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Structural Factors Controlling Tensile Yield Deformation of Semi-Crystalline Polymers

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Summary: In this work, a molecular model is proposed to account for the stress-strain relationships of spherulitic polymers. To describe the yielding behavior of spherulitic polymers, we introduced a new structural unit, i.e. the lamellar cluster, which is represented by several stacked lamellae bound by some tie molecules. It was shown that the tie molecules between the adjacent lamellar clusters produce the concentrated load acting on the cluster surface, leading to bending deformation of the lamellar cluster. The yielding behavior was explained by the disintegration of lamellar cluster due to the bending deformation.

Introduction

Semicrystalline polymers such as PE and PP prepared from the melts show spherulitic structure in which crystalline lamellae composed of folded chain crystallites radiate from its center. Tensile properties, in particular tensile yielding behavior, of these semicrystalline polymers have received a great deal of attention and study with growing use of these polyolefin materials. It has been reported that the yield process is associated with the onset of irreversible deformation such as dislocation of lamellar crystals1) and local melting process.2) However, the molecular and structural basis underlying the tensile deformation is not as well understood as would be desired. The purpose of this study is to clarify the structural factors which govern the tensile yield deformation of PP materials.

Yield Theory3)

In tensile tests, semicrystalline polymers usually show a distinct yield point as a maximum load in the stress-strain curves when deformation is done in the temperature range from T_g to T_m. As is well-known, the yielding deformation of spherulitic materials leads to a large scale transformation of the spherulitic into the fibrillar form. These conclusions have been well confirmed by a great deal of experimental work. It has been identified that tie molecules play a central role in determining plastic deformation and failure process of semicrystalline polymers since a pioneering work by Keith et al.4) and Takayanagi et al.5) Our previous work6)

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has demonstrated that the load exertion on tie molecules that bridge lamellae fragmented on yielding is directly related to the stress level just beyond yield point. Thus, tie molecules were strongly suggested to contribute to the occurrence of yielding.

The experimental results of small-angle neutron scattering of PE and PP demonstrated that the size of a chain in the melt state does not change on rapid crystallization and is usually larger than the distance between adjoining crystallites.[7,8] Therefore, these results imply that a tie molecule bounds several stacked lamellae (here it is termed the "lamellar cluster"). According to high-resolution SEM observations for a blown PE film by Tagawa et al.,[9] the piled lamellae being composed of three to ten lamellae behave as a deformation unit under blown processes. They demonstrate that the yielding process does not proceed in a single lamellar unit. Further, a similar structural unit has been also identified for spherulitic PP solids from SAXS study by Peterlin et al.[10] These experimental results suggest that the lamellar cluster plays a central role in a large-scale transformation of spherulitic structure into fibrillar form.

The author previously proposed a molecular model[11] for tensile deformation of a spherulite model in which changes in conformational free energy in the tie chains and floating chains located between adjacent lamellae within an ideal spherulite were computed as a function of interlamellar spacing, temperature and tie-chain fraction. The theory predicted the well-known characteristics that the initial strain and stress in the elastic region increase with increasing crystallinity and with decreasing temperature. In addition, we examined the stress generating from the horizontal zone and vertical zone within a deformed spherulite. As shown in Fig. 1, a contribution to the stress-strain behavior in the initial strain regions was found to be larger in the deformation of horizontal zone than in that of vertical zone.

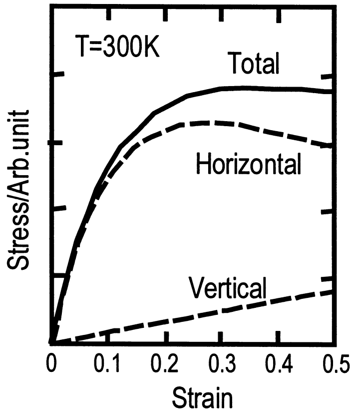

Fig. 1: Numerical results of stress-strain curve of a spherulite. Contribution of orizontal and polar zones within a deformed spherulite to the total stress strain curves.

Considering that tie molecules connect several lamellae with the amorphous region, the lamellar cluster size L can be estimated from the spatial extension of a chain in the solid state on the basis of a statistical method. The probability $P(n)$ that a chain molecule penetrates n amorphous layers can be computed by using

$$P(n) = \int_{L_c+nL_p}^{\infty} r^2 \exp\left(-2r^2/3\bar{r}^2\right)dr \Big/ 3\int_0^{\infty} r^2 \exp\left(-2r^2/3\bar{r}^2\right)dr \tag{1}$$

where $\bar{r}$ is the root mean square of the end-to-end distance. The probability for forming a tie molecule F_t proposed by Huang-Brown model[12)] is given by $P(1)$. The probability $P(n)$ monotonously decreases with increasing n and the average values $\bar{n}$ can be evaluated by using the probability density function $\rho(n) = -dP(n)/dn$. Consequently, the lamellar cluster thickness can be evaluated from

$$L = L_c + \bar{n}L_p = L_c + L_p\int_0^{\infty} n\rho(n)dn \tag{2}$$

This implies that a chain in the solid state can be considered to be confined in a box of volume L^3. Indeed, using the structural parameters of long period L_p and lamellar thickness L_c, we can estimate the thickness of the lamellar cluster of about 100 nm for PP with M_W=260k. The size of lamellar cluster was found to be more sensitive to the molecular weight rather than the microstructure such as crystallinity. Also, it is of importance to note that the modulus of lamellar cluster increases with the increasing of the crystallinity.

Considering that a high stress concentration occurs on a portion of the equatorial zone within the spherulites as also shown in Fig. 1, the external force is applied normal to the plane of lamellar clusters in the equatorial zone and this results in an opening or splaying of the amorphous phase between the lamellar clusters (see Fig. 2).

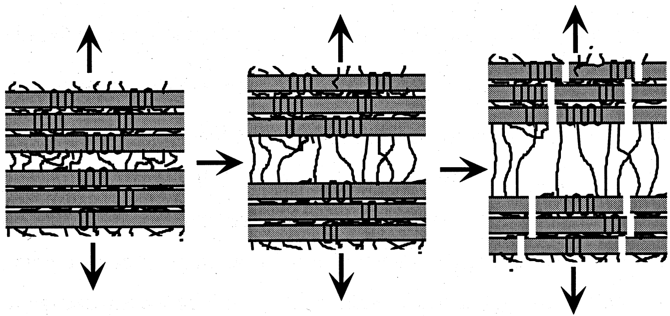

Fig. 2: Schematic illustration of interlamellar separation under a uniaxial deformation.

As illustrated in Fig. 2, the lamellar clusters latent in spherulites appear as the result of deformation inside the spherulites. Consequently, the tie molecules between the adjacent clusters support the external force and their tractive force produces the concentrated load acting on the cluster surface, leading the lamellar cluster to be bent around the active tie molecule as shown in Fig. 3.

Let the lamellar cluster be a layered composite consisting of hard and soft elastic plates of thickness L. According to the theory of elasticity, the elastic energy per a unit volume stored by the bending process is given by

$$U = \frac{2}{V_0}\int_0^{l/2} \frac{M^2}{2EI}dx = \frac{P^2 l^3}{96EIV_0} \tag{3}$$

where M is the bending moment, E is the flexural modulus of the lamellar cluster, l is the average span of bending unit, I is the cross sectional moment of interia which is given by $lL^3/12$, P is the concentrated load, and $V_0(=l^2L)$ is the volume of bending unit.

Considering that the external load is balanced by the traction force P, the stress σ can be given by P/l^2. Then, we have

$$U = \frac{1}{8E}\left(\frac{l}{L}\right)^4 \sigma^2 \tag{4}$$

Assuming that the disintegration of the lamellar cluster occurs accompanying the lamellar fragmentation when the elastic strain energy reached a critical value U^*, the stress at the onset of the disintegration, i.e. the yield stress σ_y, can be written as

$$\sigma_y = 2\sqrt{2EU^*}\left(\frac{L}{l}\right)^2 \tag{5}$$

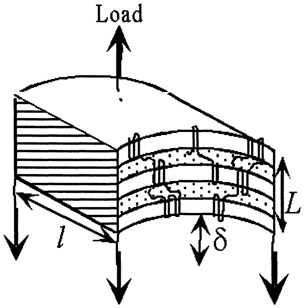

Fig. 3: Schematic illustration of a bending lamellar cluster.

This corresponds to the yielding criterion by von Mises because there is little volume changes during bending. As a consequence, the support span l in Eq. (5) can be taken as the distance between adjacent tie molecules participating in the fracture of a cluster so that l^{-2} corresponds to the area density of active tie molecules between adjacent lamellar clusters.

Huang-Brown's method predicted that the tie-molecule fraction can be estimated as the probability for forming a tie molecule per chain. This method is based on the experimental fact that the dimensions of the chains do not change on rapid crystallization.[7,8] For the precise evaluation of the tie-molecule fraction, it is necessary to take into account the possibility that a polymer chain embedded in the solid state is deeply intertwined with other surrounding chains and a majority of entanglements in the melt is preserved after crystallization. Assuming that a chain in the solid state is confined in a box of volume L^3 and the ν chains are deeply intertwined in the space, the number density ρ_n of the medium can be approximated to be ν/L^3. Since the active tie molecule exists in the space Ll^2, the probability for forming one active tie-molecule ΔF_t is approximately given by

$$\Delta F_t = \frac{1}{\rho_n L l^2} \cong \frac{1}{\nu}\left(\frac{L}{l}\right)^2 \tag{6}$$

Eq. (6) implies that the density of tie molecules is just ν times the one obtained from Huang-Brown equation. By adopting the tie molecule density $\nu\Delta F_t$, Eq. (5) is rewritten as the following equation

$$\sigma_y = 2\nu\sqrt{2EU^*}\Delta F_t \tag{7}$$

The present theory predicts the linear relationship between the yield stress and the tie-molecule density. According to Castigliano's theorem,[13] the deflection δ can be given by $\partial U/\partial P$. Provided that an applied strain ε is proportional to δL, then we have

$$U = \frac{1}{2}\sigma\left(\frac{\delta}{L}\right) \propto \frac{1}{2}\sigma\varepsilon \tag{8}$$

Comparison with Experimental Results

We performed the tensile measurements on model PPs having a constant lamellar thickness and different tie-molecule fraction which is evaluated as the probability for forming a tie molecule.[14] The tie-molecule fraction was controlled by adding a rubbery ethylene-1-hexene copolymer (EHR) into an isotactic PP on the basis of the experimental fact that the EHR molecules are dissolved in the amorphous region of PP.[15] In Fig. 4, the yield stress is plotted against the tie-molecule fraction F_t evaluated by Huang-Brown method. As predicted from

Eq. (5), we found a linear dependence of the yield stress σ_y on the tie-molecule fraction F_t with the data indicating a finite value F_t^0 at zero yield stress:

$$\sigma_y = k\,(F_t - F_t^0) = k\,\Delta F_t \tag{9}$$

where the slope k=1.33GPa is comparable to the ultimate strength of PP filament (1.5 GPa).[16)]We can consider here that the F_t^0 is ascribed to the fraction of extra tie-molecules that do not act as a stress transmitter and bind several stacked lamellae, giving rise to a lamellar cluster, and that the remainder $(F_t - F_t^0)$ can be considered to be the fraction of active tie molecules ΔF_t participating in the deformation and fracture of the lamellar clusters. According to our theory, the linear dependence of yield stress on tie-molecule fraction can be explained by the fact that the increase of tie molecules reduces the support span of the lamellae in the bending process and this results in a bending stress required for the fragmentation to increase.

According to our previous study[15)] on rheological properties of the PP/EHR blends, the addition of EHR to PP was found to vary the concentration of entanglements. Despite of the experimental results, we found the linear relationship between the yield stress and the tie-molecule fraction for the PP/EHR samples. The proportionality strongly suggests that the entangled chains residing between lamellar clusters cannot behave as the active tie molecules even if they could be formed.

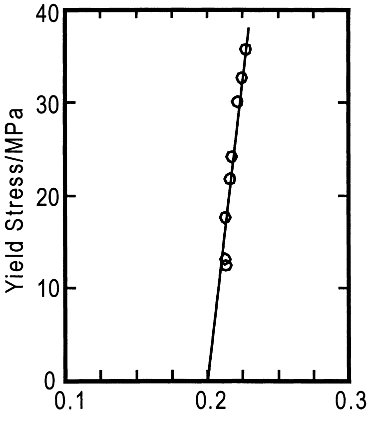

Fig. 4: The yield stress plotted against the tie-molecule fraction estimated by Huang-Brown method.

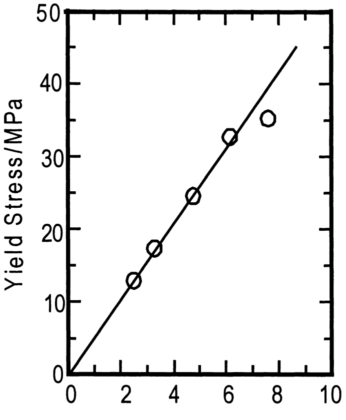

Fig. 5: Plot of the yield stress against the inverse of the yield strain.

Moreover, the present theory demonstrates that the yield strain ε_y is in inverse proportion to the yield stress according to Eq. (8). As shown in Fig. 5, this prediction was confirmed from the stress-strain data of model PPs (PP/EHR). This indicates a validity of von-Mises criterion for yielding process.

The yield energy (i.e. work of the yield) U_y is defined as the energy dissipated for yielding to take place.[17] The value of U_y can be estimated from the area under the nominal stress-strain plot from the origin to the stress drop. It is likely that U_y corresponds to the critical strain energy U^*. Provided that the lamellar clusters appear in the initial stage of deformation, the Young's modulus E_Y is related to the modulus E in Eq. (5). Then, the ratio of σ_y to $\sqrt{2E_YU_y}$ depends only on the structural variables of the sample such as tie molecule density and lamellar cluster thickness but the ratio is independent of the experimental conditions such as temperature and strain-rate. Therefore, Eq. (5) predicts that the changes in the yield stress with temperature or strain-rate are caused by the temperature or strain-rate dependence of two parameters U^* and E. As shown in Fig. 6, in which the yield stress is plotted against $\sqrt{2E_YU_y}$ using the tensile data of the PP sample, all of the data at different temperatures in the range from 273 to 373 K fall on a straight line passing through the origin as predicted from Eq. (5). This indicates a validity of the present model for the yield process of PP. Thus, it can be concluded that the fracture of lamellar clusters due to the bending mode occurs at the yield point.

The slope of the line in Fig. 6, which is evaluated to be about 1/3, gives the distance l between adjacent tie molecules participating in the fracture as predicted from Eq. (5). Using the value of L calculated from Eq. (1), we obtain $l = \sqrt{6}L \cong 240\text{nm}$. The value appears to be approximately equal to the distance estimated from TEM pictures of PE by Keith et al.[4,18] The comparison of Eq. (7) with Eq. (9) gives the following relation:

$$k = 2\nu\sqrt{2E_YU_y} \qquad (10)$$

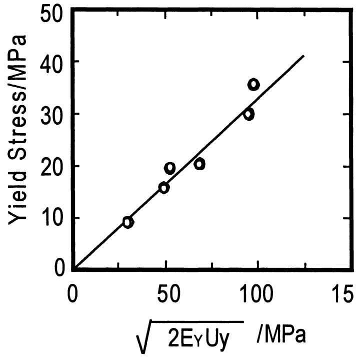

Fig. 6: Plot of the yield stress against $\sqrt{2E_YU_y}$ of PP.

Using the experimental values of k (=1.33 GPa) and $\sqrt{2E_Y U_y}$ (= 97.3 MPa) for the PP sample, which were evaluated from the stress-strain curve at room temperature, into Eq. (10) yield $\nu = 6.82$. It is of a high importance that the degree of chain intertwining can be evaluated by comparing the tie-molecule density estimated from the fracture process of lamellar cluster based on our present theory with the probability for forming one tie molecule based on Huang-Brown's statistical method.

Conclusions

In this article, we presented a theoretical approach for tensile deformation and yielding of spherulitic polymer solids on the basis of key structural variables such as molecular weight, crystallinity, and lamellar and interlamellar thickness. The present work demonstrated that tie molecules play two important roles in deformation process of semicrystalline polymer solids. Thus, one type of tie molecules acts as a transmitter of external load and the other type of tie molecules binds several stacked lamellae. We referred to the stacked lamellae as the lamellar cluster. The lamellar cluster is the middle-scale supermolecular structure, the size of which is in the order of 0.1 μm. It was shown that the tie molecules between the adjacent lamellar clusters produce the concentrated load acting on the cluster surface, leading to bending deformation of the lamellar cluster. The yielding behavior can be explained by the disintegration of the lamellar clusters accompanying lamellar fragmentation. It can be concluded that the lamellar cluster is an important structural factor that is necessary to be considered for a large-scale deformation process of semicrystalline polymers.

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References

[1] R. J. Young, P. B. Bowden, J. M. Ritche, J. G. Rider, *J. Mater. Sci.*, **25**, 441 (1987).
[2] P. Popli and L. Mandelkern, *J. Polym. Sci., Polym. Phys.*, **22**, 1491 (1984).
[3] K. Nitta and M. Takayanagi, *J. Polym. Sci., Polym. Phys.*, **38**, 1037 (2000).
[4] H. D. Keith, F. J. Padden, and R. G. Vadimsky, *J. Polym. Sci.*, A-2, **4**, 267 (1966).
[5] M. Takayanagi, K. Imada, and T. Kajiyama, *Polym. Symp.*, **15**, 263 (1965).
[6] M. Takayanagi and K. Nitta, *Macromol. Theory Simul.*, **6**, 181 (1997).
[7] D. M. Sadler and A. Keller, *Macromolecules*, **10**, 1128 (1977).
[8] J. T. Yeh and J. Runt, *J. Polym. Sci. Polym. Phys.*, **29**, 371 (1991).
[9] T. Tagawa and K. Ogura, *J. Polym. Sci., Polym. Phys.*, **18**, 971 (1980).
[10] A. Peterlin, *J. Mater. Sci.*, **6**, 490 (1971).

[11] K. Nitta, *Comp. Theor. Simul.,* **9**, 19 (1999).
[12] Y. L. Huang and N. Brown, *J. Polym. Sci., Polym. Phys.*, **29**, 129 (1991).
[13] R. L. Bisplinghoff, J. W. Mar, T. H. H. Pian, Statics of Deformable Solids, Dover, NY, 1990.
[14] K. Nitta and M. Takayanagi, *J. Polym. Sci., Polym. Phys.*, **37**, 357 (1999).
[15] M. Yamaguchi, H. Miyata, K. Nitta, *J. Appl. Polym. Sci.*, **62**, 87 (1996).
[16] M. Yamaguchi, H. Miyata, K. Nitta, T. Masuda, *J. Appl. Polym. Sci.*, **63**, 467 (1996).
[17] B. Hartmann and R. F. Cole, *Polym.Eng.Sci.*, **23**, 13 (1983).
[18] R. G. Vadimsky, H. D. Keith, F. J. Padden, *J. Polym. Sci.* A-2., **7**, 1367 (1964).