Thermal Shrinkage of Fibrous Polymers by Partial Melting of Crystalline Regions

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Relations among the relative shrinkage, orientation distribution function and orientation factor were investigated for fibrous polymers on the basis of the shrinkage theory proposed in previous paper. It was shown that the orientation distribution function was written as an exponential function of λ, and the orientation factor f_a in amorphous regions was represented by a parabola curve with respect to ΔG or (S/λ).

INTRODUCTION

Thermal shrinkage of fibrous polymers along the fiber axis may be mainly caused by partial melting of crystalline regions, the decrease in the number of pseudo cross-links in amorphous regions, the decrease in orientation of amorphous chains and re-crystallization in amorphous regions. Above all, the thermal shrinkage by partial melting of crystalline regions and the decrease in the number of pseudo cross-links in amorphous regions have been already investigated theoretically in the previous papers.[1~3] These theoretical treatments of thermal shrinkage were discussed on the basis of Flory's melting theory on polymer-diluent systems and on cross-linked polymer systems.[4,5]

Fischer[6] has indicated that the dimensional stability of crystalline polymers was closely related to the mechanism of partial melting of crystalline regions. Conformational entropy of amorphous chains may substantially affect the dimensional stability of crystalline polymers. This conformational entropy of amorphous chains was discussed in detail by Zachmann.[7,8]

In this paper, thermal shrinkage of fibrous polymers by partial melting will be discussed in terms of the orientation distribution function and the orientation factor in amorphous regions.

THEORETICAL TREATMENT

Relation between Relative Shrinkage and Orientation Distribution Function of Amorphous Chains

According to Flory,[4,9] the change in Gibbs free energy accompanying disappearance of crystalline regions in polymer in the absence of diluent, when the crystalline length is constant at a given temperature, is given by

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$$(h_u - Ts_u) - (h_x - Ts_x) - (2\sigma_e/\zeta) = kT[(1/x\lambda) - (1/\zeta)\ln\{(x-\zeta+1)/x\}] \qquad (1)$$

h_u : heat of fusion per structural unit.

s_u : entropy of fusion per structural unit.

h_x : heat of transition per structural unit due to pseudo cross-links in amorphous regions.

s_x : entropy of transition per structural unit due to pseudo cross-links in amorphous regions.

σ_e : surface free energy per structural unit.

ζ : length of crystallite in number of units.

λ : amorphous fraction.

x : total number of structural units in a polymer molecule.

k : Boltzmann's constant.

T : absolute temperature.

Whereas, the relation between the amorphous fraction λ and the relative shrinkage S is given by[1]

$$\lambda = SL_c/(L_c - L_a) \qquad (2)$$

where, L_c and L_a are the lengths of sample in totally crystalline and totally amorphous states, respectively. Substituting eq. (2) in eq. (1), we obtain a relation between S and T

$$\frac{1}{S} = A\frac{1}{T} - \frac{xL_c}{k(L_c - L_a)}\frac{1}{\zeta}\ln\left(\frac{x-\zeta+1}{x}\right) \qquad (3)$$

in which,

$$A = \frac{xL_c}{k(L_c - L_a)}\left\{(h_u - Ts_u) - (h_x - Ts_x) - \frac{2\sigma_e}{\zeta}\right\}$$

Further, the Gibbs free energy change ΔG [ΔG is equal to $(h_u - Ts_u) - (h_x - Ts_x) - (2\sigma_e/\zeta)$, the left hand term in eq. (1)], is regarded to be approximately governed by the conformational entropy of amorphous chains,[6] and hence

$$\Delta G = kT\frac{1}{\phi}\left(\frac{\partial\phi}{\partial n} + \frac{\partial\phi}{\partial r}\frac{dr}{dn}\right) \qquad (4)$$

where, ϕ is the conformation factor, r the end-to-end distance in an amorphous chain, and n the number of segments per an amorphous chain.

Since the conformation factor ϕ for Gaussian and Langevin chains is, respectively, given by

$$\phi = \Delta V(3/2\pi nb^2)^{3/2}\exp(-3r^2/2nb^2), \text{ Gaussian chain} \qquad (5)$$

$$\phi = B\Delta V\left(\frac{\sin h\beta}{\beta}\right)^n\exp(-\beta r/b), \text{ Langevin chain} \qquad (6)$$

where, $\beta = L^*(r/nb)$, L^*: Inverse Langevin function, B: normalization constant, ΔV: arbitrary volume, and b: length of a segment, the following equations are obtained for Gaussian and Langevin chains.

$$\Delta G = kT(3/2n^2b^2)(r^2 - nb^2 - 2rnb\cos\gamma), \text{ Gaussian chain}, \qquad (7)$$

$$\Delta G = kT(-3/2n) + \ln\left(\frac{\sin h\beta}{\beta}\right) - \beta\cos\gamma), \text{ Langevin chain}, \qquad (8)$$

If r is changed by partial melting of crystallites, then it may be assumed that the melting in the side face of crystallite does not occur and, thus, $2(1-\lambda)/\zeta$ becomes constant. Therefore, the term $2(1-\lambda)/\zeta$ is disappeared by differentiation of ΔG by λ, so that $-2\sigma_e/\zeta$ in ΔG is neglected, and hence

$$\Delta G = (h_u - Ts_u) - (h_x - Ts_x)$$

The orientation distribution function $F(\gamma)$ in Langevin chain is represented by[10]

$$F(\gamma) = \frac{fb}{4\pi kT} \frac{1}{\sinh(bf/kT)} \exp\{L^*(r/nb)\cos\gamma\} \tag{9}$$

where, f is the force, and γ is the angle between the direction of a segment and the end-to-end distance vector. From eq. (9), the following equation is obtained.

$$-(3/2n) + \ln\left(\frac{\sinh\beta}{\beta}\right) - \beta\cos\gamma = -(3/2n) - \ln(4\pi) - \ln F(\gamma) \tag{10}$$

With respect to Gaussian chain, the orientation distribution function $F(\gamma)$ is represented by[10]

$$F(\gamma) = \frac{3r}{4\pi nb \sinh(3r/nb)} \exp(3r\cos\gamma/nb) \tag{11}$$

Therefore, in this case, the following equation is obtained.

$$(3/2n^2b^2)(r^2 - nb^2 - 2rnb\cos\gamma) = -\ln(4\pi) - (3/2n) - \ln F(\gamma) \tag{12}$$

Thus, for both Gaussian and Langevin chains, ΔG is given as a function of $F(\gamma)$ by an identical equation as

$$\Delta G = kT\{-\ln(4\pi) - (3/2n) - \ln F(\gamma)\} \tag{13}$$

Substituting eq. (13) in eq. (3), one obtains relation between the orientation distribution function $F(\gamma)$ and the relative shrinkage S

$$k\{-\ln(4\pi) - (3/2n) - \ln F(\gamma)\} = \frac{k(L_c - L_a)}{xL_c}\frac{1}{S} - \frac{1}{\zeta}\ln\left(\frac{x-\zeta+1}{x}\right) \tag{14}$$

Further, A in eq. (3) is represented by

$$A = \{-\ln(4\pi) - (3/2n) - \ln F(\gamma)\}\frac{xTL_c}{L_c - L_a} \tag{15}$$

Therefore, the orientation distribution function $F(\gamma)$ is written as

$$F(\gamma) = C\exp\left\{-\frac{A(L_c - L_a)}{xTL_c}\right\} \tag{16}$$

with

$$C = \exp\left\{-\left(\frac{3}{2n} + \ln 4\pi\right)\right\}$$

Relation between the degree of polymerization x and the force f, in reversible process of thermal deformation, is represented by[3]

$$N_A/f = xL_c/kA \tag{17}$$

where N_A is the Avogadro number. Therefore, substituting eq. (17) in eq. (16), we obtain the orientation distribution function $F(\gamma)$ represented by

$$F(\gamma) = C \exp\left\{-\frac{f(L_c - L_a)}{TR}\right\} = C \exp\left(-\frac{N_A \Delta G}{TR}\right) \tag{18}$$

In addition, as ΔG was expressed as a function of S by

$$N_A \Delta G = ARS/x\lambda, \tag{19}$$

substitution of eq. (19) in eq. (18) leads to the following equation.

$$F(\gamma) = C \exp\left\{-\frac{A}{Tx}(S/\lambda)\right\} \tag{20}$$

$$F(\gamma) = C \exp\left\{-\frac{fL_c}{TR}(S/\lambda)\right\} \tag{21}$$

If the second term in the right hand of eq. (3) is neglected, then eq. (3) is written as

$$S = T/A \tag{22}$$

and hence one obtains the following equations by substituting eq. (22) in eq. (20) or in eq. (21).

$$F(\gamma) = C \exp(-1/x\lambda) \tag{23}$$

or

$$F(\gamma) = C \exp/(-fL_c/RA\lambda) \tag{24}$$

Thus, $F(\gamma)$ was represented by exponential functions of λ.

By combining eqs. (4) and (13), the orientation distribution function $F(\gamma)$ is expressed as a function of ϕ by

$$\ln C - \ln F(\gamma) = \partial \ln\phi/\partial n \tag{25}$$

Therefore, the relative shrinkage is finally represented by the following equation by combining eqs. (20), (21), and (25).

$$S = (\lambda/fL_c)\{TR(\ln C - \ln F(\gamma)\} = (\lambda/fL_c)TR(\partial \ln\phi/\partial n) \tag{26}$$

Relation between Relative Shrinkage and Orientation Factor of Amorphous Chains

The orientation factor f_a of amorphous chains is generally represented by[11]

$$f_a = 1 - \frac{3r/nb}{L^*(r/nb)} \tag{27}$$

and the average value, $\langle\cos^2\gamma\rangle$, of $\cos^2\gamma$ is given as

$$\langle\cos^2\gamma\rangle = 1 - \frac{2r/nb}{L^*(r/nb)} \tag{28}$$

Hence, f_a is represented by

$$f_a = \frac{3\langle\cos^2\gamma\rangle - 1}{2} \tag{29}$$

On the other hand, the length L_a of the sample in totally amorphous state is given by

$$L_a = L_c(\langle\cos^2\gamma\rangle)^{1/2} \tag{30}$$

Thus, from eqs. (29) and (30), f_a is alternatively given by

$$f_a = \frac{3}{2}\left(\frac{L_a}{L_c}\right)^2 - \frac{1}{2} \tag{31}$$

Moreover, from eqs. (2) and (31), f_a is expressed as a function of S/λ by

$$f_a = 1 - 3(S/\lambda) + (3/2)(S/\lambda)^2 \tag{32}$$

Combination of eqs. (19) and (31) gives a relation between f_a and ΔG.

$$f_a = (3/2)(x/Ak)^2(\Delta G)^2 - 3(x/Ak)\Delta G + 1 \tag{33}$$

Thus, it was shown that f_a is a quadratic function of S/λ or of ΔG.

Conformational Entropy and Entropy of Fusion

According to eq. (19), difference ΔS between the entropy of fusion and the entropy of transition in amorphous regions is represented by

$$\Delta S = (s_u - s_x) = \frac{h_u - h_x}{T} - \frac{AkS}{x\lambda T} \tag{34}$$

Hence, substituting eq. (22) in eq. (34), one obtains

$$\Delta S = \frac{h_u - h_x}{T} - \frac{k}{x\lambda} \tag{35}$$

If $h_u = h_x$, then,

$$\Delta S = -k/x\lambda \tag{36}$$

The entropy difference ΔS shown in eqs (34)–(36) should be equal to the conformational entropy of amorphous chains, hence, this quantity is indicated by the following equations for Gaussian and Langevin chains, by the use of eqs. (7) and (8).

$$\Delta S = k\left\{\frac{3}{2n^2b^2}(r^2 - nb^2 - 2rnb\cos\gamma)\right\}, \quad \text{(Gaussian chain)} \tag{37}$$

$$\Delta S = k\left\{-\frac{3}{2n} + \ln\left(\frac{\sin h\beta}{\beta}\right) - \beta\cos\gamma\right\}, \quad \text{(Langevin chain)} \tag{38}$$

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