15A, 15C2/2003C001

Hot drawing behavior of copolymer of propylene with butene-1 by time-resolved WAXD/SAXSmeasurements

Takashi SAKURAI[1*], Yoshinobu, NOZUE[1], Tatsuya KASAHARA[1], Noboru YAMAGUCHI[1],
Kohji TASHIRO[2] and Yoshiyuki AMEMIYA[3]
[1]Petrochemicals Research Laboratory, Sumitomo Chemical Co., Ltd., 2-1 Kitasode Sodegaura City, Chiba 299-0295, Japan
[2]Graduate School of Science, Osaka University, Toyonaka City, Osaka 560-0043, Japan
[3]Graduate School of Frontier Sciences, Univ. of Tokyo, Kashiwanoha, Kashiwa City, Chiba 277-8561, Japan

Introduction

In polyolefin materials, the structural distribution on the crystalline level is the key factor governing the mechanical properties. As for the propylene/butene-1 copolymer, butene-1 is favorably incorporated in the crystalline phase with the expansion of crystal lattice, because of the similarity of crystal chain conformation between isotactic polypropylene and isotactic polybutene-1 [1]. This comonomer inclusion in the polypropylene sequences should affect the deformation behavior and resultant mechanical properties.

The purpose of this study is to examine the effects of the comonomer inclusion on the deformation behaviour in film manufacturing process. Structural developments during the hot drawing process have been investigated by carrying out time-resolved SAXS/WAXD measurements.

Experimental

The sample used here is copolymer of propylene with butene-1 polymerized by isospecific metallocene catalyst system, reported by Hosoda et al [1]. The molecular characteristics of the sample are listed in Table 1.

The sample specimen cut from the melt-crystallized sheet of 1.0mm in thickness was set in a tensile tester installed in the path of synchrotron X-ray beam. The specimen was uniaxially stretched with a strain rate of 60 mm/min at 413K.

The WAXD and SAXS measurements were conducted at the BL-15A beam line. For tracing the structural change in the specimen during drawing, time-resolved two-dimensional (2D) WAXD and SAXS patterns were measured with 0.5 sec time slices by using a CCD X-ray detector [2].

Results and Discussion

2D WAXD and SAXS patterns observed in the hot drawing process are shown in Figure 1. The 2D WAXD pattern before drawing (0sec) exhibited the Debye-Scherrer rings. These rings were changed into the arcs at the timing of the onset of yielding and necking (10-20sec). Beyond necking (25-50sec), the azimuthal spread of the reflections became narrower, indicating that the crystal orientation increased with draw ratio. It is noted here that the 2D WAXD pattern exhibits not only *c*-axis orientation of crystallites but also *a**-axis orientation of crystallites along the drawing direction.

The 2D SAXS pattern before stretching consisted of rings. It transformed to the elliptical pattern in the yielding and necking regions. In the draw region beyond necking, the 2D SAXS pattern showed a two-bar pattern with the scattering maximum on the horizontal direction and the streak-like pattern along the vertical direction. When the copolymer of propylene with butene-1 is drawn at temperature below melting point, it is thought that the fragmented lamellae with the *a**-axis orientation of crystallites is formed along the drawing direction in addition to the stacked lamellae with *c*-axis orientation of crystallites along the drawing direction.

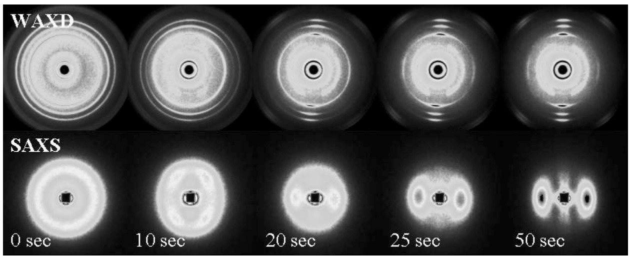

Fig 1. 2D WAXD and SAXS patterns observed in the hot drawing process. The horizontal line is the drawing direction.

Table 1. The molecular characteristics of sample

Comonomer Content[a] (mol%)	Mw[b]	Mw/Mn[b]	CXS fraction[c] (wt%)	[η][d]	Tm[e] (°C)	Tc[e] (°C)	Density (g/cm^3)	Crystallinity (wt%)
2.7	330,000	2.2	0.1	2.0	148.5	110.2	0.902	60

[a] Determined by ^{13}C NMR. [b] Determined by GPC. [c] Fraction soluble in *p* -xylene at 20°C [d] Intrinsic viscosity determined by Ubbelohde viscometer. [e] Crystallization and melting temperatures determined by DSC.

References

[1] S. Hosoda et al., *Polymer* 43, 7451 (2002).
[2] Y. Amemiya et al., *Rev. Sci. Instrum.* 66, 2290 (1995).

* sakurait2@sc.sumitomo-chem.co.jp