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Heterogeneous structure of poly(glycolic acid) fiber studied with differential scanning calorimeter, X-ray diffraction, solid-state NMR and molecular dynamic simulation

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ABSTRACT

The heterogeneous structures of poly(glycolic acid) (PGA) fibers which have been used as bio-degradable suture were studied by differential scanning calorimeter (DSC),X-ray diffraction and ^{13}C solid state NMR. The ^{13}C cross polarization NMR spectra without magic angle spinning of the stretched fibers observed by changing the angle between the fiber axis and the magnetic field clearly showed the heterogeneous structures which consist of three components; well-oriented, poorly-oriented and isotropic amorphous components. The local structure, distribution of the fiber axis and fraction of each component were determined quantitatively. Change in the heterogeneous structure by changing the stretching method in the sample preparation and by changing the stretching ratio was also monitored. The X-ray diffraction data of the fibers are in good agreement with the ^{13}C CP NMR data. Change in the heterogeneous structures correlate with change in the thermal properties observed by DSC method. The molecular dynamic simulation showed the generation of trans conformation of PGA chain and also change in the fraction of other conformations by stretching, which supports the experimental results obtained above and gives additional structural information.

1. Introduction

A semi-crystalline biodegradable polyester, Poly(glycolic acid)(PGA) [1–5] has been successfully used as suture materials after stretching the amorphous fiber. However, the main disadvantage of PGA for sutures is its high stiffness and therefore the polymer is processed in a multi-filament form to increase flexibility. In addition, the physical properties and related structures change largely by the processing condition such as stretching.

Chatani et al. [6] determined the crystal structure of stretched PGA fiber by X-ray diffraction method. The dimensions of the orthorhombic unit cell were reported to be $a = 5.22$ Å, $b = 6.19$ Å and c (fiber axis) $= 7.02$ Å. Two PGA chains with planar zig-zag conformation passing through the unit cell permit tight molecular-packing and close approach of the ester groups. However, the stretched PGA fibers are generally heterogeneous and therefore it is necessary to obtain more structural and dynamical information for such a heterogeneous sample which is closely related with the physical properties.

The solid-state NMR has been used for structural and dynamical studies of PGA. Sobczac et al. [7] used ^{13}C CP/MAS NMR to study phase structure and morphology of PGA sutures (Dexon). De Oca et al. [8] studied dynamics of un-stretched isotropic and highly-stretched PGA fibers by second-moment analysis of ^{1}H NMR signal and spin-lattice relaxation time, T_1 analysis by solid-state ^{1}H pulse NMR. They also studied theoretical modeling to explain the elastic behavior of PGA crystals [9]. The tensile modulus is higher along the fiber axis than the other directions. There is a good correction between the experimental modulus (294 GPa) and the theoretical predictions. However, the glass transition temperature, T_g determined experimentally is higher than the T_g value predicted theoretically. They speculated that such a higher shift of T_g is due to the existence of "oriented amorphous component".

We also studied the structure and dynamics of as-spun and stretched PGA fibers by solid echo ^{1}H NMR and WAXD methods [10]. The observed WAXD patterns of highly-stretched fibers showed sharp diffraction peaks from which the crystallinities of stretched fibers with the stretching ratios of 2.5, 2.8 and 3.2 were determined to be 0.50, 0.51 and 0.52, respectively. However, the

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observation of the ^{1}H spin–spin relaxation time (T_2) of these stretched fibers, showed quite different tendencies. The fractions of the "hard" component for the stretched PGA fibers with the stretching ratios of 2.5 and 3.1 were determined to be 0.62 and 0.93, respectively, at 120 °C, from the deconvolution of the observed ^{1}H FID signals. Thus, the picture of the heterogeneous structures is different depending on the analytical methods which indicate what kinds of structures are reflected in the different analytical methods.

The ^{13}C CP/MAS NMR has been frequently used for study heterogeneous polymer structure from the chemical shifts and line shape analyses including several relaxation time observations. However, MAS techniques sometimes delete important structural information instead of peak resolution and intensity enhancements. Thus, ^{13}C CP NMR observation in oriented and non-oriented samples without MAS spinning is sometimes effective for the ^{13}C carbon such as carbonyl carbon with large chemical shift anisotropies. Actually, we successfully applied ^{13}C CP NMR without MAS spinning to study the heterogeneous structures of *Bombyx mori* and *Samia cynthia ricini* silk fibers [11–16], and also stretched synthetic polymers such as poly(ethylene terephthalate) [17], poly(L-lactic acid) [18] and ply(ε-caprolacton) [19]. Importantly, such a ^{13}C CP NMR spectrum has been obtained as a function of the angle between the fiber axis and external magnetic field, which gives detailed information on the heterogeneous structures by analyzing the observed spectra on the basis of orientation-dependent spin interaction tensors.

In this paper, the heterogeneous structures of poly(glycolic acid) (PGA) fibers prepared by different stretching condition and stretching ratio will be studied by differential scanning calorimeter (DSC), X-ray diffraction and ^{13}C solid state NMR. Change in the conformation of PGA molecule by stretching will be also monitored theoretically by the molecular dynamics simulation.

2. Experimental part

2.1. Materials

PGA was synthesized by Mitsui Chemicals, Inc. and its molecular weight was determined to be about 2×10^5 using the gel permeation chromatography (GPC) method. PGA fibers were prepared at 230 °C from the molten state. After cooling them at room temperature, the amorphous fibers were stretched by two different methods. For case A (Pre-heated method); 10 cm of un-stretched PGA fibers were held on a tensile strength instrument for 1 min just above T_g of PGA and then, the fibers were stretched at the rate of 100 mm/min at 62 °C. The stretched samples were prepared to 1.5 and 3.5 times which were defined to be the ratio of stretched fiber length to original untreated fiber length. For case B (After-heated method); 10 cm of un-stretched PGA fibers were stretched at the rate of 100 mm/min. at 23 °C (below T_g) and then, the fibers were heated at 62 °C for 1 min. The stretching ratios were the same as those in case A. The tensile strength was measured at room temperature with an extension rate of 100 mm/min while keeping the gauge length, 100 mm. The heterogeneous structures of the stretched fibers prepared by these two methods are different even if the stretching ratio is the same.

2.2. DSC measurement

The DSC measurements were carried out with a Perkin–Elmer Pyris 1 instrument to observe T_g and T_m temperatures. To avoid a change of T_m of the PGA fiber sample by its shrinkage, the fibers were bound by a fine metal wire and coiled on the sample pan while keeping a strain of the fibers. The heating rate was 10 °C/min. T_g was determined from the mid-point of specific heat transition.

2.3. X-ray diffraction measurement

Wide-angle X-ray diffraction (WAXD) of the un-stretched and stretched PGA fibers was observed by a Rigaku RINT2500 X-ray instrument utilizing nickel-filtered CuK_α radiation (wave length $\lambda = 1.54$ Å) at room temperature. PGA fibers were rolled and mounted carefully to avoid further stretching of the samples on a holder.

2.4. Solid-state NMR

^{13}C solid state NMR experiments were performed at 23 °C using a Bruker AVANCE400 WB spectrometer at resonance frequencies of 100.6 MHz for ^{13}C nuclei. The ^{13}C CP/MAS NMR spectra were recorded under observation conditions, a CP contact time of 3 ms, a repetition time of 5 s, a spinning speed of 7 KHz and the numbers of scans were 4 k. The ^{13}C CP NMR spectra of the blocks of uniaxially stretched PGA fibers were also obtained under similar observation conditions without MAS spinning. In this observation, a home built probehead with a 1 cm square coil for ^{13}C observation with ^{1}H decoupling was used. The angle of the fiber axis and the magnetic field was changed. Typically, 12k scans were accumulated for each spectrum. The ^{13}C chemical shift tensors of the carbonyl carbons of these samples were obtained by fitting the line shape of amorphous PGA fibers [17]. The simulations of the angle-dependent ^{13}C CP NMR spectra on the basis of chemical shift anisotropies were performed by the least-square method [17–19].

2.5. Molecular dynamic simulation

The molecular dynamics (MD) and molecular mechanics (MM) calculations were carried out by using 'Material Studio 4.1 Discover' module (Accelrys Inc.). All of the simulations were performed by using pcff force field (Accelrys Inc.). The model of initial amorphous PGA structure before stretching was reproduced as follows. The 18 PGA chains with 20 polymerization degree and with all trans conformations were generated on the computer according to the crystal structure of stretched PGA fiber by X-ray diffraction method [6]. Then 2 Å was added to the distance of the inter-chains along *a* and *b* axes to produce amorphous state. The infinite bulk system of the infinite repeated polymer chains, periodic boundary condition, was set. Then, MD simulations were performed at 10,000 steps at 1000 °C under external shear stress of 0.3 GPa which was set parallel to the fiber axis, *c* axis. Then, additional MD simulation under equivalent hydrostatic pressure of 1.0 GPa and then annealing was performed. The amorphous PGA structure with density of 1.50 determined experimentally [20] for amorphous PGA sample was obtained. The stretching of such amorphous PGA chains was performed as follows. 4 Å was added to the original chain length of each chain selected from 18 chains and then MD simulation was performed at 50,000 steps (50 psec) at 100 °C under the fixed co-ordinates of the end atoms of the PGA molecule. The same process was repeated for 18 PGA chains. Then MM calculation was then performed to minimize the conformational energies. This process (adding each 4 Å to the end-to-end distance of the stretched PGA chain) was repeated and conformational distribution of the PGA chains was obtained under increase in the stretching ratio. Finally, the stretched PGA chains with stretching ratio from 1.0 to 1.91 for each 0.11 increase were obtained. The internal rotation angles of the C–C or C–O bonds of PGA molecules after MD and then MM calculations were plotted to examine conformational change by stretching.