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熱可塑性エラストマーのポリマーアロイ構造の分析

Analysis of polymer alloy structure of thermoplastic elastomer

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1. Background and research objectives

Segmented polyurethane (TPU) polymer chains have a hard segment portion as the cross-linking point and a soft segment as the elongation portion. This TPU is expected to be the next-generation thermoplastic elastomer. However, it is difficult to use TPU alone in components with large deformation of more than 100% because it produces very large permanent strain when repeatedly elongated up to 300%. It is an important academic and practical issue to clarify the cause of this permanent strain and to reduce it. This problem has not been solved in previous spectroscopic studies. In this measurement, the structure of TPU were examined in detail by measuring the SAXS of each when the TPU was unstretched, stretched to 300%, and returned to zero strain.

2. Experimental

Experiments were performed with SAXS and WAXD simultaneous measurements, camera length 1958.830 mm, wavelength 1.5 Å, and R-AXIS IV. The samples used were Nisshinbo (Mobilon bands Blue and Brown) and BASF (70 and 80). The TPU was stretched in situ to 300% using a stretching machine and secured to the frame. The time between fixation and measurement is 5 minutes; after 5 minutes, stress relaxation is nearly at apparent equilibrium.

3. Result and discussion

Figure 1 shows the results of measuring the size L of hard segment aggregates from the first peak in SAXS for a number of types of TPUs with different hard segment lengths and their periods. The more cleanly and densely aggregated the hard segment portion is, the shorter the length of L becomes. In many studies, the long period observed in this TPU is mistakenly thought to be the distance between hard segments, but this is not the case.

Figure 2 shows a schematic of the SAXS pattern and the structure of TPU in the unstretched, 300% stretched, and post-shrinkage permanent strain states, respectively. In the unstretched state, the cylindrical hard segment aggregates are oriented randomly.At 300% elongation, they STREAK only in the meridional direction. Therefore, it can be seen that the majority of the cylindrical aggregates are aligned in the stretched direction. When the TPU is shrunk from this state to the original state, the SAXS pattern is not in the original ring state, and four strong spots remain. This is because the hard segment aggregates that have been aligned by stretching do not completely return to their original random positions, but are fixed in a somewhat tilted state in the direction of stretching, which is the cause of the permanent strain.

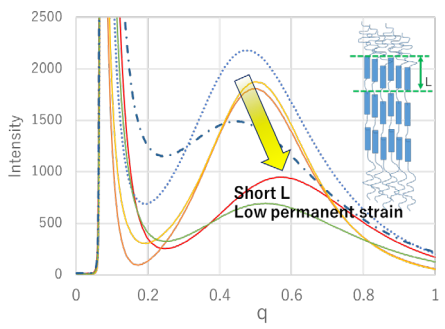

Fig.1 SAXS pattern of TPU

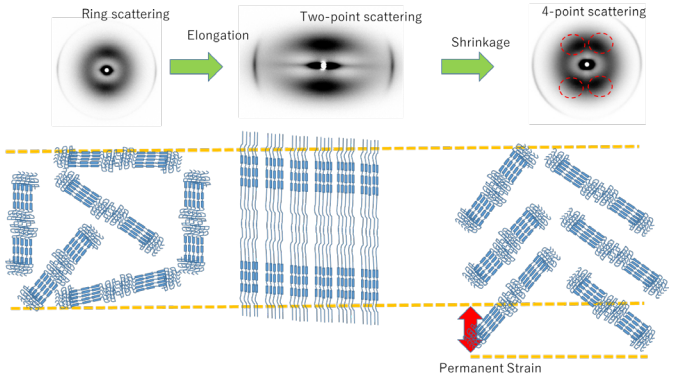

Fig.2 Permanent strain occurs due to the orientation of hard ment aggregates