectric measurements. The γ relaxation and σ_{ionic} dielectric contributions are not influenced by hydration. α mode is governed by a VFT behavior. A plasticization phenomenon due to water molecules is observed. VFT fit parameters are reported in Table 4. The ideal glass temperature T_{∞} is located at 56 °C below the calorimetric Tg in the dry state.

Eq. (2) allows us to calculate the equivalent relaxation time $\tau_{eq, DSC}$, approximately 30 s, for a heating rate of 20 °C/min and reported in Fig. 7. The calorimetric Tg is consistent with the mechanical and dielectric measurements.

In order to shed some light on the molecular origin of these relaxation dynamics and to study the effect of crosslinking, the dielectric permittivity of PHPMA in the dry and RH states was studied. Due to the weak mechanical properties of PHPMA, DMA analyses could not be performed.

In Fig. 8, relaxation times temperature dependence of PHPMA are reported on an Arrhenius diagram. In the glassy state, the secondary relaxations are governed by the Arrhenius law and the fitted parameters are reported in Table 5. These γ , β_{sw} , β modes of PHPMA are consistent with those observed in PU.

The γ relaxation process is associated with the rotation of the $-OH$ side groups as in PHEMA [32]. In the PU, all the $-OH$ functions do not react with the $-NCO$ functions to form the PU function. The γ mode remains relatively constant with water molecule presence, as a con-

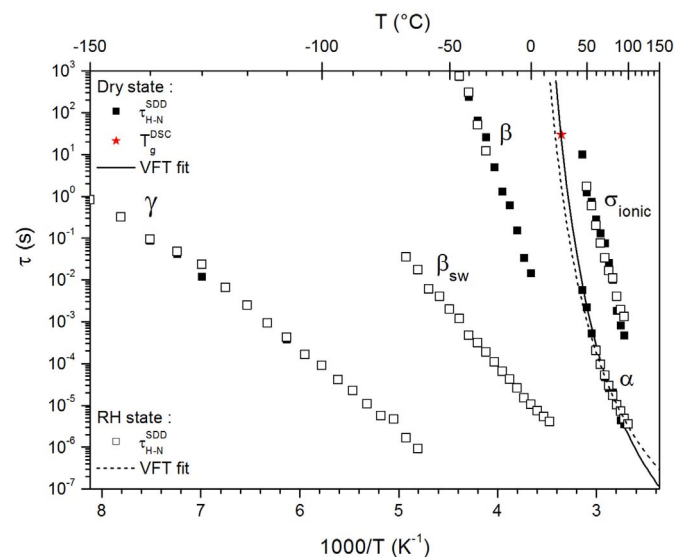


Fig. 8. Arrhenius diagram of relaxation times of PHPMA at dry and RH states. Lines correspond to VFT fit.

Table 5

Arrhenius fit parameters for the secondary relaxations and σ_{ionic} in PHPMA at dry and RH states.

State	Dry		RH	
	τ_0 (s)	E_a (kJ/mol)	τ_0 (s)	E_a (kJ/mol)
γ	7.10^{-15}	34 ± 1	2.10^{-15}	35 ± 1
β_{sw}	–	–	1.10^{-15}	52 ± 1
β	9.10^{-27}	127 ± 2	1.10^{-27}	131 ± 2
σ_{ionic}	1.10^{-30}	187 ± 2	1.10^{-30}	188 ± 2

Table 6

VFT fit parameters of the α relaxation in PHPMA at dry and RH states.

Mode	State	τ_0 (s)	T_∞ ($^\circ\text{C}$)	α_f ($^\circ\text{C}^{-1}$)
α	Dry	1.10^{-10}	-20 ± 2	$8.5.10^{-4}$
	RH	8.10^{-10}	-22 ± 1	1.10^{-3}

firmation of Janacek [20] interpretation on PHEMA swollen (with different concentrations of water or other polar solvents) by mechanical experiments. Janacek et al. show that its γ mode gradually disappears with increasing diluent concentration but its temperature location is constant. Gates et al. [22] mention that the activation energy of the γ mode is constant for cross-linked HEMA, DHPMA and their copolymers, and not dependent from hydration. But Lustig et al. [57] observed for PHEMA a slight decrease toward lower temperatures with water content, while Shen et al. [58] for PHEMA and PHPMA noted the opposite. In this work, the activation energy value for the γ relaxation is about 34 kJ/mol. This result is in agreement with the ones previously established for polyacrylic systems with hydroxyl groups as PHEMA [22,32,59,60] or PHEA [61].

In RH state, the β_{sw} mode is also observed. Literature reports that it is shifted toward lower temperatures as water content increases for the PHEMA [62] and for the PHEA [19]. This mode has been associated with water molecules in interaction with hydroxypropyl group on the polymer side chain [20]; i.e. a complex $-\text{OH}$ side groups/water. A part of $-\text{OH}$ side groups involve in the γ process is transformed into the β_{sw} process. The activation energy is 52 kJ/mol which is consistent with the values from literature [60,61].

As already observed in DMA, the β mode is hidden by the β_{sw} relaxation. Only a few points can be fitted with the HN function in the RH state. The secondary mode β corresponds to the rotation of the ester side group [20]. The activation energies in the dry and hydrated state are close. In the literature, the temperature of the β mode slightly decreases with water content [57,58]. The activation energy values obtained for the β mode are similar to those reported for PHEMA [59,24].

At higher temperatures, the σ_{ionic} obeys an Arrhenius behavior and is not influenced by hydration. The activation energy of the secondary modes between PHPMA and PU are close. There is no influence on these modes when PHPMA is crosslinked. Only, the ionic conductivity σ_{ionic} is modified. The activation energy is higher in the PHPMA.

A VFT behavior is observed for the PHPMA α mode. The VFT fit parameters are reported in Table 6. The ideal glass transition temperature T_∞ , located in the vicinity of -20 $^\circ\text{C}$, is 45 $^\circ\text{C}$ below the calorimetric T_g in the dry state ($T_g(\text{PHPMA}) = 25$ $^\circ\text{C}$). In the same way as PU, the point ($T_g(\text{PHPMA}), \tau_{eq, DSC}$) has been reported in Fig. 8, and is in good agreement with VFT fit. The α relaxation for the PU is shifted to higher temperatures as compared to the PHPMA by crosslinking limiting the degrees of freedom of the main chain segments involved in the glass transition.

5. Conclusions

Mechanical and dielectric relaxations have been applied to thorough investigation of the dynamic molecular mobility of PHPMA and PU in dry and RH states. The combination of DMA and DDS has brought to light the correlation between the response of this mobility under mechanical and electric field.

At low temperature in the dry state, two secondary relaxation modes γ and β were identified in PHPMA and PU. The molecular origin of the γ mode is the rotation of the $-\text{OH}$ side group in PHPMA. The β secondary relaxation mode is attributed to the rotation of the ester side group. Their relaxation times are not modified by humidity and crosslinking. For RH conditions, the β_{sw} mode has been observed and associated with water molecules in interaction with $-\text{OH}$. This mode isn't modified by crosslinking. At high temperature in the dry state, the α relaxation of PHPMA is shifted to higher temperatures in PU due to crosslinking.

Once hydrated, a plasticization phenomenon appears for PHPMA and PU. In dielectric analysis, an ionic conductivity σ_{ionic} is associated with ions accumulation at electrodes. This phenomenon is not influenced by humidity but by crosslinking. Finally, the good consistency between DMA and DDS results allows us to significantly improve the knowledge of molecular/dynamic structure relationships of PHPMA base PU coating.

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