Molecular Dynamics of PGA Bioabsorbable Polymer
During Isothermal Cold Crystallization

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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 $\tau = \frac{1}{2\pi f_{\text{max}}}$ where $f_{\text{max}}$ is the frequency at maximum loss for the main $\alpha$ 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 hydrolysis 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 $\alpha$ 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 $\alpha$ 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