



Water-driven segmental cooperativity in polyvinyl butyral

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ABSTRACT

Measurements of thermogravimetry, dynamic mechanical and dielectric analysis, and infrared absorption have been performed in polyvinyl butyral (PVB) to investigate the effect of absorbed water on relaxation dynamics. Increasing water content plasticizes PVB, also causing a growing intermolecular cooperativity mainly for the secondary relaxation motions. Mechanical and dielectric β -relaxations for dry- and wet-PVB fit onto the same Arrhenius plots showing the very close nature of underlying mechanisms. In particular, the sub-glass mechanical β -relaxation in wet-PVB exhibits a frequency factor which increases up to 10^{16} s^{-1} , disclosing an activation entropy as high as about 59 J/Kmol . It is suggested the existence of cooperative transitions of relaxing side units in adjacent chains, mainly driven by bridges formed through water molecules between the hydroxyl groups of vinyl alcohol segments. Below the glass transition temperature T_g , the bridges are mechanically stable and give rise to an increase of the elastic modulus by more than a factor 2 when compared to that of a fully dry-PVB.

1. Introduction

Polyvinyl butyral (PVB) is a random *ter*-polymer mainly composed of vinyl alcohol and vinyl butyral with relatively small amount of vinyl acetate [1–3], which is widely used in different industrial and technological applications, such as automotive laminated glasses, paints and adhesives. It is well recognized that good adhesion efficiency to a variety of surfaces is strictly related to the glass transition of the polymeric matrix, the lower the glass transition temperature T_g the higher the softening at room temperature. In this respect, a number of plasticizers are usually added to commercial PVB in order to lower its T_g [3–5]. The capacity to absorb and hold significant amount of plasticizers while preserving a good stability of transparency against sunlight and elasticity makes PVB as the most suitable candidate for structural adhesives and interlayer safety glass. Usually, PVB is exposed to environments where water is ubiquitous and interest to investigate the nature of water interactions with PVB and its influence on the structural properties is of primary importance for its use. Moisture acts as a plasticizer for polymers [6–8] giving rise to a decrease of T_g and enhancing the flexibility of the backbone and extended exposition to atmospheric moisture during standard working condition can modify their physical properties, causing mechanical, dielectric and optical instability. The interaction mechanism moisture-polymer can follow different routes, such as in some specific polymers where plasticization

occurs over the region of the glass-rubber transition and anti-plasticization is observed in the glassy region. A typical example of this is nylon 66 [9], where the water sorption gives rise to mechanical bridges between the amide groups which decreases T_g , but depresses severely the secondary relaxation observed below T_g , also producing an increase of the storage modulus over the same temperature region.

With the aim to explore the influence of water over the relaxation dynamics of PVB, we have performed an investigation of mechanical and dielectric spectroscopy on samples having controlled amount of water, using as a reference the behavior observed in a fully dry PVB. The effect of absorbed water on the state of hydrogen bonds in PVB was also investigated by analyzing the evolution of the infrared band associated to O–H stretching ($3000\text{--}3600 \text{ cm}^{-1}$). It has been found that addition of water up to the maximum uptake content plasticizes PVB shifting to lower temperatures both the primary (α) and secondary (β) relaxations, while enhancing the strength of the β -relaxation by a factor as high as 5 and the elastic modulus by more than a factor 2.

2. Experimental details

2.1. Samples and thermogravimetry

PVB (average MW 40,000–70,000), with about 80 wt% of vinyl butyral, 18–20 wt% of vinyl alcohol and 0–2 wt% of vinyl acetate, was

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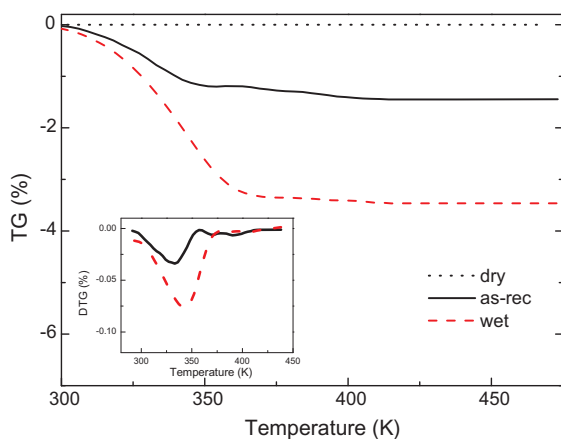


Fig. 1. Temperature dependences of the weight loss (%) of dry- (dotted line), as-rec (solid line) and wet- (dashed line) PVB. Inset reports the derivative thermogravimetric behaviors.

purchased from Sigma Aldrich. As determined by thermogravimetry analysis (TGA), thin layers (200–300 μm thickness) of as-received PVB (as-rec PVB) had an initial water content of 1.5 wt%. They have been dried under vacuum of about 10^{-4} mbar at 45 $^{\circ}\text{C}$ for 48 h, in order to have samples fully without water (dry-PVB). Then, the layers were kept in the liquid H_2O environment for the time necessary to ensure an equilibrium liquid content (about 24 h), determined by subsequent weighing of the samples until reaching a constant value. Liquid H_2O used was distilled water, further deionized ($\sigma < 0.1 \mu\text{S}$) and purified with a mixed-bed resin and filters by Milli-Q water system. The liquid content of the layers was measured by TGA at a constant heating rate of 5 K/min in a Setaram thermogravimetric analyzer by maintaining the experimental chamber under a controlled atmosphere of nitrogen. The study of thermal stability indicates the temperature range where the materials keep unchanged their specific characteristics without undergoing any degradation processes.

Fig. 1 compares the weight loss percentages as a function of temperature from 25 $^{\circ}\text{C}$ up to 160 $^{\circ}\text{C}$ of wet sample with those of dry- and as-rec PVB. As the temperature is increased from room temperature, wet- and as-rec PVB evidence weight loss due to the desorption of the absorbed liquid, without no degradation processes. These features more clearly appear in the derivative TG (DTG), where the weight loss is strongly enhanced and revealed as a large peak, inset of **Fig. 1**. The temperature and the area of the peak are related to the maximum rate of weight loss and to the percentage of desorbed liquid, respectively. Indeed, the amount of the lost liquid is quite close to the values of liquid uptake (LU), obtained by the relation

$$LU (\%) = \left(\frac{W_w - W_d}{W_d} \right) * 100$$

where W_w and W_d are the weights of wet and dry layers, respectively: $LU = 1.5\%$ for as-rec PVB and $LU = 3.7\%$ for wet PVB.

2.2. Dynamic mechanical and dielectric analysis

The real and imaginary parts of the complex elastic modulus, $E^* = E' + iE''$ (E' and E'' being the storage and the loss moduli, respectively), were determined over the 120–373 K temperature range and at selected frequencies between 0.1 Hz and 30 Hz by using a dynamic mechanical thermal analyzer [10]. The samples were tested in a configuration of single cantilever driven in bending mode with a fixed displacement (± 20 m). A heating rate of 2 K/min was employed over the whole temperature range. Measurements of E' and E'' were taken by performing a single thermal ramp on PVB samples and by collecting the data at all the selected frequencies at regular temperature intervals during the dynamic heating. The experimental chamber was kept under

a controlled atmosphere of nitrogen during each test.

Dielectric permittivity (ϵ') and loss (ϵ'') were also investigated between 120 and 373 K in non-isothermal condition with a heating rate of 2 K/min using a Rheometric Scientific Dielectric Thermal Analyzer (DETA) over the frequency interval between 0.3 Hz and 30 kHz. Also in this case, measurements of ϵ' and ϵ'' were taken by performing a single thermal ramp on PVB samples and by collecting the data at all the selected frequencies at regular temperature intervals during the dynamic heating. Samples having cylindrical shape were sputtered by gold on both sides for electrodes. The sputtered electrodes gave better electrical contact between polymer and capacitance bridge. The samples were kept between two plates (platinum electrodes, 30 mm diameter) and the measurements were performed by increasing temperature under nitrogen atmosphere. It is worth emphasizing that both mechanical and dielectric experiments have been performed on samples (dry, as-rec and wet) cut from the same layer and having rectangular and cylindrical shapes, respectively.

2.3. Infrared spectroscopy

To study the role of water on vibrational dynamics of PVB polymeric layers, dry circular samples having a diameter of about 2.5 cm and a thickness of about 250 μm were preliminarily dipped in H_2O at room temperature for 24 h, i.e. the time necessary to reach an equilibrium liquid content of 3.7%. Then, the wet-PVB samples were placed into a cryostat under dynamical vacuum at 45 $^{\circ}\text{C}$ and analyzed at regular time intervals by a FT-IR spectrometer from Perkin-Elmer to observe the variations of the frequency and the intensity of the absorption bands associated with water absorption. In this case, the samples analyzed were cut from the same layer also used for thermogravimetry, mechanical and dielectric experiments.

3. Results and discussion

To identify the mechanical relaxations observed in PVB samples, the temperature behaviors of the loss (E'') and storage (E') moduli of as-rec PVB, a polymer already studied by dielectric [11,12] and mechanical [12,13] spectroscopy, is shortly described. As the temperature is increased from 120 K to about 250 K, E'' of amorphous PVB (**Fig. 2a**) increases and passes through the β -relaxation peak at about 185 K (at a frequency of 3 Hz). Above this region, E'' shows the α -relaxation peak, typical of cooperative segmental motions of amorphous chains at the glass transition. It is worth noting that the temperature range of the α -relaxation coincides with that of water desorption (see **Fig. 1**) and a decrease of water content during dynamic heating of the sample above room temperature is to be expected. Hence, the observed temperatures of α -peaks are purely indicative and lower temperatures are to be expected by preserving the water content. Both the relaxation peaks are thermally activated and shift to higher temperatures as the mechanical driving frequency is increased. The storage modulus E' exhibits a considerable inflection in the same temperature region, where the β -peak is observed, and a sharp fall associated to the α -relaxation at higher temperatures (**Fig. 2b**).

Over the frequency range explored, the peak temperatures $T_{p,\beta}$ of β -relaxation follow an Arrhenius behavior (inset of **Fig. 2a**) giving the average activation energy $E_{\beta,mech} = 50.6$ kJ/mole with a characteristic frequency $\omega_0 = 4.31 * 10^{15} \text{ s}^{-1}$.

Similar features are also observed by dielectric measurements. The temperature dependences of ϵ' and ϵ'' (**Fig. 3a** and **b**) reveal the β -relaxation peak at temperatures below T_g and the α -relaxation peak at higher temperatures. Also in this case, the β -peak follows an Arrhenius behavior (inset of **Fig. 3a**) giving the average activation energy $E_{\beta,dielect} = 50.5$ kJ/mole with a characteristic frequency $\omega_0 = 1.95 * 10^{15} \text{ s}^{-1}$. It is worth noting that the values of E_{β} are close to those previously obtained by dielectric (52.1 kJ/mole [11]) and mechanical (54.4 kJ/mol [13]) measurements in similar PVB polymers.

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