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Molecular Dynamics of PGA Bioabsorbable Polymer During Isothermal Cold Crystallization

Galder Kortaberria, Amaia Jimeno, Puy Arruti, Koro de la Caba, Pedro Remiro, Arantxa Eceiza,* Iñaki Mondragon*

Summary: An investigation was carried out on the molecular dynamics of poly(glycolide) (PGA) in its completely amorphous state and during isothermal cold crystallization. Experimental results were generated over a wide range of frequency and temperature by broad-band dielectric spectroscopy (DRS). The variation of the average relaxation time (defined as $\tau = 1/2\pi f_{max}$ where f_{max} is the frequency at maximum loss for the main α relaxation) has been studied during cold crystallization and the temperature dependence of this average relaxation time for completely amorphous and crystallized samples has been analyzed. This behaviour has been modelled by Havriliak-Negami and Vogel-Fulcher equations. The sensitiveness of the segmental dynamics to the degree of crystallinity has been analyzed, taking into account the relaxing segments and the amorphous layers between lamellae. Supporting evidence about the thermal behaviour of the polymers has been obtained with DSC. Complementarily, the evolution of the morphologies obtained during crystallization processes has been followed by optical microscopy.

Keywords: biopolymers; crystallization; dielectric relaxation spectroscopy; molecular dynamics; relaxation time

Introduction

Biodegradable aliphatic polyesters like poly(glycolide) (PGA) are well known bioabsorbable and biocompatible semicrystalline polymers. Originally limited to the commercial sutures application, they have extend their use to different areas of surgery including dental and fracture repair and ligament reconstruction [1–6], due to their capability of biodegradation through hydrolisis of the ester linkage and the formation of decomposition products which are normal intermediated of cell metabolism[7]. Many investigations [8, 9] have been made to understand the degradation behaviour of these kind of polymers during in vitro and in vivo biochemical applications, being evident that the crystallinity dominates the degradation behaviour.

In the other hand, the effect that the crystalline phase exerts on the α dynamics of the amorphous phase during crystallization is an interesting point [10]. The work presented herein addresses this problem experimentally by using broadband dielectric relaxation spectroscopy (DRS) over a range of frequency and temperature to monitor dynamics during cold crystallization of above mentioned bioabsorbable polymer.

As a starting point it is usefull to ask how the segmental α process in a completely amorphous but crystallizable polymer is altered once the crystals begin to form. This has been studied experimentally over a limited range of frequency and temperature by directly comparing the dielectric spectra

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"Materials + Technologies" Group, Departamento de Ingeniería Química y Medio Ambiente, Escuela Universitaria Politécnica, Universidad del País Vasco/ Euskal Herriko Unibertsitatea, Pza. Europa 1, 20018 San Sebastian (Spain).
Fax: (+34)943017140
E-mail: galder.cortaberria@ehu.es;
arantxa.eceiza@ ehu.es

of crystalline and completely amorphous samples and by continuously monitoring the dielectric response during crystallization. The effect of crystallinity on the average relaxation time τ (related to the frequency of the maximum loss) for the α process is found to be complex and dependant upon the type of polymer. How one can account for these different trends in τ is of interest.

The principal objectives of this preliminary study are (1) to investigate the effect of cold crystallization on molecular dynamics over a wide range of frequency and temperature and (2) to elucidate the effect that the crystalline phase exerts on the main relaxation process before and during cold crystallization comparing the dielectric response of amorphous and crystallizing samples. This behaviour is modeled by the Havriliak-Negami equation [11] and parameters like relaxation time are obtained.

Experimental

The poly(glycolide) PGA polymer studied in this work was kindly supplied by Ethicon Johnson & Johnson with an average molar mass M_w of about 80.000 g/mol. DRS measurements were carried out in a Novocontrol Alpha high resolution dielectric analyzer that covers a frequency range between 3 μHz and 10 MHz. The instrument is interfaced to a computer and equipped with a Novocontrol Novocool cryogenic system for the temperature control. Supporting evidence was obtained from Differential Scanning Calorimetry (DSC) by using a Mettler Toledo DSC822 with scans at 10 °C/min and Optical Microscopy Eclipse E600 with Mettler FP82 HT hot stage device.

Results and Discussion

Two approaches have been undertaken to investigate the effect of crystallization on the molecular dynamics of the biopolymer. The first approach consists on analyzing the relaxation spectra of completely amorphous samples. The second one focuses on in-situ monitoring of the dielectric response during isothermal cold crystallization. For melt crystallization the frequency window used is not enough to follow the evolution of the main relaxations (higher frequencies are needed). Before presenting the DRS results, we briefly review the thermal behaviour of PGA as evaluated by DSC.

DSC thermogram for completely amorphous PGA is shown in Figure 1. Traces were obtained on heating samples quenched from the melt into liquid nitrogen, rendering the sample completely amorphous.

The glass transition, T_g, is observed at around 45 °C. Cold crystallization and melting occurs at 115 °C and 220 °C respectively. Obtained values are in agreement with those found in literature [10–12].

We now present the dielectric results. The relaxation spectra for the completely amorphous sample is examined first. Since the permittivity and loss are related by Kramers-Kronig transform, only loss data are presented in figures. Figure 2 shows the dielectric loss in the frequency domain with temperature as parameter for completely amorphous PGA. Solid lines represent the modeling by Havriliak-Negami equation.

A low intensity β relaxation is observed below T_g as it can be seen at 30 and 40 °C. The α process is clearly seen at temperatures higher than T_g. Below these temperatures this process overlaps with conductivity, as high loss values indicate. The α process is complex thermodielectrically speaking, and the loss peak becomes slightly narrower with increasing temperature. This behaviour has been modeled by Havriliak-Negami equation, isolating both relaxations and conductivity term and obtaining relaxation time (τ) values, for being compared with those obtained for crystallizing samples. As an example, Figure 3 shows the isolated α process as obtained from Havriliak-Negami equation.

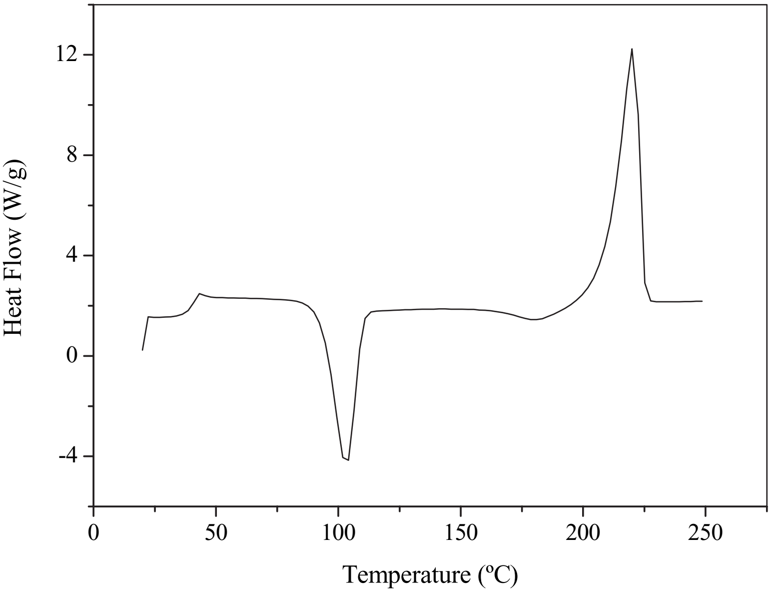

Figure 1.
DSC heating scan for completely amorphous PGA.

The temperature dependence of the relaxation time is examined next. In Figure 4 relaxation time obtained from Havriliak-Negami is plotted as a function of reciprocal temperature for completely amorphous samples. It is well known that the α process in glass-formers deviates from a thermally activated Arrhenius

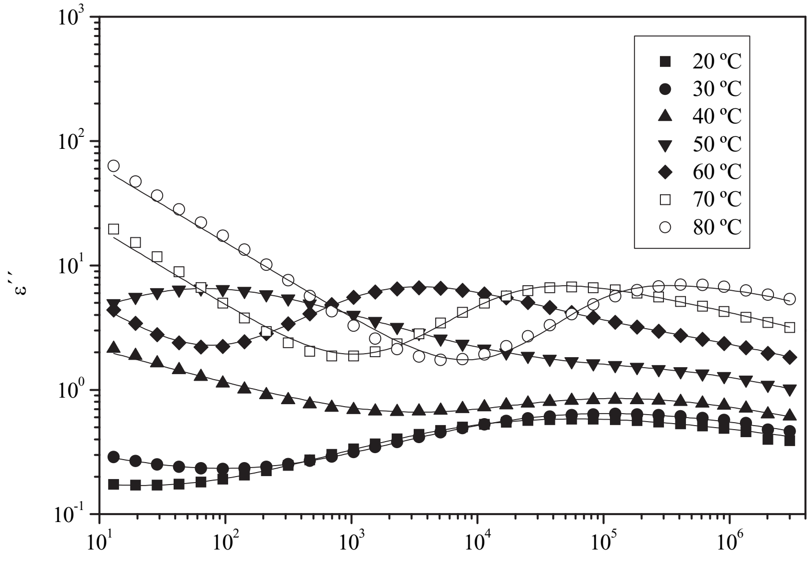

Figure 2.
Dielectric loss in the frequency domain with temperature as a parameter for completely amorphous PGA. Solid lines indicate Havriliak-Negami equation.

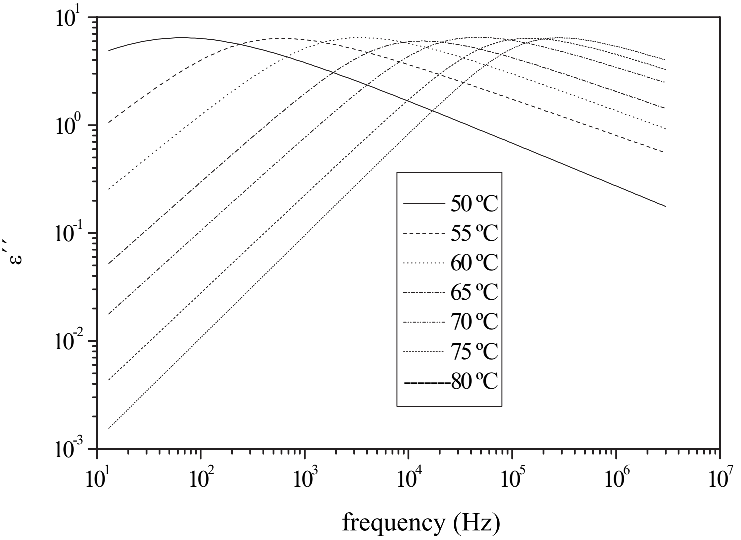

Figure 3.
Isolated α process at several temperatures, as obtained from Havriliak-Negami.

functional form and that much stronger temperature dependence is observed. Such behaviour is generally modeled by the Vogel-Fulcher equation, represented by the solid line in Figure 4. An excellent fit was obtained, with the following fit parameters: τ_0 (attempt frequency) = 3, 2E-19 s^{-1}, E_a (activation energy) = 3,9E-01 eV, and T_v (Vogel temperature) = 210 K. All these values fall in the same range than those found in the literature for similar biopolymers[12,13].

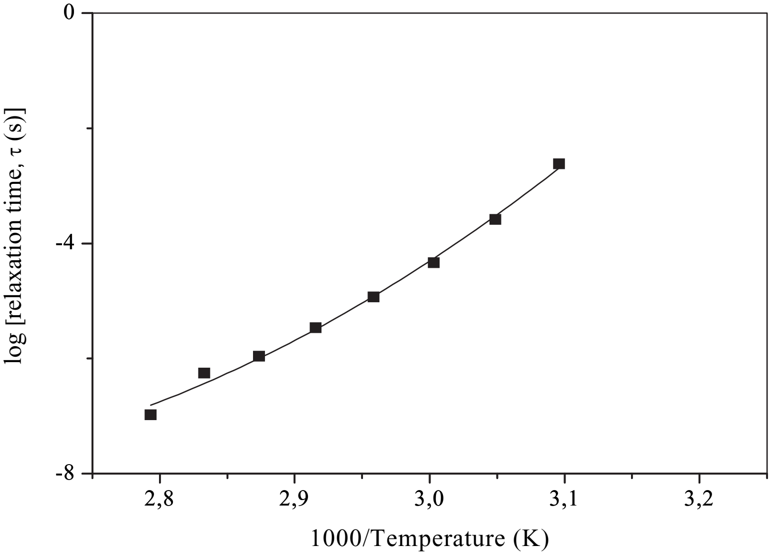

Figure 4.
Relaxation time as a function of reciprocal temperature for completely amorphous PGA. Solid line indicates Vogel-Fulcher equation.

Since the molecular origin of a relaxation process is generally related to its morphological environment, it was anticipated that much could be learned about relaxation dynamics by monitoring dielectric response during the temporal evolution of crystalline morphology. This goal was accomplished by conducting in-situ real-time DRS measurements during cold crystallization of samples. We emphasize that the spectra recorded in each sweep are representative of an *isostructure* (constant degree of crystallinity) at a given stage of crystallization, because the time scale for a sweep is short (less than 40 s) in comparison with the time scale for crystallization. Isothermal frequency sweeps were carried out for PGA at 70 and 80 °C with time as a parameter. Figure 5 (a) and (b) show dielectric loss in the frequency domain at different times during crystallization of PGA at 70 and 80 °C respectively. Solid lines represent the modeling by Havriliak-Negami equation.

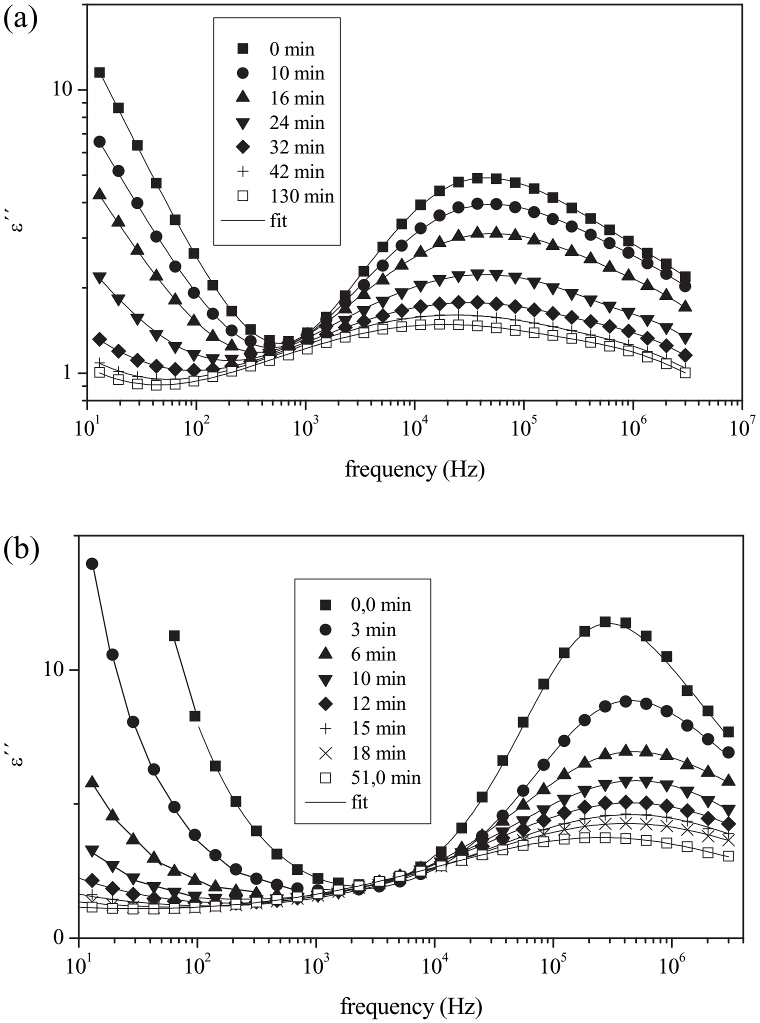

Figure 5.

Dielectric loss in the frequency domain with time as a parameter during the cold crystallization process of PGA at (a) 70 °C and (b) 80 °C. Solid lines indicate Havriliak-Negami equation.

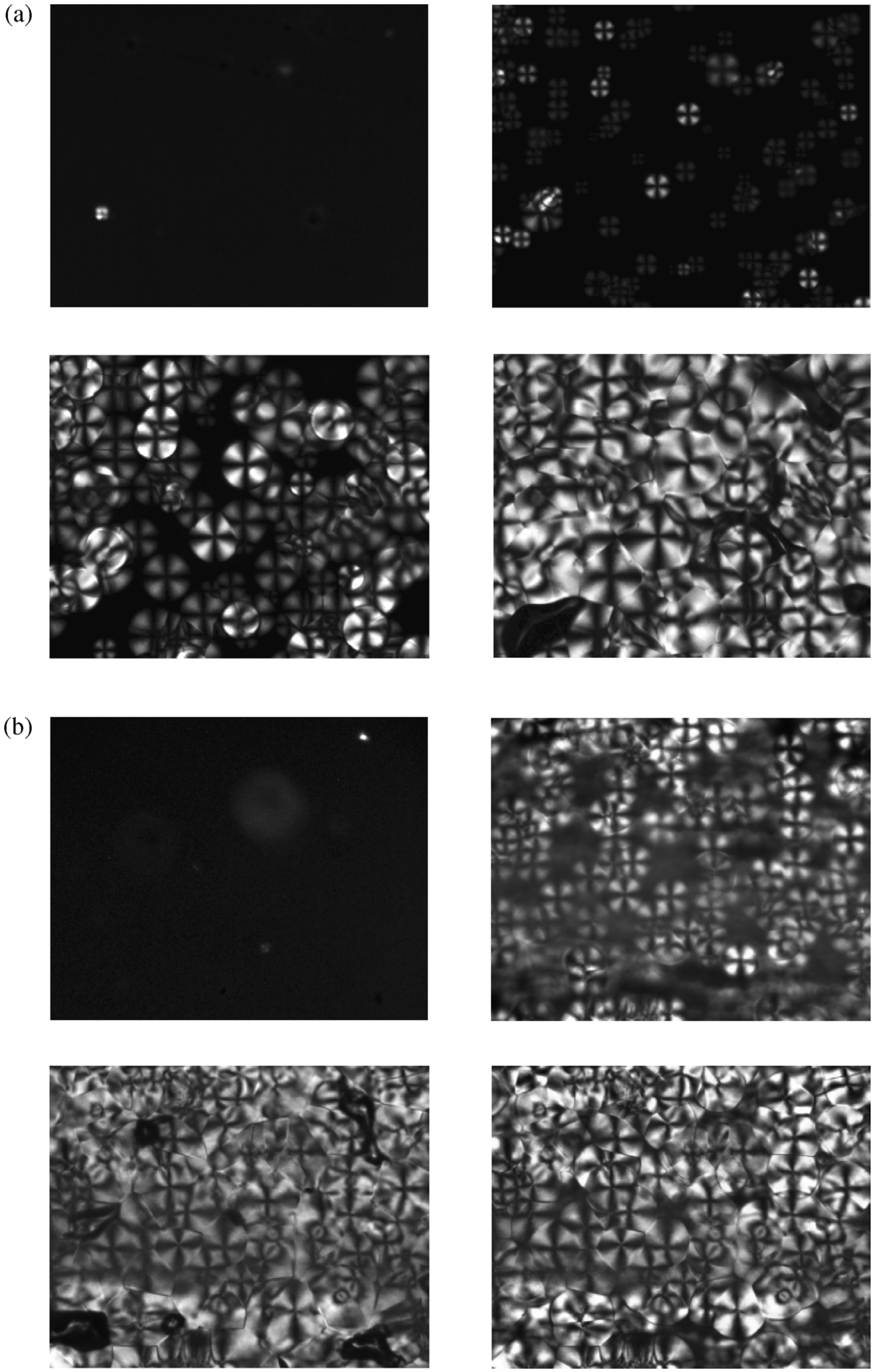

Figure 6.
(a) Optical micrographs during cold crystallization at 70 °C of PGA at 0, 25, 50 and 100 minutes (b) Optical micrographs during cold crystallization at 80 °C at 0, 5, 15 and 25 minutes.

It can be seen that the magnitude of the loss peak and the relaxation strength decrease while the frequency at maximum loss remains unchanged (and consequently relaxation times) as crystallization progresses. Spectra of crystallizing samples broaden during crystallization. At early stages of the process, there is an important conductive component, as reflect the high values of loss at low frequency, which is clearly decreasing with crystallization.

It is worth to note that as we mentioned above relaxation times remain unchanged during crystallization. Moreover, relaxation times obtained from these spectra are equal to those obtained for completely amorphous samples at 70 and 80 °C and fall on the same line presented in Figure 4, thus indicating that the initiation and development of crystallization process does not affect the relaxation time. Many authors have found the same conclusion working with flexible-chain homopolymers like poly(vinylidene fluoride) (PVDF) or homopolymer blends like poly(vinylidene) poly-(methylmethacrylate) PVDF/PMMA [14, 15]. The observed insensitivity of the segmental dynamics to the difference in the degree of crystallinity implies that the domain size of this segmental motion is sufficiently small that the growing crystals do not perturb dipole relaxation, what is to say that the characteristic size of the cooperatively rearranging domains is less than the thickness of the amorphous layer between lamellae [13, 15].

To facilitate the visualization of the development of crystals, we show in Figure 6 (a) and (b) a series of optical micrographs taken at different times during cold crystallization at the same conditions than in DRS measurements. It can be seen the formation and growth of the spherulites. No further exploration of the morphological details vis-à-vis the dynamics was made in this preliminary study, which will be completed with the use of atomic force microscopy (AFM) to follow the development of morphologies in more detail.

Conclusion

Regarding the segmental α dynamics in PGA measured by dielectric relaxation spectroscopy before and during the cold crystallization process, the following can be concluded:

The intensity and the dielectric relaxation strength of the process decrease with increasing degree of crystallinity. The average relaxation time, however, remains unaffected by the formation of lamellar crystals. This insensitivity of those segmental dynamics to the difference in the degree of crystallinity implies that the characteristic size of the cooperatively rearranging domains is less than the thickness of the amorphous layer between lamellae. The domain size of the segmental motion is sufficiently small that the growing crystal units do not perturb dipole relaxation.

The behaviour is modeled by Havriliak-Negami and Vogel-Fulcher equations and obtained parameter values are in agreement with those found in the literature.

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