

Using Raman Imaging to Visualize Structural Changes in Polymers and Elastomers During Deformation

早大 (正) *ベルツ モルテン、(正) 山口 健、(正) 柳沢 雅広、(非) 会田 昭二郎、(非) 本間 敬之

Morten Bertz*, Ken Yamaguchi**, Masahiro Yanagisawa*, Shojiro Kaita**, Takayuki Homma*

*Waseda University, ** Bridgestone Corporation

1. Introduction

A detailed molecular understanding of the structural changes during deformation is key to designing and optimizing sustainable materials for challenging mechanical applications. Here, we use Raman imaging to investigate the spatial and temporal propagation of microstructural changes during uniaxial deformation in several model polymers, the well-studied semi-crystalline thermoplastic polyethylene (PE) and the novel thermoplastic elastomer ethylene-styrene-butadiene (ESB).

2. Materials & Methods

Raman imaging was performed using a Phalanx Raman microscope (Tokyo Instruments) equipped with a 532 nm laser and a 5x objective lens (Fig. 1 A). The incident laser light was polarized parallel to the direction of deformation. In a typical experiment, an area of 1.6×1.6 mm was imaged at 50 μm resolution during stepwise stretching by scanning a beam array of 11×11 beams across the sample. Low-density PE films (100 μm thickness) were obtained commercially. ESB samples (87.5% ethylene, 5.6% styrene, 6.9% butadiene, 1 mm thickness) were prepared by Bridgestone Corporation. Small incisions were applied to the samples to ensure that necking occurs within the observation region.

3. Results

Fig. 2A shows characteristic spectra of PE obtained before and after stretching. The intensity of the peaks at 1130 cm^{-1} (symmetric C-C stretching of long trans regions) and 1060 cm^{-1} (asymmetric C-C stretching) changes during deformation indicating an orientation of the polymer backbone along the pulling axis. In addition, CH_2 bending of orthorhombic crystalline regions (1420 cm^{-1}) also changes relative to CH_2 bending of amorphous regions

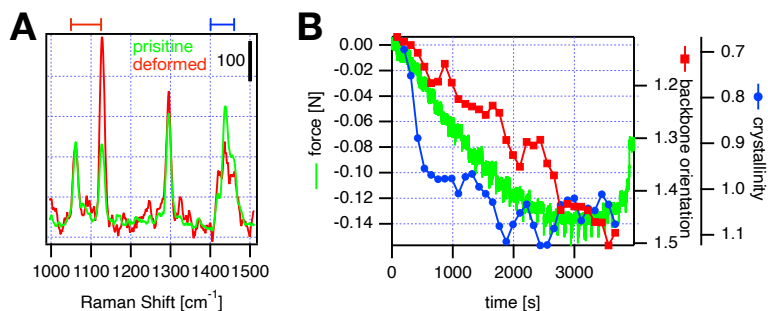


Fig. 2 Uniaxial stretching of polyethylene: (A) spectra of undeformed (green) and deformed (red) PE. (B) Force response and conformational changes of the film during deformation.

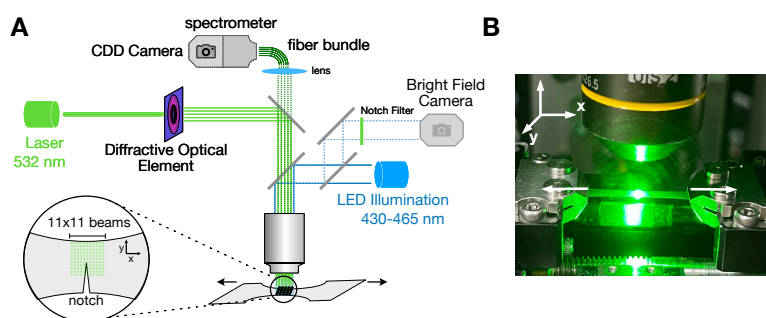


Fig. 1 Schematic of the experiment: Uniaxial stretching of thin polymer samples is probed by simultaneous multipoint Raman microscopy and video imaging. (A) Schematic of the optical setup. (B) Photograph of the sample mounted in the custom stretching apparatus.

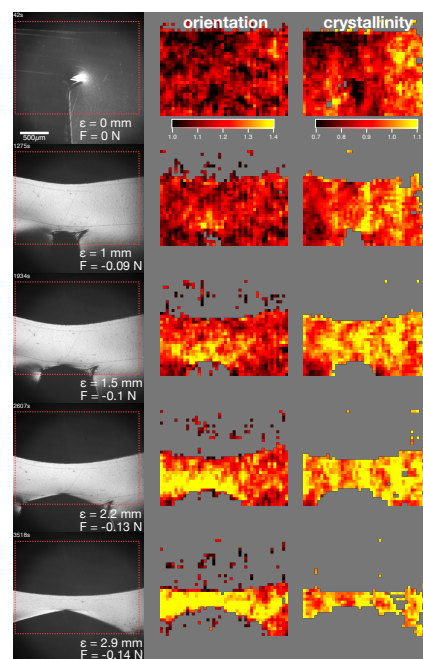


Fig. 3 Wide-field Raman imaging of a PE film during stretching: Left column: bright-field images. Center column: PE backbone orientation. Right column: PE crystallinity

(1460 cm^{-1}), which suggests that changes in the orientation of crystalline chains and overall crystallinity occur during the deformation process [1,2]. Fig. 3 displays the spatial distribution of the changes in orientation and crystallinity during the deformation of PE obtained from Raman imaging. Changes in crystallinity (right) can be observed throughout the necking region even at low deformations while the reorientation of the polymer backbone originates from regions of high local strain at the bottom of the neck. The time course of these changes (Fig. 2B) measured at the center of the observation region suggests that the increase in crystallinity, which is likely due to the reorientation of the crystalline domains along the pulling axis, quickly reaches a plateau after the application of stress while backbone orientation continues to increase up to the point of rupture.

ESB, a co-polymer of ethylene, styrene, and butadiene, exhibits the Raman signature of its constituents (Fig. 4A). In addition to the familiar peaks of PE, peaks stemming from styrene (phenyl ring breathing at 1000 cm^{-1} and 1030 cm^{-1}) and butadiene (C=C stretching at 1660 cm^{-1}) can be observed. Deformation of the sample by uniaxial extension results in the change of the relative intensity of several of these peaks (Fig. 4A red trace). The polyethylene (PE) component exhibits a change in orientation and crystallinity, as observed for the pure PE sample. In addition, the intensity of C=C stretching increases during deformation, indicating an orientation of the butadiene

(BD) component along the pulling axis. Fig. 5 displays the spatial distribution of the structural changes during ESB deformation focusing on the PE component. Reorientation of crystalline domains precedes skeletal reorientation, as was the case for pure PE, but there are a number of notable differences: Whereas crystalline orientation in pure PE changed sharply upon the application of force, the change in ESB is more gradual and correlates well with the force applied to the sample (Fig. 4B). Accordingly, changes in crystallinity are first detected

at the bottom of the necking region where the sample experiences the highest local strain. These findings suggest the presence of softer segments in ESB that are initially deformed. Furthermore, crystallinity reaches a maximum in ESB that coincides with the yield point of the polymer (Fig. 4B) and starts decreasing after the polymer is deformed further. This indicates the destruction of crystalline domains at high strain. The skeletal orientation of the PE and BD components of ESB exhibit similar behavior to that of pure PE and increase throughout stress application (Fig. 4B).

4. Discussion

Our results demonstrate that operando Raman imaging can provide a wealth of insights into the structural-mechanical relationships of the building blocks of a complex co-polymer during deformation. In future work, we aim to investigate the remaining components of ESB, styrene and butadiene, to gain a fuller molecular understanding of the deformation mechanism of thermoplastic elastomers.

Acknowledgements

This work was supported by the JST A-STEP program 「プラズモンセンサを用いた超高感度表面・界面分析用表面増強ラマン顕微鏡の開発」 (JPMJTR202K).

References

- [1] Kida, T., Oku, T., Hiejima, Y. & Nitta, K.-h. Deformation mechanism of high-density polyethylene probed by in situ Raman spectroscopy. *Polymer* **58**, 88-95 (2015).
- [2] Kida, T. Raman Spectroscopic Analyses of Structure–Mechanical Properties Relationship of Crystalline Polyolefin Materials. *Nihon Reoroji Gakkaishi* **50**, 21-29 (2022).

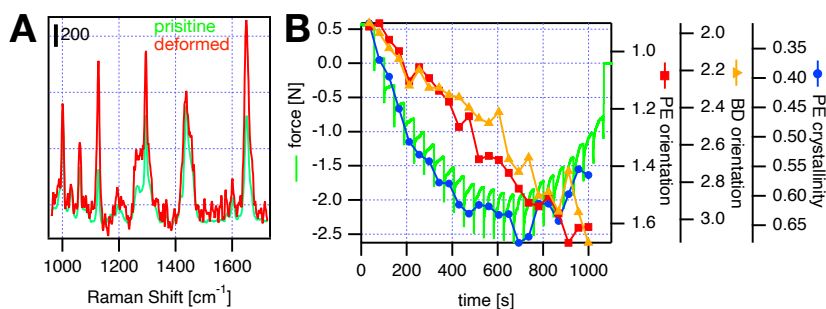


Fig. 4 Uniaxial stretching of ESB: (A) Characteristic spectra of undeformed (green) and deformed (red) ESB. (B) Force response and conformational changes during uniaxial stretching.

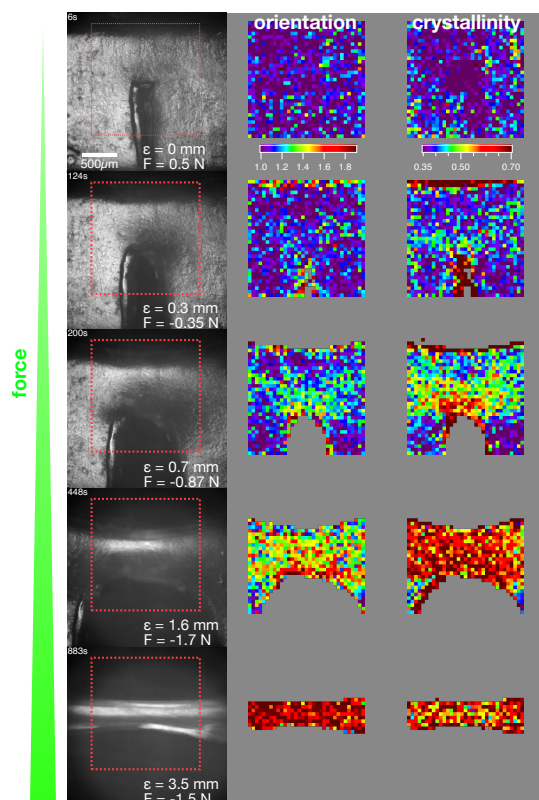


Fig. 5 Raman imaging of ESB during deformation: Sample morphology (left), orientation (center) and crystallinity (right) of the ethylene component of ESB at various points in time during the stretching experiment