

The Spatial Correlation between Crystalline and Amorphous Orientations of Isotactic Polypropylene during Plastic Deformation: An *in situ* Observation with FTIR Imaging*

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Abstract On the basis of research method in FTIR imaging, we made a heterogeneous thin film of isotactic polypropylene (*i*PP) that contains a few large spherulites (~150 μm) which are surrounded by small spherulites (~15 μm) for tensile testing. The evolution processes of crystalline and amorphous orientations of *i*PP are monitored with its characteristic peaks at 998 and 973 cm^{-1} , respectively. By introducing the correlation images, the analysis demonstrates the relationships between the orientation evolutions of crystalline and amorphous phases in a space of 250 $\mu\text{m} \times 250 \mu\text{m}$ detecting area. During the plastic deformation, crystalline orientation is higher than amorphous orientation outside the large spherulite, while that is opposite inside the region. In addition, the evolutions of crystalline and amorphous orientations almost keep a positive correlation.

Keywords: Isotactic polypropylene; FTIR imaging; Deformation; Orientation evolution.

INTRODUCTION

The macroscopic properties of semi-crystalline polymers are strongly dependent on their crystalline and amorphous microstructures. It has been reported that a major contribution to strength and toughness of semi-crystalline polymers comes from plastic deformation, during which both the crystalline and amorphous phases are involved^[1, 2]. Moreover, the relative contributions from the two phases change with the extent of deformation^[3, 4]. Recent true stress-strain experiments revealed that the tensile deformation of semi-crystalline polymers is strain-controlled and that the deformation mechanism changes at a critical value of strain^[5–7]. The onset of transition process depends on the interaction between the entanglement state in the amorphous phase and the stability of the crystal blocks^[8, 9].

Deformation mechanisms of the crystalline and amorphous phases in *i*PP materials have been extensively studied in the past decades^[10–15]. Bourson *et al.* proposed that the shearing mechanism in amorphous phase plays a major role in the initial deformation stage, followed by the crystalline chains pulling-out mechanism in stress-softening deformation stage^[16]. Michler *et al.* compared the different orientation behaviors between crystalline orientation (f_c) and amorphous orientation (f_{am}) in α - and β crystals of *i*PP^[17]. Aside from independent

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contribution of the crystalline and amorphous phases to the molecular orientation, the interconnection between f_c and f_{am} during tensile deformation has been also studied^[18–20]. Song *et al.* found that the difference in deformation history did not affect the relationship between f_c and f_{am} of a quenched *i*PP sample. They suggested that the lamellar orientation was simply determined by the deformation of the surrounding amorphous chains at the earlier stage of the necking propagation through the sampling area.

The polarized infrared spectroscopy has been applied to quantify the molecular orientation in both the crystalline and amorphous phases using the infrared dichroism^[13, 17, 21], whereas it is not suitable for heterogeneous parent phases study because of the analysis averaged over the sample. FTIR imaging technique enables chemical visualization by combining the spectral and spatial information^[22–29]. The apparatus of FTIR imaging usually consists of spectrometer and infrared microscopy with a focal plane array (FPA) detector. Compared with microscopic infrared dichroism, this improvement allows scanning from all pixels covering the detecting areas at the same time, and thousands of infrared spectra can be acquired at a spatial resolution near to the diffraction limit in a few minutes. Therefore, FTIR imaging combined with polarized radiation offers a possibility to investigate the anisotropic distribution and chemical information simultaneously. Li *et al.* reported that the distribution of molecular orientation in uniaxially drawn polymer films^[19, 30–33]. Recently, the spatial correlation between f_c and f_{am} during tensile deformation has been investigated in polyethylene system^[34]. By introducing the subtraction images between f_c and f_{am} , the method enables to visualize the different contributions from the crystalline and amorphous phases to the molecular orientation.

In this work, microstructure information of a heterogeneous *i*PP sample was studied during tensile deformation using a combination of miniature tensile tester and *in situ* FTIR imaging with polarized radiation. The sample was first fixed at a suitable temperature until a large spherulite with diameter of around 150 μm was formed, and then the melt was quenched to room temperature where small spherulites formed around it. By following the characteristic bands of crystalline and amorphous phases at 998 and 973 cm^{-1} , respectively, the orientation and crystallinity distributions at different macroscopic strains were obtained. The experimental results show that some correlations exist between the orientations of crystalline and amorphous phases in a space of 250 $\mu\text{m} \times 250 \mu\text{m}$ detecting area during tensile deformation.

EXPERIMENTAL

Materials

The *i*PP sample used in this study has a weight-average molecular weight of 720 $\text{kg} \cdot \text{mol}^{-1}$ and a polydispersity index of 4.8, and was kindly supplied by SABIC-Europe. *i*PP film with a thickness of about 100 μm obtained by compression molding was first heated to 220 $^{\circ}\text{C}$ for 10 min to erase thermal history, and then decreased to 135 $^{\circ}\text{C}$ for isothermally crystallization, until the spherulite size reached around 150 μm . Subsequently, the film was cooled to room temperature rapidly stimulating the formation of small spherulites of about 15 μm around it. For uniaxial tensile test, the sample was cut into rectangular shape with length and width of 25 mm and 3 mm, respectively. The detecting region was positioned in the center of the sample.

Tensile Test and *in situ* FTIR Imaging Measurement

In current work, the sample with an initial length of 3 mm was mounted between two clamps of a homemade miniature tensile tester and deformed with a constant tensile speed of 0.3 $\mu\text{m} \cdot \text{s}^{-1}$ at room temperature. Due to low tensile speed, the test could be regarded as a quasi-static process. The deformation process was monitored by *in situ* FTIR imaging combined with Bruker HYPERION 3000 microscope and 64 $\times$ 64 elements FPA detector and a Specac KRS5 polarizer. Sample was measured in absorbance mode in the region of 250 $\mu\text{m} \times 250 \mu\text{m}$. The imaging pixel size is 3.9 $\mu\text{m} \times 3.9 \mu\text{m}$ measuring in the wavenumber range 3800–900 cm^{-1} .

FTIR imaging measurements were carried out during the stretching of sample in different steps, with a polarizer adjusted alternatively parallel and perpendicular to the tensile direction. The baselines of the spectra were carefully adjusted using the OPUS 5.5 package. Peak height was considered to be the integral intensity of a characteristic band in this study. Dichroic ratio R is calculated as the ratio between parallel and perpendicular polarized intensities as below:

$$R = \frac{A_{//}}{A_{\perp}} \quad (1)$$

The dichroic ratio is related to the orientation function f by following relation:

$$f_{//} = \frac{R-1}{R+2} \cdot \frac{R_0+2}{R_0-1} \quad (2)$$

R_0 is the perfect dichroic ratio. In this case it is assumed that the polymer chains are all oriented towards the tensile direction, and R_0 is given by:

$$R_0 = 2 \cot^2 \psi \quad (3)$$

ψ is the angle between the polymer chain axis and the transition moment of the investigated absorption peaks of the group oscillations. In this work, the orientation functions in the crystalline and amorphous phases are calculated using peaks of 998 and 973 cm^{-1} , respectively. The IR bands of *i*PP have been well assigned. The π -band at 998 cm^{-1} involves the CH_3 rocking, the $\text{C}-\text{CH}_3$ stretching, the CH bending and the CH_2 twisting modes in the crystalline phase, while the π -band at 973 cm^{-1} belongs to the CH_3 rocking and the axial and equatorial $\text{C}-\text{C}$ stretching modes in both the amorphous and the crystalline phases. The 973 cm^{-1} vibration is associated with both crystalline and amorphous phases. Thus, the orientation function for amorphous phase can be obtained through an indirect way^[13, 18, 19]. The average orientation function is derived on the basis of the two-phase model by the following equation:

$$f_{\text{av}} = X_c \cdot f_c + (1 - X_c) \cdot f_{\text{am}} \quad (4)$$

In Eq. (4) f_{av} is the average orientation and X_c is the degree of crystallinity, which is estimated from the intensity ratios of the absorption peaks at 998 and 973 cm^{-1} :

$$X_c = \frac{\varepsilon_0(973)}{\varepsilon_0(998)} \cdot \frac{A_0(998)}{A_0(973)} \quad (5)$$

In Eq. (5) ε_0 is the extinction coefficient of the absorption band and A_0 is the structural absorbance. The ratio $\varepsilon_0(973)/\varepsilon_0(998)$ was estimated using DSC crystallinity measurements and found to be 0.56^[17].

RESULTS AND DISCUSSION

Figure 1(a) shows the engineering stress-strain curve of the *i*PP sample. Three different stages can be distinguished. The first stage, $0 < \text{macroscopic strain } \varepsilon < 0.5$, corresponds to the elastic deformation behavior of the *i*PP. A linear increase of stress σ with ε can be found until σ achieves 17 MPa at yield point of $\varepsilon = 0.5$. The second stage, $0.5 < \varepsilon < 8$, corresponds to the strain softening and necking propagation. Stress decreases significantly when necking occurs, then followed by a symmetric propagation of the neck shoulders towards the specimen heads at almost a constant σ of 14 MPa. The last stage is strain hardening region ($8 < \varepsilon < 10$), which shows a small increase of the stress from 14 to 16 MPa.

Optical micrographs of *i*PP spherulite at different macroscopic strains are inserted (Fig. 1b). At strain $\varepsilon_2 = 2$, the necking propagation front is observed. As displayed in Fig. 1(b), the local darkening band first appeared in the left side of the micrograph and the necking front gradually passes over the whole spherulite afterwards. As strain increases, spherulite changes its shape from sphere to ellipsoid accompanied with two tails along the tensile direction. In the last strain hardening region, spherulite deformation is obvious.

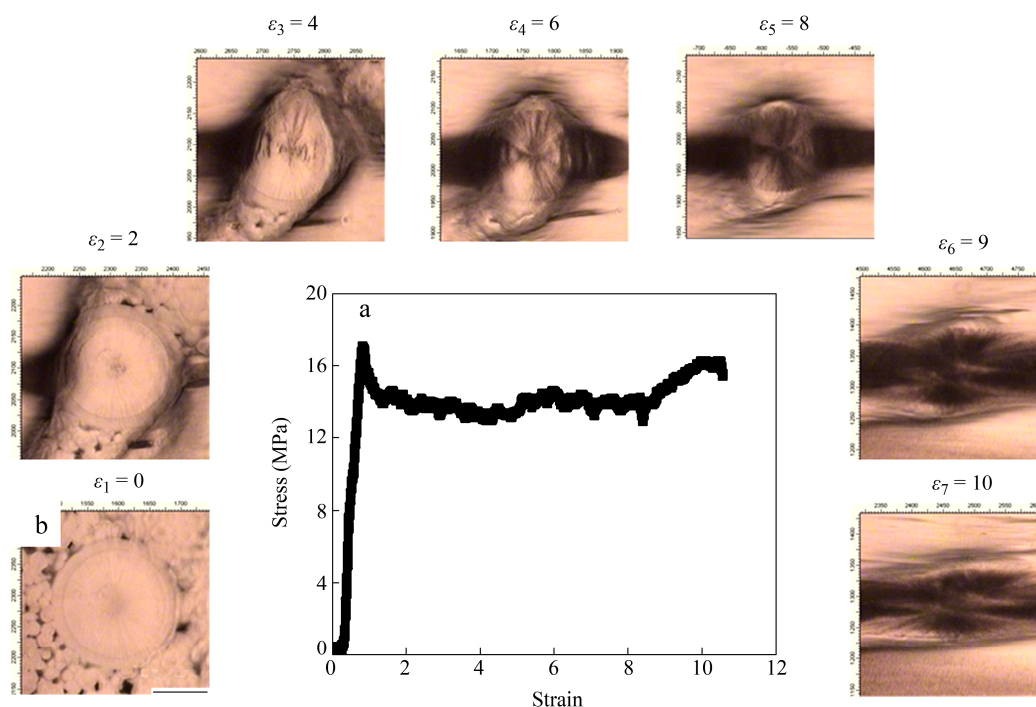


Fig. 1 (a) Engineering stress-strain curve and (b) the selected optical micrographs at different macroscopic strains (The scale bar is 50 μm . Tensile direction is horizontal.)

Figure 2(a) shows the optical micrograph at $\varepsilon_4 = 6$, where the spherulite has been exceeded by necking propagation. The corresponding FTIR spectra of two different locations at point I and point II are presented in Fig. 2(b). At the point I inside the spherulite, the intensities of the absorption bands at 998 and 973 cm^{-1} with radiation polarized parallel (solid lines) to tensile direction are almost as those with same as that perpendicular polarization (dash lines). It means that orientation of polymer chains does not take place within the spherulite. At the point II outside the spherulite, the intensities of 998 and 973 cm^{-1} of the solid line are stronger than those of the dash line. As 998 and 973 cm^{-1} bands have $\psi = 0^\circ$ and the absorption is the strongest with radiation polarized parallel to the helix axis^[31], which suggests crystalline and amorphous chains are oriented towards tensile direction.

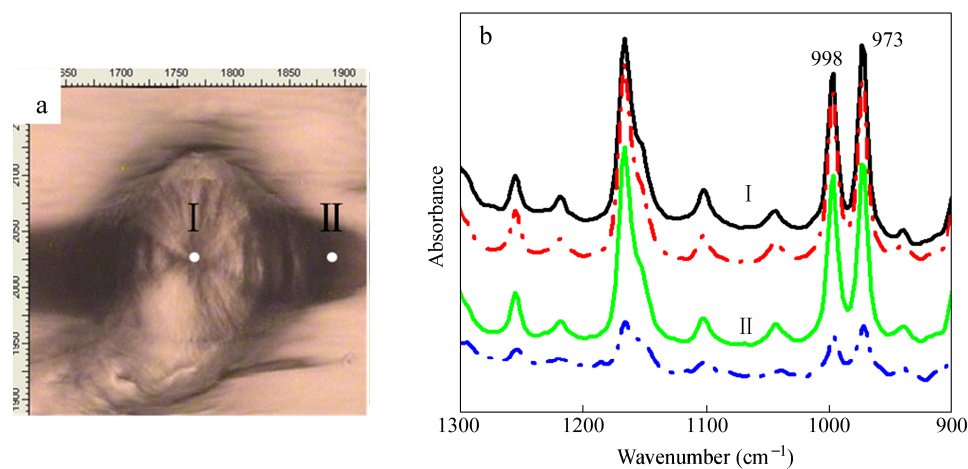


Fig. 2 (a) The optical micrograph at macroscopic strain of 6; (b) Corresponding FTIR spectra of point I and II. The solid and dashed lines are spectra with radiation polarized parallel and perpendicular to tensile axis, respectively.

The orientation distribution images of crystalline and amorphous phases at different macroscopic strains are shown in Figs. 3(a) and 3(b), respectively. Both of the orientations are evaluated with $\psi = 0^\circ$ through Eq. (2) and then plotted into 2D distribution images with 64×64 elements by matrix command in MATLAB software. The area of each image is consistent with Fig. 1(b). The value of each pixel is expressed as a color bar at the right side. The color red represents a high value of orientation. Before tensile test ($\varepsilon_1 = 0$), images of crystalline and amorphous orientations both show a uniform distribution with a value around zero. After yielding, at $\varepsilon_2 = 2$, a clear contrast of orientation distribution appears. Both f_c and f_{am} show a dramatic level-up outside the spherulite, which is confirmed by the appearance of the red area on the left, while no obvious change is observed inside the spherulite. When strain is up to 8, the red and yellow regions extend around the spherulite, indicating that polymer chains are drastically oriented except for the spherulite area. As increase to strain hardening region ($\varepsilon > 8$), the degrees of crystalline and amorphous orientations increase significantly inside the spherulite. The crystallinity distributions during tensile deformation are displayed in Fig. 3(c). During the plastic deformation, a higher crystallinity always locates exactly in the center of the large spherulite. The contour of the crystallinity distribution is consistent with that of optical micrograph. As larger spherulite has higher crystallinity and lamellar thickness than the surrounding small spherulites^[35, 36], it is mechanically stable to resist the necking to some extent. Both orientation distributions of crystalline and amorphous phases indicate a similar inhomogeneous pattern.

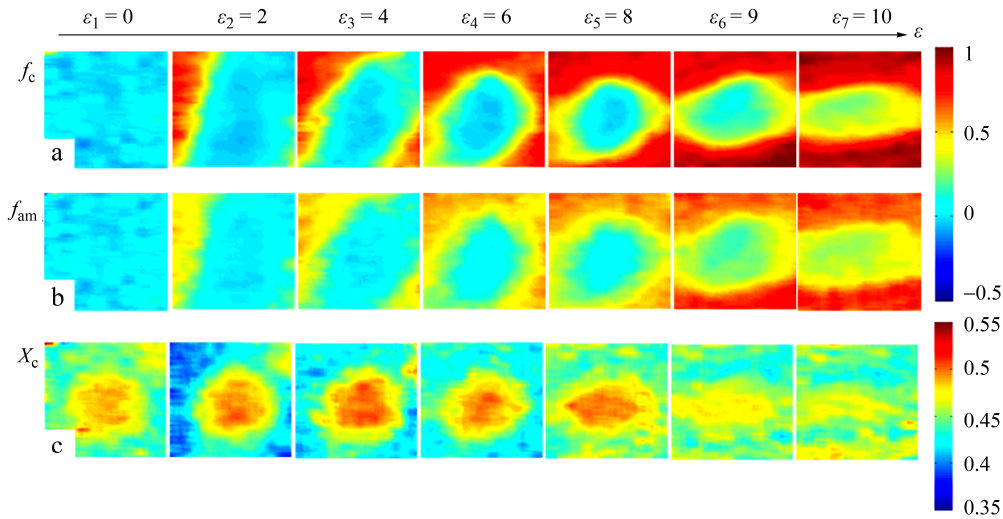


Fig. 3 The distribution images of crystalline orientation (f_c) (a) and amorphous orientation (f_{am}) (b) at different macroscopic strains; (c) The crystallinity (X_c) distributions during tensile deformation

The evolutions of orientation and crystallinity during tensile deformation are shown in Fig. 4. Each image is obtained with MATLAB software by subtracting values of two adjacent orientation or crystallinity image in Fig. 3. In the initial deformation stage, a dramatic decline of X_c can be found outside the spherulite accompanying with the increase of orientation on the left side in the images of S_{2-1} . In plastic deformation stage, lamellae slips have already occurred. The crystalline molecules cannot sustain the tensile stress and thus partial destruction of the original crystals takes place. Crystalline and amorphous chains in surrounding small spherulite experience a fast transformation from the random state to highly oriented alignment. As strain increases, the fragmentation crystals or the molten chains recrystallize along the tensile direction to form fibrils, which induce an increase in the X_c outside the spherulite (see images of S_{3-2}). Meanwhile, orientation directions move around the spherulite, indicating that the spherulite is subjected to shear stress as result of non-uniformity necking process. Afterwards, the degree of crystalline orientation inside the spherulite shows a small increase in the images of S_{4-3} . It should be pointed out that apparent orientation does not occur inside the spherulite during

necking propagation. Thus, the negative value of Δf_c implies that crystalline chains are oriented in perpendicular to the tensile direction. On further deformation, orientation increases in the compression direction outside the spherulite (see images of S_{5-4}), which suggests that spherulite deformation begins to take place and induces an increase of X_c at the edge of the spherulite.

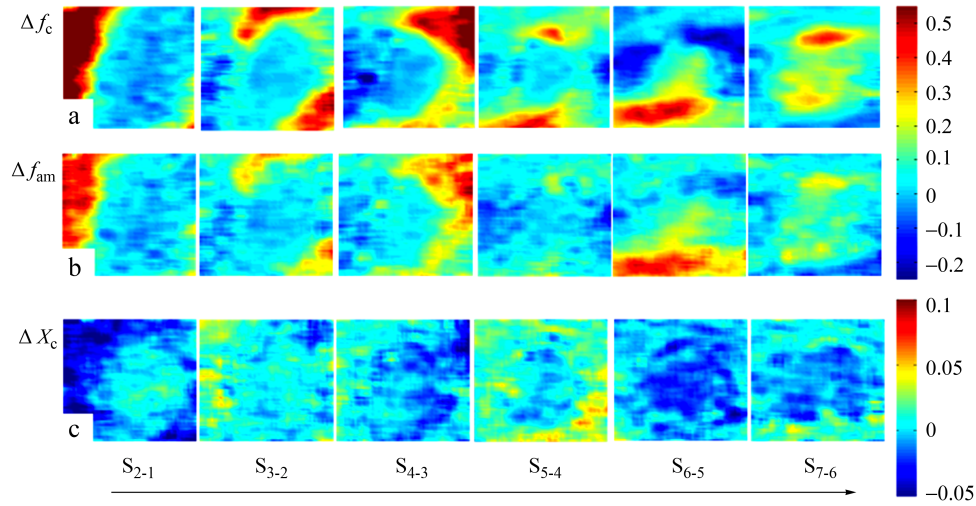


Fig. 4 The evolutions of crystalline orientation (Δf_c) (a) and amorphous orientation (Δf_{am}) (b) during tensile deformation; (c) The crystallinity evolutions (ΔX_c) during tensile deformation

After entering into strain hardening region, spherulite deformation is obvious and crystals destruction occurs inside the spherulite, resulting in a dramatic decline of X_c accompanying with the increase of orientation in the image of S_{6-5} . These important changes mean that stress transfer from the surrounding small spherulites to the large spherulite. The stress concentration induces local orientation which is in agreement with our previous experimental observation from continuous elongation of polybutene-1 film^[32]. Note here that the deformation of spherulite morphology could account for the decrease in orientation along the tensile direction. In the last deformation stage, the spherulite is further compressed because of the orientation increase in the corresponding area (see images of S_{7-6}). The slight decrease of X_c indicate that there is no fibril formation inside the spherulite.

For analysis of the relationship between f_c and f_{am} during tensile deformation, the distribution images of f_c/f_{am} and f_c-f_{am} at different macroscopic strains are displayed in Figs. 5(a) and 5(b), respectively. Before tensile test, f_c/f_{am} presents random distribution at around 1, which corresponds to 0 of f_c-f_{am} . The initial states of orientation in crystalline and amorphous phase are almost the same. After tensile deformation, the values of f_c/f_{am} and f_c-f_{am} are always larger than 1 and 0 outside the spherulite, which indicate the degree of crystalline orientation is higher than that of the amorphous orientation. The higher degree of crystalline orientation comparing with amorphous orientation is attributed to the faster relaxation of amorphous phase than crystalline phase^[37-39]. On the contrary, $-1 < f_c-f_{am} < 1$ and $f_c-f_{am} < 0$ are found inside the spherulite. Amorphous orientation is slightly higher than the crystalline part, which coincides with the feature in the elastic region. Most likely the relative orientation degree of crystalline and amorphous phases inside and outside the spherulite is related to the interplay between the amorphous entanglement density and the stability of crystal blocks. The larger spherulite is crystallized at 135 °C, which has thicker lamellae and lower entanglement density than its surroundings with nonisothermal crystallization. The thicker lamellae inside the spherulite and higher entanglement density outside the spherulite imply a higher stress that is generated when the sample is stretched. It is worth pointing out that the deformation experiment was performed at room temperature, the annealing effect on entanglement will be ignored.

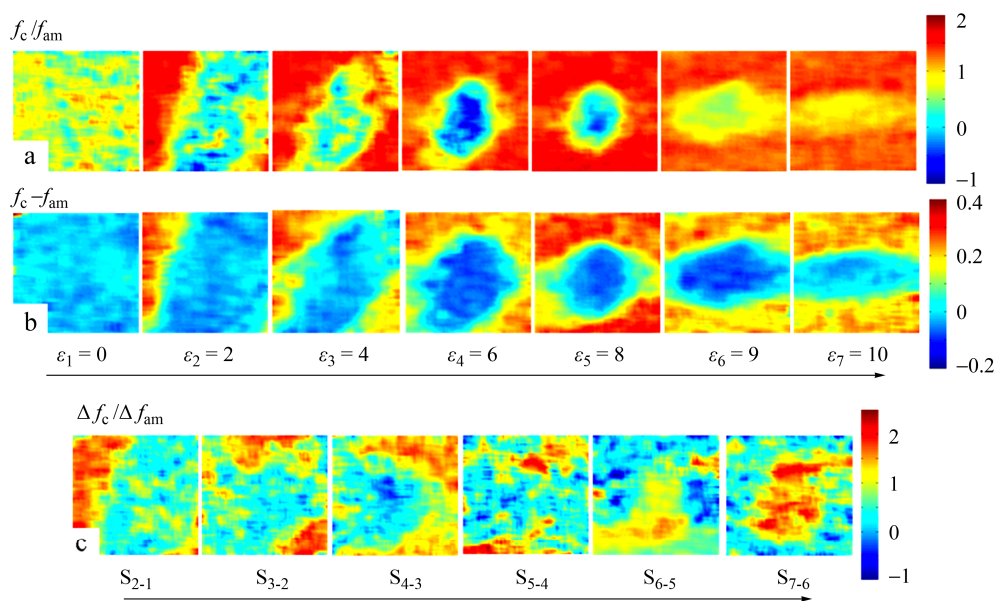


Fig. 5 The distribution images of f_c/f_{am} (a) and $f_c - f_{am}$ (b) at different macroscopic strains; (c) The differential of orientation evolutions between crystalline and amorphous phases during tensile deformation

During necking propagation, f_c/f_{am} keeps the initial random distribution inside the spherulite before $\varepsilon < 6$. Once the necking passed over the spherulite at strain of 6, a negative value of f_c/f_{am} between -1 and 0 can be derived from the inside region, which indicates molecular chains in crystalline and amorphous phases are oriented towards opposite directions. According to the orientation evolutions described above, the crystalline chains with a low degree of orientation are perpendicular to the tensile direction inside the spherulite, while amorphous chains are oriented towards the tensile direction. The difference in the direction of f_c and f_{am} inside the spherulite may be ascribed to the crosshatched structures of α -crystal, which are composed of parent lamellae and daughter lamellae at around 80° or 100° . After entering into strain hardening region, molecular chains in parent lamellae and daughter lamellae are both oriented towards the tensile direction. Distributions of f_c/f_{am} reach uniform with positive ratio inside the spherulite.

Through the above results, two mechanical processes are identified in *iPP* spherulite during stretching at room temperature. Changes in orientation and crystallinity first appear outside the spherulite in necking propagation region, and then take place inside the spherulite in strain hardening region. Figure 5(c) shows the differential of orientation evolutions between crystalline and amorphous phases ($\Delta f_c/\Delta f_{am}$) during tensile deformation. The evolutions of f_c and f_{am} almost keep a positive correlation. In necking propagation region, the change of f_c is faster than that of f_{am} outside the spherulite under the effect of shear and compression, which is opposite to the inside of the spherulite. The differential results confirm that the crystalline orientation is easier to take place when external stress is applied. Therefore, the crystalline chains tend to be oriented quickly inside the spherulite when larger deformation of spherulite occurs.

CONCLUSIONS

In the present study, spherulite deformation in *iPP* films is investigated using *in situ* FTIR imaging with polarized radiation. The results indicate that crystalline and amorphous phases are oriented inhomogeneous following the deformation behavior of spherulite. During necking propagation, molecules outside the large spherulite are oriented preferentially. Only a little change of orientation occurs inside the spherulite. After the necking passed over the spherulite, it is found there are two opposite orientation directions between crystalline and amorphous phases. Afterwards, both crystalline and amorphous chains are oriented towards the tensile

direction in strain hardening region. Meanwhile, obvious deformation of spherulite occurs accompanying with a decrease in crystallinity inside the large spherulite. Moreover, the degree of amorphous orientation is slightly higher than the crystalline part inside the spherulite during the plastic deformation, while it is opposite outside the spherulite. The results also indicate the positive correlations between the orientation evolutions in crystalline and amorphous phases. In addition, the crystalline chains are oriented faster than the amorphous chains when stress is applied.

REFERENCES

- 1 Meijer, H. and Govaert, L., *Prog. Polym. Sci.*, 2005, 30: 915
- 2 Galeski, A., *Prog. Polym. Sci.*, 2003, 28: 1643
- 3 Jiang, Z.Y., Tang, Y., Rieger, J., Enderle, H. and Lilge, D., *Macromolecules*, 2010, 43: 4727
- 4 Jiang, Z.Y., Tang, Y., Men, Y.F., Enderle, H. and Lilge, D., *Macromolecules*, 2007, 40: 7263
- 5 Hobeika, S., Men, Y.F. and Strobl, G., *Macromolecules*, 2000, 33: 1827
- 6 Hiss, R., Hobeika, S., Lynn, C. and Strobl, G., *Macromolecules*, 1999, 32: 4390
- 7 Al-Hussein, M. and Strobl, G., *Macromolecules*, 2002, 35: 8515
- 8 Men, Y.F., Rieger, J. and Strobl, G., *Phys. Rev. Lett.*, 2003, 91: 095502
- 9 Men, Y.F. and Strobl, G., *Macromolecules*, 2003, 36: 1889
- 10 Peterlin, A., *J. Mater. Sci.*, 1971, 6: 490
- 11 Bowden, P. and Young, R., *J. Mater. Sci.*, 1974, 9: 2034
- 12 Wu, P. and Vandergiessen, E., *Mechanics Research Commun.*, 1992, 19: 427
- 13 Su, R., Wang, K., Zhang, Q., Chen, F., Fu, Q. and Xu, W., *J. Phys. Chem. B.*, 2009, 113: 7423
- 14 Gsell, C. and Dahoun, A., *Mat. Sci. Eng. A-Struct.*, 1994, 175: 183
- 15 Bartczak, Z., Galeski, A., Argon, A. and Cohen, R., *Polymer*, 1996, 37: 2113
- 16 Martin, J., Poncot, M., Hiver, J. and Bourson, P., *J. Raman. Spectrosc.*, 2013, 44: 776
- 17 Huy, T., Adhikari, R. and Lupke, T., *J. Polym. Sci., Part B: Polym. Phys.*, 2004, 42: 4478
- 18 Song Y., Nitta K. and Nemoto, N., *Macromolecules*, 2003, 36: 1955
- 19 Song Y.H., Nitta, K. and Nemoto, N., *Macromolecules*, 2003, 36: 8066
- 20 Song Y.H. and Nemoto, N., *Polymer*, 2006, 47: 489
- 21 Parthasarthy, G., Sevegney, M. and Kannan, R., *J. Polym. Sci., Part B: Polym. Phys.*, 2002, 40: 2539
- 22 Vogel, C., Wessel, E. and Siesler, H., *Macromolecules*, 2008, 41: 2975
- 23 Hikima, Y., Morikawa, J. and Hashimoto, T., *Macromolecules*, 2013, 46: 1582
- 24 Hikima, Y., Morikawa, J. and Hashimoto, T., *Macromolecules*, 2012, 45: 8356
- 25 Cong, Y.H., Hong, Z.H., Zhou, W.M., Chen, W. and Li, L.B., *Macromolecules*, 2012, 45: 8674
- 26 Cong, Y.H., Hong, Z.H., Qi, Z.M., Zhou, W.M. and Li, L.B., *Macromolecules*, 2010, 43: 9859
- 27 Su, F.M., Li, X.Y., Zhou, W.M., Chen, W., Li, H.L. and Li, L.B., *Polymer*, 2013, 54: 3408
- 28 Su, F.M., Li, X.Y., Zhou, W.M., Zhu, S.S., Ji, Y.X. and Li, L.B., *Macromolecules*, 2013, 46: 7399
- 29 Snively, C.M. and Koenig, J., *J. Polym. Sci., Part B: Polym. Phys.*, 1999, 37: 2353
- 30 Li, H.L., Zhou, W.M., Ji, Y.X., Hong, Z.H., Miao, B. and Li, L.B., *Polymer*, 2013, 54: 972
- 31 Hong, Z.H., Cong, Y.H., Qi, Z.M., Li, H.L., Zhou, W.M. and Li, L.B., *Polymer*, 2012, 53: 640
- 32 Chen, W., Li, X.Y., Li, H.L., Su, F.M., Zhou, W.M. and Li, L.B., *J. Mater. Sci.*, 2013, 48: 4925
- 33 Li, J., Li, H.L., Meng, L.P., Li, X.Y., Chen, L. and Chen, W., *Polymer*, 2014, 55: 1103
- 34 Hikima, Y., Morikawa, J. and Hashimoto, T., *Macromolecules*, 2011, 44: 3950
- 35 Young, R., *Philosophical Magazine*, 1974, 30: 85
- 36 Brooks, N. and Mukhtar, M., *Polymer*, 2000, 41: 1475
- 37 Seguela, R. and Rietsch, F., *Polymer*, 1986, 27: 532
- 38 Pazur, R. and Ajji, A., *Polymer*, 1993, 34: 4004
- 39 Butler, M., Donald, A. and Ryan, A., *Polymer*, 1998, 39: 39