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Effect of temperature and HV monomer concentration on parameters of the unit cell of the PHB/HV biopolymer crystal

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Changes of the unit cell parameters in the crystalline phase of the poly(β-hydroxy-butyrate-*co*-valerate) (PHB/HV) containing 0, 6, 15 and 22 mol% HV, during heating from room temperature to the melting point, were studied. It was found that unit cell expansion occurred with increasing HV monomer concentration from 0 mol% to 22 mol%. The increase in lattice parameters a and b are almost linear with increasing concentration and the concentrational expansion coefficients in the direction a and b are about 6×10^{-4} (mol%HV)$^{-1}$ and 3×10^{-4} (mol%HV)$^{-1}$, respectively. The parameter c (fibre axis) remains unchanged. Temperature change causes unit cell expansion characterized by significant change of the parameter a only, with the linear coefficient of thermal expansion of about 1.3×10^{-4} °C^{-1}. © 1997 Elsevier Science Ltd. All rights reserved.

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Introduction

At low concentration of the HV monomer (below 30 mol%) the statistical copolymer of biological origin, PHB/HV, crystallizes in the PHB type of crystalline lattice with orthorhombic unit cell ($P2_12_12_1$) and parameters[1] $a = 5.76$, $b = 13.20$ and $c = 5.96$ Å. Bluhm *et al.*[2] and Mitomo *et al.*[3] showed that increasing concentration of HV in the PHB/HV copolymer causes the increase of the elementary cell along the a direction, while Marchessault *et al.*[4] indicated that change along the b direction also takes place. It was also found that, as a consequence of the isodimorphism with PHB/HV, the increase of HV content does not change the type of the crystalline lattice (PHB type) up to a concentration of about 30 mol%. At higher concentrations of HV the copolymer crystallizes in the PHV type crystalline lattice. We have shown that increasing temperature causes expansion of the elementary cell of the PHB homopolymer along the parameter a, the coefficients of thermal expansion in the a direction being an order of magnitude higher than that for b and c parameters[5]. Martinez-Salazar *et al.*[6] studied spherulite cracking and thermal expansion of PHB/HV copolymers and found a similar order of magnitude of thermal expansion coefficients for a and b parameters.

In this work we have re-examined the combined effect of temperature and concentration of HV monomer on the change of parameters of the elementary cell in the crystalline phase of the PHB/HV biopolymer at HV concentrations below 30 mol%. We have estimated the coefficient of concentrational expansion and given new values for the thermal expansion coefficient.

Experimental

Powdered samples of PHB/HV obtained from ICI Biological Products Division (Billingham, UK) were used as received. X-ray data were collected on a Philips powder diffractometer (model PW1050, with CuK_α radiation) using a controlled heating module (Anton Paar, model HTK 10). The parameters a and b of the elementary cell, as a function of the composition and temperature, were determined from the position of the diffraction maxima (0 2 0) and (1 1 0). The peaks were registered using a proportional counter in a wide enough interval of Bragg angles (about four half-widths of the measured peaks). The position of diffraction maxima was optimized by fitting the measured counts in Gaussian profile of the peak, and taking into account the profile of the amorphous halo below the peak, which was approximated linear (for 0 2 0) and quadratic (for 1 1 0) functions.

Thermal expansion of PHB/HV (6 mol%HV) was also measured by dilatometry (TMA-2940 TA Instruments) at a heating rate of 5°C min^{-1} in the temperature range 23–150°C. Injection moulded 2 mm thick samples were heated up to 150°C (close to T_m) and then quenched in cold water.

Results and discussion

Parameters of the elementary cell of the PHB/HV crystal phase with HV concentration varying from 0 mol% up to 22 mol% were determined from WAXS data. The temperature varied from ambient to the melting point of the polymer. It was found that expansion of the orthorhombic elementary cell occurred with increasing temperature and HV content, characterized by linear elongation of parameters a and b, while parameter c was unchanged. This expansion occurred under the influence of both factors up to limiting values

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of the elementary cell, where a phase change took place. The phase change could be either melting (above T_m) or transition from PHB to PHV type unit cell (above 30 mol% of HV).

The measured values of the cell parameters *a* and *b* for PHB/HV are fitted in a linear function having the form

$$x = x_0(1 + A\theta)$$

where x_0 are corresponding values of the cell parameters at 0°C or 0 mol%HV, *A* represents the thermal or concentrational coefficients of expansion, while θ represents variables temperature or HV content. *Table 1* displays the measured values of the parameters *a* and *b* for PHB/HV cell at different temperatures and different HV monomer concentration. *Table 2* shows values for both thermal and concentrational expansion coefficients for the given cell parameters. The thermal expansion coefficients in this work are compared with the recalculated corresponding average values of previously published data[6].

Both *a* and *b* parameters vary almost linearly with the change of HV concentration with coefficients α_a and α_b, characterizing the rate of the *a* and *b* parameter increase with the increase of HV concentration. They are found to be 6×10^{-4} and 3×10^{-4} $(\text{mol\%HV})^{-1}$, respectively. In *Figure 1*, the relative expansion (%) along the *a* and *b* axes with increasing HV content is shown. As can be seen, this expansion at lower HV concentration is approximately the same. At higher HV concentration (above 15 mol%HV) the increase of the parameter *a* is faster, causing the expansion coefficient α_a to be higher than α_b in the whole range of investigated HV concentrations. A similar change of the parameter *a* with HV content in PHB/HV has also been observed by other authors[3,4].

Figure 2 indicates that increasing temperature at a fixed HV concentration causes expansion of the elementary cell

Table 1 PHB/HV cell parameters *a* and *b* as a function of HV content and temperature

HV (mol%)	0	6	15	22
T(°C)	*a*(±0.01 Å)			
30	5.74	5.76	5.78	5.83
50	5.76	5.77	5.80	5.85
70	5.78	5.79	5.81	5.86
90	5.79	5.81	5.82	5.87
110	5.81	5.82	5.84	5.89
130	5.82	5.83	5.85	5.90
150	5.84	5.85	5.87	5.92
160	5.85			
b (±0.02 Å)	13.20	13.24	13.27	13.30

Table 2 Thermal (λ) and concentrational (α) expansion coefficients for PHB/HV for the *a* and *b* parameter

mol%HV	λ_a (°C^{-1}) ×10^4	λ_a (from ref. 6) (°C^{-1}) ×10^4	λ_b (°C^{-1}) ×10^5	λ_b (from ref. 6) (°C^{-1}) ×10^5
0	1.4 ± 2	2.5	2	3.3
6	1.3 ± 2	2.4	0.3	2.9
12		3.2		0.34
15	1.2 ± 2	2.7	−0.7	0.34
19		2.1		0.34
22	1.2 ± 2		−2	

$\alpha_a = (6 \pm 1) \times 10^{-4}$ $(\text{mol\%HV})^{-1}$ $\alpha_b = (3 \pm 1) \times 10^{-4}$ $(\text{mol\%HV})^{-1}$

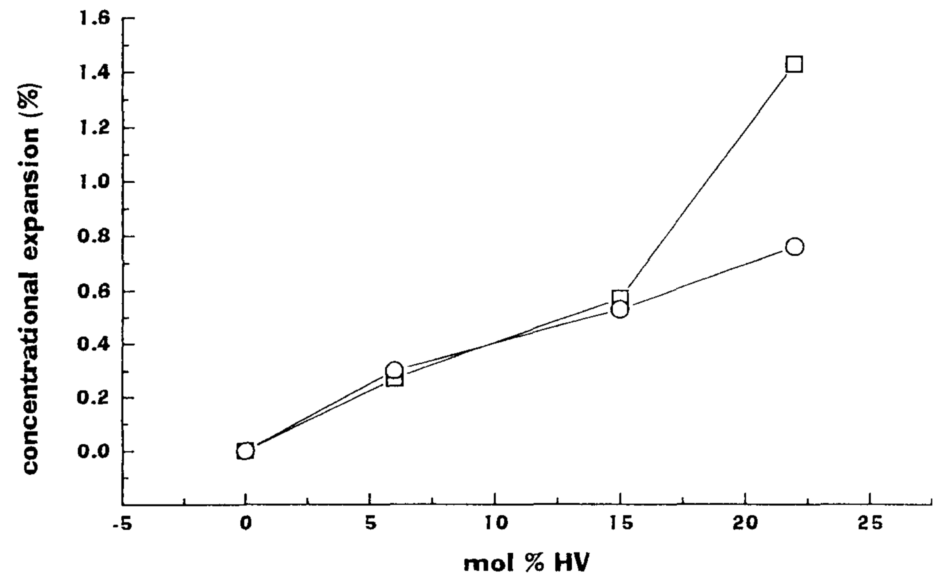

Figure 1 Relative concentrational expansion of the PHB/HV unit cell along *a* (□) and *b* (○). Data for parameter *a* averaged over temperature

of PHB/HV through the parameter *a*, λ_a being the coefficient of thermal expansion. The average value obtained for λ_a at different concentrations of HV monomers in PHB/HV is around 1.3×10^{-4} °C^{-1}, and in good agreement with the corresponding reported coefficient for PHB[5].

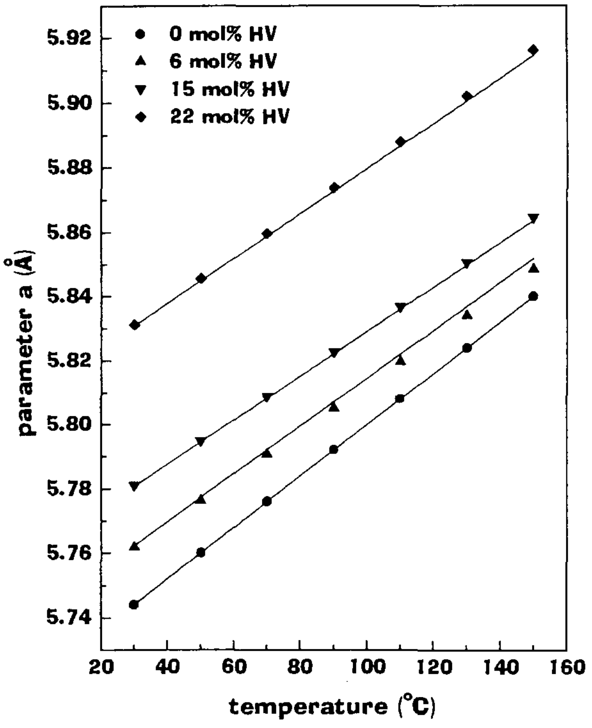

Figure 2 Thermal expansion of the PHB/HV unit cell along *a* for different HV content

According to our measurement the cell parameter *b* does not vary significantly with temperature. As can be seen from *Table 2*, in both works the thermal expansion coefficients along the *b* direction are one to two orders of magnitude lower than those for the *a* direction, and they are comparable with the thermal expansion coefficient for the *c* direction[5]. The value for the thermal expansion coefficient of the *a* parameter ($\lambda_a = 1.3 \times 10^{-4}$ °C^{-1}) obtained by the authors of this paper is one half the value of the corresponding average value (2.6×10^{-4} °C^{-1}) in the Martinez-Salazar paper[6].

Taking into account the effect of both factors on expansion of the elementary cell in the crystalline phase of PHB/HV, the parameters *a* and *b* could be related to temperature end concentration of HV by the expressions

$$a(T, \text{mol\%HV}) = a_{00}(1 + \lambda_a T)(1 + \alpha_a \, \text{mol\%HV})$$

$$b(\text{mol\%HV}) = b_0(1 + \alpha_b \, \text{mol\%HV})$$

The values $a_{00} = 5.72$ Å (for 0 mol%HV and 0°C) and $b_0 = 13.20$ Å (for 0 mol%HV) are obtained from the linear fit.

The t.m.a. diagram of PHB/HV (6%HV) is shown in *Figure 3*. The average thermal expansion coefficient over the whole temperature range of the measurement was 1.63×10^{-4} °C^{-1} and in good agreement with the average value (1.3×10^{-4} °C^{-1}) obtained from the X-ray study. Thermal expansion coefficients at particular temperatures are indicated on the experimental curve. The increase of α around 100°C and its variation at 120°C may reflect the crystalline–amorphous–crystalline domain reorganization described in our previous paper[7].

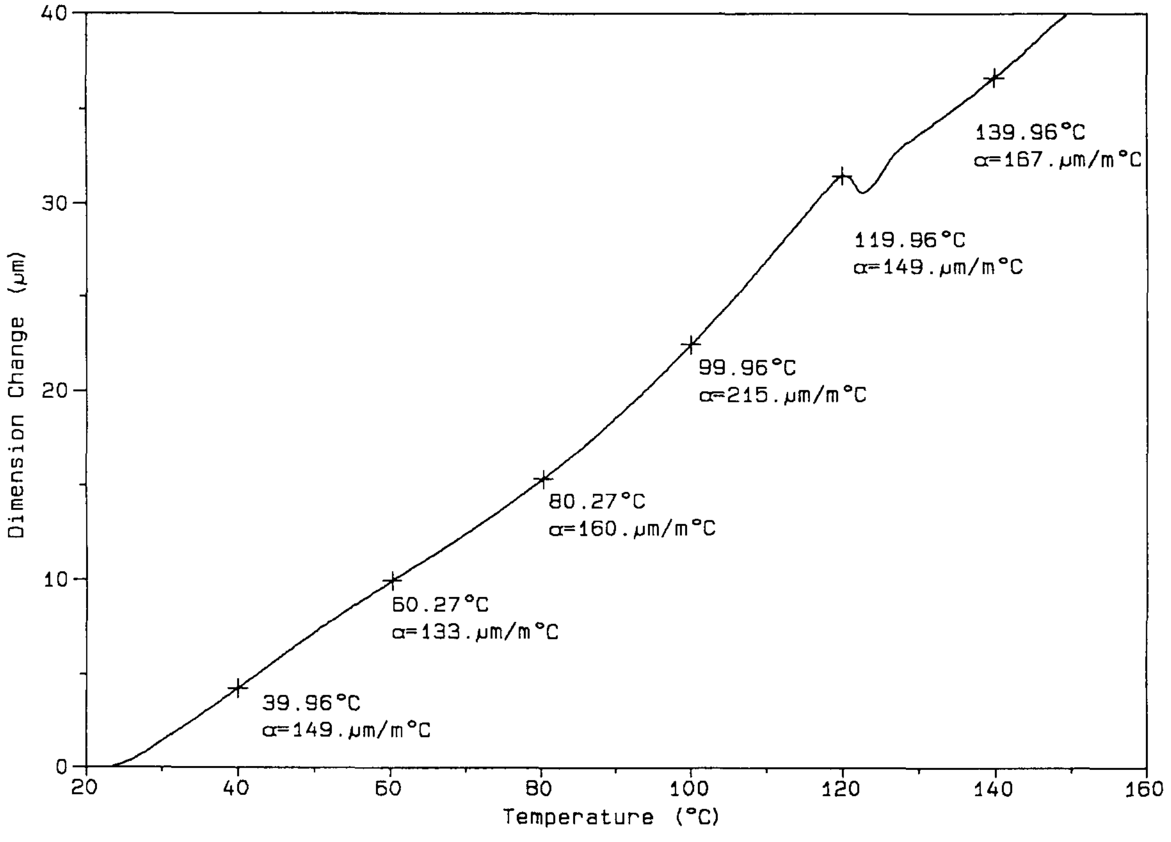

Figure 3 T.m.a. diagram of PHB/(6 mol%HV)

Conclusion

The effect of temperature and HV monomer concentration on the dimensions of the elementary cell of the crystalline phase in the PHB/HV biopolymer, for the PHB type of crystalline cell (<30 mol%HV), is characterized by the linear change of the a and b parameters. Increasing the HV concentration causes the increase of both cell parameters, but the increase in parameter a is faster ($\alpha_a > \alpha_b$), assuming the whole range of investigated concentrations. Increasing temperature, however, increases the parameter a dominantly ($\lambda_a \gg \lambda_b$). The total increase of the cell parameter a under the influence of both factors is bounded by limiting value of about 5.90 Å. For PHB/HV at room temperature this limiting value can be reached by an increase of the HV content up to 30 mol%, or a temperature increase for both PHB homopolymer and PHB/HV copolymer up to the melting point.

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