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

D. Dupenne[a,b], A. Roggero[b], E. Dantras[b], A. Lonjon[b,*], T. Pierré[a], C. Lacabanne[b]

[a] IRT A. de Saint Exupéry, 118 route de Narbonne, 31432 Toulouse Cedex 4, France
[b] CIRIMAT, Université de Toulouse, CNRS, UPS, 118 route de Narbonne, 31062 Toulouse Cedex 09, France

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ABSTRACT

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 βsw 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 Tg [3–19]. Although the mechanical and dielectric behaviors of poly(2-hydro-xyethyl 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-trimethylcyclo-hexyl 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 (HVLP) 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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$$f_{eq,DSC} = \frac{v}{2\pi a \delta T} \tag{1}$$

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

The associated relaxation time can be determined:

$$\tau_{eq,DSC} = \frac{1}{2\pi f_{eq,DSC}} \tag{2}$$

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 $150\,^\circ\text{C}$ at constant angular frequencies, with an heating rate of $3\,^\circ\text{C/min}$. 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 $150\,^\circ\text{C}$ by $5\,^\circ\text{C}$ 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}:

$$\varepsilon_T^*(\omega) = \varepsilon_\infty + \frac{\varepsilon_s - \varepsilon_\infty}{[1 + (i\omega\tau_{HN})^{\alpha_{HN}}]^{\beta_{HN}}} \tag{3}$$

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 $\varepsilon_T'(\omega)$, thus virtually eliminating the contributions of purely dissipative phenomena.

$$\varepsilon_{KK}''(\omega) = \frac{\sigma_0}{\varepsilon_0 \omega_0} + \frac{2}{\pi} \int_0^\infty \varepsilon_{(\omega)}' \frac{\omega_0}{\omega^2 - \omega_0^2} d\omega \tag{4}$$

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]:

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

where τ_{0a} 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]:

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

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.
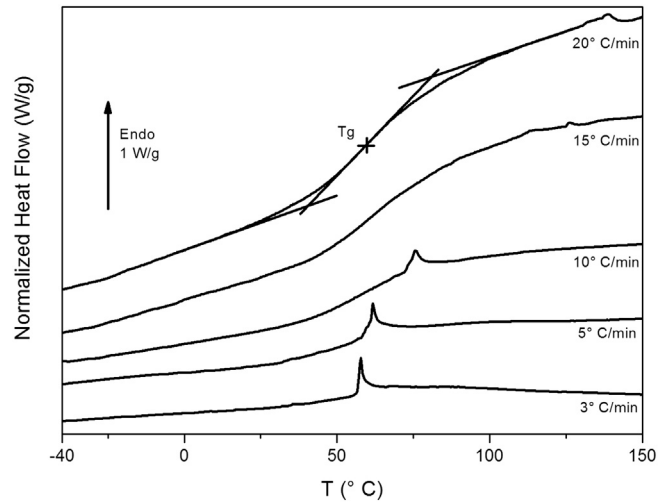

Fig. 1. DSC thermograms of PU for various heating rates (2nd heating). Lines correspond to the inflection point method.

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 $60\,^\circ\text{C}$. 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 $-145\,^\circ\text{C}$ and 0.6 GPa at $20\,^\circ\text{C}$. At high temperature, the rubbery plateau is around 2 MPa. Between $30\,^\circ\text{C}$ and $110\,^\circ\text{C}$, 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