



熱可塑性ウレタンエラストマーの永久ひずみ低減 Elucidation of the Cause of Permanent Strain Reduction in Thermoplastic Urethane Elastomers

YAMASHITA Yoshihiro¹, TASHIRO Kohji²

¹University of Fukui, ² Aichi Synchrotron Radiation Center

Keywords : Thermoplastic polyurethane, permanent strain, SAXS, WAXD

1. Date of measurement

2022/11/17 BL8S3 (2 shift)

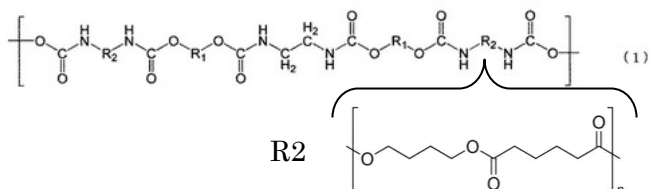
2022/11/18 BL8S3 (2 shift)

2. Abstracts.

Thermoplastic elastomers are rapidly replacing conventional natural rubber materials because of their recyclability. For example, their disposal has become a major social problem in automobile tires. In this study, we focused on polyurethane, a representative thermoplastic elastomer. Although it has excellent strength and elastic modulus, it has a drawback that its permanent strain is larger than that of natural rubber. SAXS and WAXD investigations revealed that the cause is due to the crystallization of soft segments and rearrangement of hard segments caused by elongation of the rubber.

3. Background and research objectives

The molecular structure of polyurethane elastomer (TPU) is shown in Figure 1. Permanent strain is mainly due to the crystallinity of the soft segment corresponding to R2. Therefore, it is important to reduce the crystallinity of the R2 portion. However, along with that, the structure of the hard segment including isocyanate bonds is also affected. In this study, we used SAXS to investigate the effect of soft segments consisting of different R2 on the structure of hard segments.

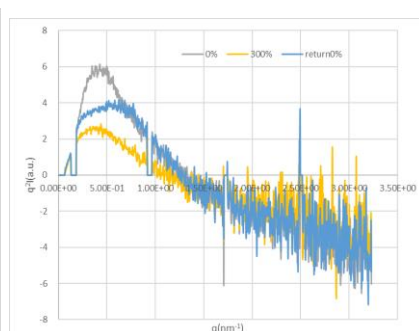
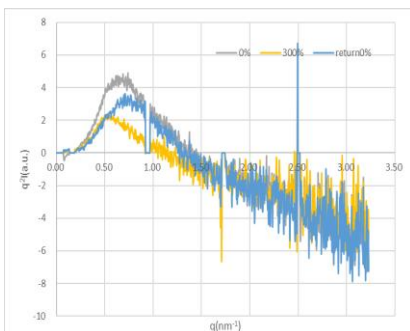
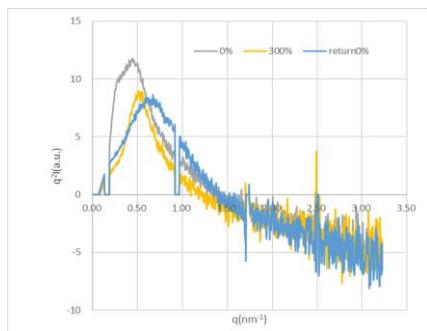


4. Experimental

Experiments were performed with SAXS and WAXD simultaneous measurements, camera length 1958.830 mm, wavelength 1.5 Å, and PILATUS. The samples used were BASF (hardness 70 and 80).

Fig.1 polyurethane elastomer

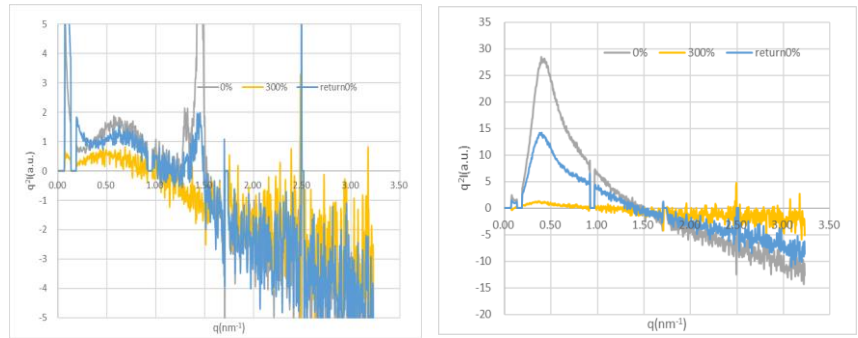
5. Result and discussion



(a) polybutylene adipate terephthalate (b) ethylene glycol

(c) ethylene glycol copolymer-1

SAXS measurements of TPU with polybutylene adipate terephthalate as the soft segment with the R2 component are shown in Figure 2(a); results with the R2 component replaced with an amorphous ester component are shown in Figure 2(b)~(e). These results indicate that elongational deformation changes the structure of the hard segment.



(d) ethylene glycol copolymer-2 (e) Same soft segment as (a) with a larger proportion of hard segment

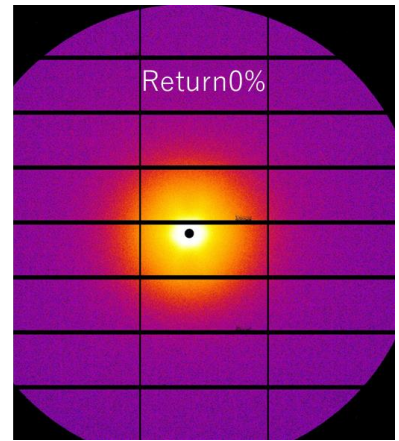
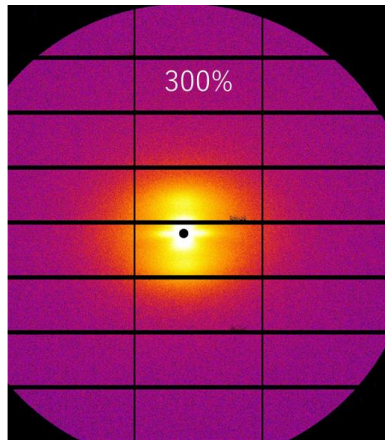
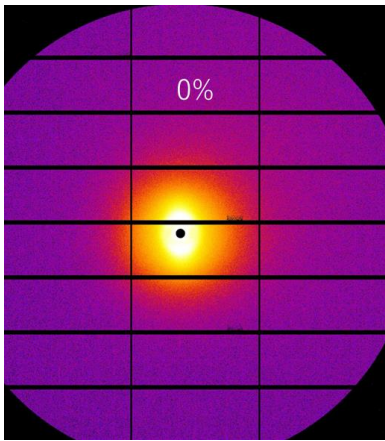
Fig.2 SAXS profiles of TPU

We compared the long period in the undeformed state with that at 0% strain after 300% elongation. First, the original polybutylene adipate terephthalate soft segment (a) showed an increase in long period, but the length of the long period did not change in elongation. However, the length of the long period did not change with elongation, but the hard segments were oriented in the direction of stretching. When the soft segments in (b) and (c) were made more similar to rubber elasticity, the distance between the hard segments widened when the strain was returned to 0% after 300% elongation. This may be due to the fact that the hard segments remained slightly aligned by stretching. In case (d), where the soft segments were brought closer to the rubber elasticity, the structure of the hard segments became less visible than in the case of stretching. This may be due to the fact that the hard segments have a smaller cohesive structure than in (a)~(c), or that the structure has collapsed due to stretching. When the strain in sample (d) was returned to 0%, the distance between the hard segments recovered to almost the same position as in the unstretched sample. This sample (d) also had the lowest permanent strain. When the percentage of hard segments in (e) was increased from that in (a), the change in the long-period distance was also smaller.

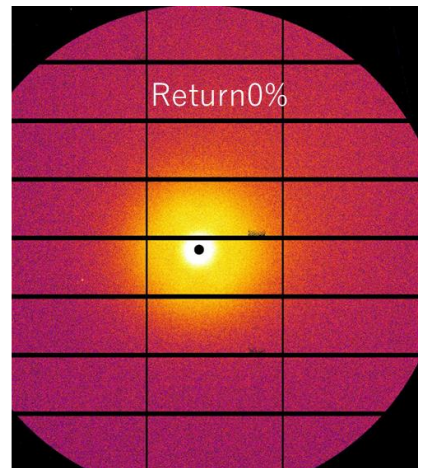
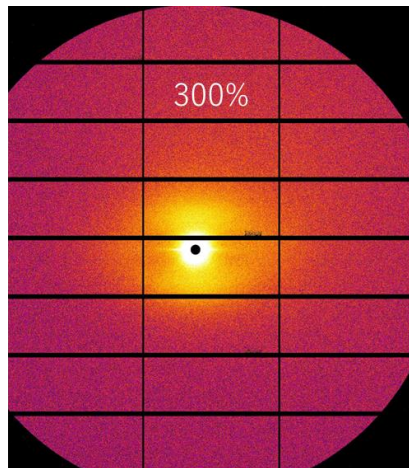
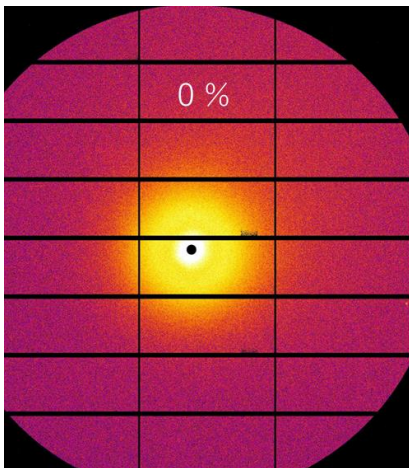
From these results, it can be considered that the orientation of hard segments caused by elongation is not maintained after strain recovery, but returns to the undeformed state, which contributes to the reduction of permanent strain.

6. Future Issues

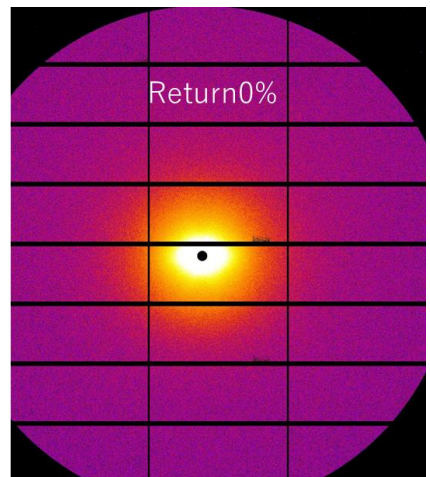
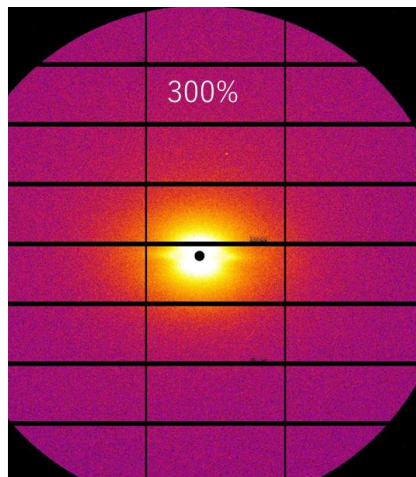
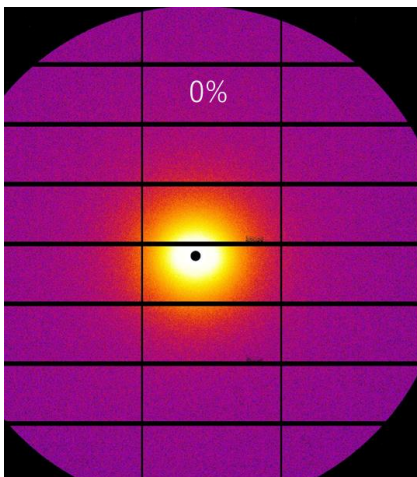
Since the rate of structural change due to stretching seems to be very fast, time-resolved SAXS measurements at an acquisition rate of less than 1 second while stretching with a stretcher attached are necessary.



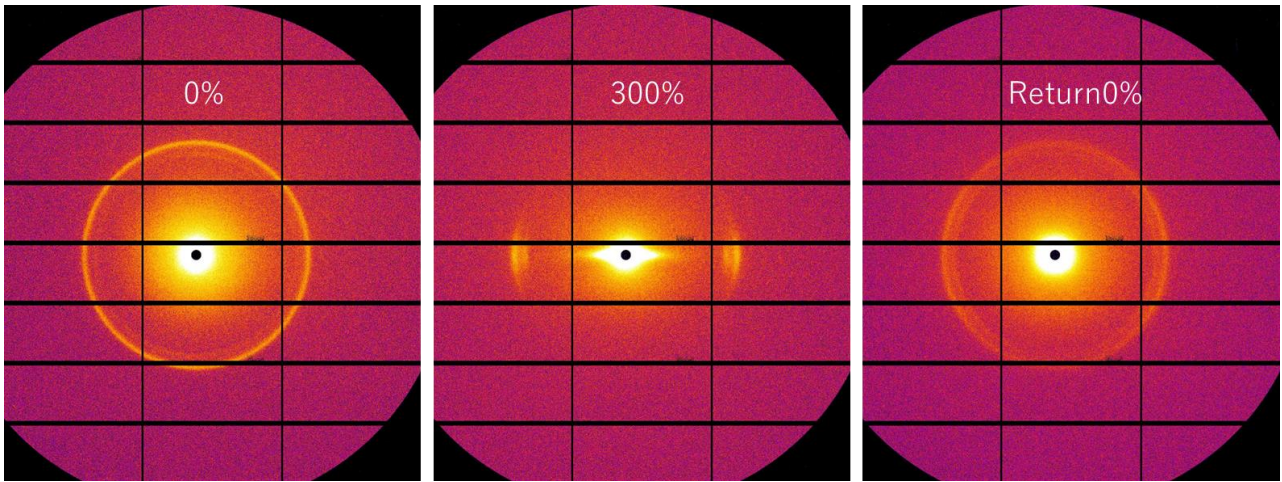
(a) polybutylene adipate terephthalate



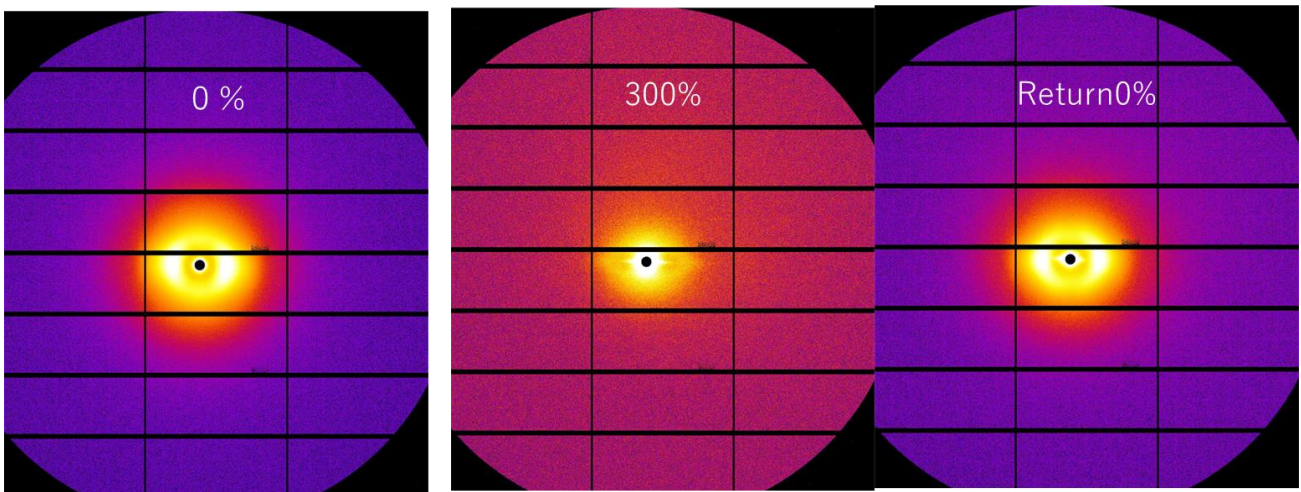
(b) ethylene glycol



(c) ethylene glycol copolymer-1



(d) ethylene glycol copolymer-2



e) Same soft segment as (a) with a larger proportion of hard segment

Fig.3 SAXS patterns in all ring directions of TPU

7. References

1. Furukawa M., J. Society of Rubber Sci. &Tech., Japan, Vol.783(2010), pp 278-283