



Molecular dynamics of fully biobased poly(butylene 2,5-furanoate) as revealed by broadband dielectric spectroscopy



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ABSTRACT

This work presents the molecular dynamics of both fully amorphous and semicrystalline poly(butylene 2,5-furanoate) (PBF). Broadband dielectric spectroscopy experiments were combined with temperature modulated differential scanning calorimetry measurements. The results showed that the subglass molecular dynamics is characterized by the existence of two dielectric relaxation processes, being the faster one associated to the glycolic subunit, whereas the slower relaxation was assigned to the link in between the ester group and the furan ring. Crystallization affected differently the contribution of these two components. Additionally, crystallization had a stronger effect on the α relaxation process, related to the segmental dynamics of the amorphous phase. In the semicrystalline state, the PBF amorphous phase was described as being composed by different fractions, including a completely rigid one, with distinctly slower mobilities and reduced contributions to the dielectric relaxation, compared to the fully amorphous polymer.

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1. Introduction

The increasing awareness concerning the use of fossil fuels and human impact on the environment has led to a renewed strong interest in the use of sustainable resources for energy and materials [1–3]. Among the different renewable raw materials that have been used for the preparation of bioplastics, furan-based monomers have attracted considerable attention; the most important example being represented by 2,5-furandicarboxylic acid (2,5-FDCA). This monomer is mainly used for the synthesis of poly(ethylene-2,5-furanoate) (PEF), considered the most credible biobased alternative to poly(ethylene terephthalate) (PET) [1–5]. In fact, PEF displays more attractive thermal and mechanical response and improved barrier properties than PET: higher glass transition

temperature (T_g) (358 K vs 349 K) and lower melting temperature (T_m) (484 K vs 520 K) [4,5], a 1.6 times higher Young's modulus [6], 11 times lower oxygen permeability [7], 19 times lower carbon dioxide permeability [8] and a 5 times lower water diffusion coefficient [9]. Last but not least, the production of PEF would decrease the non-renewable energy use of about 40–50% and the greenhouse gas emissions of 45–55% ca. with respect to PET [10]. Furthermore, other 2,5-furan dicarboxylate-based polymers have been synthesized using aliphatic diols with different lengths, for example, sugar diols like isosorbide, benzylic structures like 1,4-bis(hydroxymethyl) benzene, and bisphenols like hydroquinone [6]. In this framework, it has been recently reported the synthesis of the poly(butylene 2,5-furanoate) (PBF) and its copolymers: these reports showed that PBF had good thermal, mechanical [6,11–18] and barrier properties [11], in line with those expected for possible industrial applications such as food packaging.

As reported in the literature [5,11,17] several of these furan-based polymers can crystallize under the appropriate conditions, leading to the development of a semicrystalline material, *i.e.* a polymer composed by phase-separated amorphous and crystalline areas. This fact is very interesting from the applications point of

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view since semicrystalline polymers have enhanced thermal and mechanical properties, and better chemical resistance. However, polymer crystallization is a complicated process that might significantly alter the properties of the remaining amorphous phase [19]. A powerful way of investigating the semicrystalline polymer amorphous phase is by probing its molecular dynamics; particularly, the segmental relaxation is directly connected with the characteristics of the glass transition process, and polymer crystals impose structural constraints affecting these segmental motions [19–22]. However, the details of these effects can be hardly anticipated. Recently, Dimitriadis et al. showed that in PEF, polymer segments could be located within an amorphous fraction with restricted mobility, different from that in the fully amorphous polymer, leading to possible implications in the mechanical and gas barrier properties [5]. This result was obtained using broadband dielectric spectroscopy on samples prepared by following different protocols that resulted in various degrees of crystallinity. In this same work authors also identified the so-called rigid amorphous fraction (RAF) [19–23] to account for the reduced contributions to the dielectric relaxation and the specific heat capacity jump at the glass transition temperature (T_g). The RAF is considered as the result of extreme constraints on the amorphous phase when crystallinity is well developed [19–23].

In this work we report a detailed study on the dielectric relaxation behavior of fully amorphous and cold crystallized PBF, using broadband dielectric spectroscopy. First, we have evaluated the low temperature regime, where we studied the role of glycol length, acid structure and crystallization on the local molecular dynamics, described by the simultaneous presence of two relaxation processes. Then, we have studied the segmental relaxation of this polymer, making special emphasis on how the amorphous phase in the semicrystalline state was affected by the surrounding crystals. In this way, we have interpreted our data using different amorphous fractions, not necessarily phase-separated, that compose the amorphous phase of the semicrystalline material.

2. Experimental section

Poly(butylene 2,5-furanoate) (PBF) was synthesized and characterized as described elsewhere [11]. The PBF chemical structure is presented in Fig. 1.

Broadband Dielectric Spectroscopy (BDS) measurements were carried out in a Novocontrol broadband dielectric spectrometer. This technique allows the study of the complex dielectric permittivity, $\varepsilon^*(\omega) = \varepsilon'(\omega) - i\varepsilon''(\omega)$, where $\varepsilon'(\omega)$ is the dielectric constant and $\varepsilon''(\omega)$ the dielectric losses, as a function of the applied electric field frequency ($\omega = 2\pi f$, f being the frequency) and temperature (T). BDS measurements were performed over a broad frequency window, $10^{-1} \leq f(\text{Hz}) \leq 10^7$, using a Novocontrol Alpha S dielectric interface. The temperature was controlled by a nitrogen jet (Quatro from Novocontrol), with a temperature error during every single frequency sweep of ± 0.1 K. Samples for dielectric studies were prepared by melt-pressing, allowing to obtain homogeneous films. These samples were pressed between two circular gold electrodes

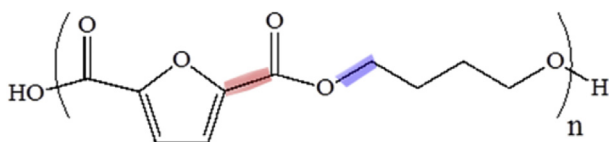


Fig. 1. Poly(butylene 2,5-furanoate) (PBF) molecular structure. Red and blue highlighted bonds are those related to the β_2 and β_1 movements respectively, as discussed in section 3. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

of 40 mm diameter (lower electrode) and 20 mm diameter (upper electrode). In order to avoid any possible short-circuits, Teflon spacers (100 μm thick) were used.

The dielectric studies were conducted as stated in the following lines. The as-prepared PBF film was placed inside the spectrometer cryostat and heated up to 453 K ($T_m(\text{PBF}) = 437$ K [11]), while continuously monitoring its dielectric signal. This final temperature was maintained for 3 min and, immediately afterwards, the sample cell was submerged into a liquid nitrogen reservoir, allowing the sample to reach a temperature of 77 K within a few minutes, and kept at this temperature for 10 min. This procedure permitted to prepare a melt-quenched PBF sample, labeled from now on as **mq-PBF**. For this sample BDS measurements were carried out on heating from 213 K to 393 K. Once the final temperature was reached, the sample cell was again submerged into a liquid nitrogen reservoir and a second heating run was performed, in the range 213 K–353 K. In this last case, as detailed in section 3 and going in line with recent reports [11], the PBF is found in its semicrystalline state. Then, this sample will be denoted from now on as **sc-PBF**.

In general, BDS data analysis was carried out in terms of the Havriliak-Negami (HN) formalism, where the dielectric function follows the relation [24]:

$$\varepsilon^*(\omega) = \varepsilon_\infty + \sum_x \Delta\varepsilon_x \left[1 + (i\omega\tau_{\text{HN}_x})^{b_x} \right]^{-c_x} + \left(\frac{\sigma_{\text{DC}}}{i\varepsilon_0\omega} \right) \quad (1)$$

where $\Delta\varepsilon$ is the dielectric strength of the relaxation and τ_{HN} a characteristic relaxation time; b and c ($0 < b, bc \leq 1$) are shape parameters related to the symmetric and asymmetric broadening, respectively. The summation in equation (1) extends over all the processes present in the experimental window at a specific temperature. Also, the last term in this equation accounts for the contribution of charge carriers to the dielectric signal, where σ_{DC} is the DC conductivity and ε_0 the vacuum permittivity.

From τ_{HN} , the peak relaxation time (τ_{max}) was calculated using the equation [24–26]:

$$\tau_{\text{max}} = \frac{1}{2\pi f_{\text{max}}} = \tau_{\text{HN}} \left[\sin \frac{b\pi}{2+2c} \right]^{-1/b} \left[\sin \frac{bc\pi}{2+2c} \right]^{1/b} \quad (2)$$

where f_{max} is the frequency of maximum loss, and the rest are the HN-function parameters.

Differential Scanning Calorimetry (DSC) measurements were carried out using a TA Instruments Q2000 with a liquid nitrogen cooling system. Temperature-modulated experiments were conducted at a mean rate of 3 K/min, using a 60 s period and ± 0.5 K amplitude. Samples for DSC experiments were prepared by encapsulating about 5 mg of PBF in aluminum pans. For the DSC analysis the specific heat increment (Δc_p) associated with the glass transition of the amorphous phase, was calculated from the area under the curve of the heat flow derivative with respect to the temperature, in the region $278 \leq T(\text{K}) \leq 333$. The glass transition temperature (T_g) was determined from the maximum of the peak. The crystal phase heat of fusion (ΔH_m) was calculated from the difference between the enthalpy associated with the melting endotherm and the cold-crystallization exotherm whenever present.

3. Results

Fig. 2 shows the PBF dielectric loss as a function of the applied electric field frequency, for three representative temperatures: 228 K, 323 K and 353 K. Specifically, left column in Fig. 1 shows the

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