Deformation Mapping by Combining Optical and Raman Microscopy

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1. Introduction

Understanding the relationship between structural and mechanical properties of polymers is key to optimizing their performance. Here, we employ a combination of high-resolution Raman microscopy and optical imaging paired with image analysis to elucidate the mechanism of plastic deformation using the semi-crystalline polymer polypropylene as a model system.

2. Materials & Methods

Multipoint Raman microscopy was carried out using a Phalanx Raman microscope (Tokyo Instruments) equipped with a 523 nm laser and a 4x objective lens (Fig. 1A). The sample was stretched in 50 µm steps using a custom-built stretching apparatus (Fig 1B) as described previously [1]. For each extension step, an area of 1.6×1.6 mm was imaged at 15 µm spatial resolution. Simultaneous video imaging (512×512 pixel resolution) was performed using 430 nm illumination.

The optical flow analysis was performed in ImageJ or OpenCV. All custom code is available on request. Image sequences for the optical flow analysis were acquired while stretching the sample in 5 µm steps.

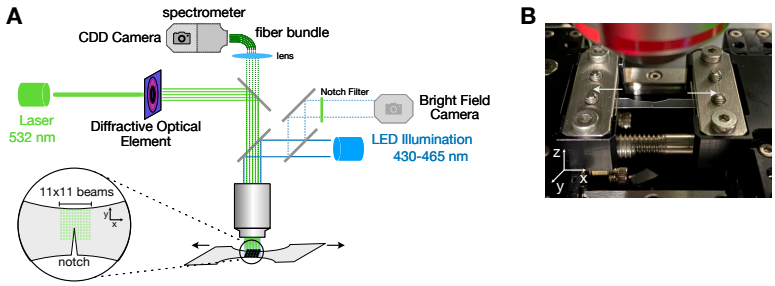

Fig. 1 Schematic of the experiment: Uniaxial stretching of thin polymer samples is probed by simultaneous multipoint Raman microscopy and video imaging. (A) Schematic of the optical setup. (B) Photograph of the stretching apparatus

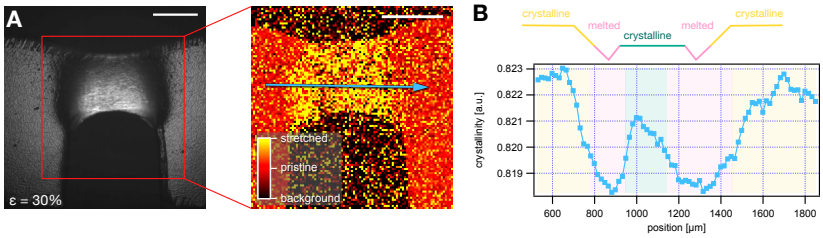

Fig. 2 Microstructural changes of polypropylene during stretching. (A) Brightfield image of the stretched sample at 30% strain (left) and Raman mapping of the degree of crystallinity (ratio of peaks at 808 and 842 cm^{-1}) in the imaged region (red box in the brightfield image). (B) Line profile across the necking region (blue arrow in (A)). The scale bar is 500 µm.

3. Results

Stretching polypropylene exhibits the typical features of plastic deformation. After reversible visco-elastic stretching, the polymer film undergoes necking after reaching a yield point and is further deformed during the strain-softening regime. We applied a small incision to the sample to ensure that necking occurs in the observation region (see inset in Fig. 1A). A snapshot of the deformed polymer during the strain-softening phase is shown in Fig. 2A. At this stage, the sample has been significantly deformed by the applied external strain. Raman imaging of the necking region (boxed region in the brightfield image) in Fig. 2A reveals that the ratio of the Raman peaks at 808 cm^{-1} and 842 cm^{-1}, which is commonly used to assess the degree of crystallinity of polypropylene [2], changes during stretching, which indicates a localized loss of crystallinity induced by the deformation. The neck of the sample exhibits low crystallinity (yellow) whereas the regions flanking the neck have higher crystallinity (red). This illustrates how stress disrupts the ordered lamellar structures of semicrystalline polypropylene. Analyzing the degree of crystallinity across the necking region provides further insight into the deformation mechanism: The line profile of crystallinity computed across the necking region (blue arrow in Fig 2A) follows a characteristic W shape (Fig 2B): The undeformed polymer bordering the neck has the highest crystallinity whereas the deformed region at the center of the neck exhibits intermediate crystallinity. This deformed region is flanked by two minima of crystallinity. This points to a deformation-induced melting-recrystallization process, which has been proposed as the mechanism underlying the deformation of polypropylene [3].

While Raman imaging can elucidate the structural changes that occur during uniaxial stretching of polypropylene, correlation of these changes with the mechanical behavior of the polymer requires further analysis, in particular local strain maps. To this end,

we performed a deformation analysis on sequences of brightfield images acquired during uniaxial stretching. In contrast to strain gauges, deformation maps obtained by optical imaging reveal, in a quantitative fashion, the full-field strain of the sample and work at any length scale. We employed an algorithm based on optical flow since this technique does not rely on specular patterns applied to the sample [4]. A strain map of polypropylene undergoing stretching is displayed in Fig. 3. While the algorithm (in principle) allows sub-pixel resolution, the vector field of the deformation map (Fig. 3B) is displayed at a resolution of 8×8 pixel (23×23 µm) for clarity. The analysis reveals that at 17% strain, which is past the yield point of the polypropylene film, local strain is highly heterogeneous. The center of the necking region is characterized by low local strain whereas the borders between the necking and non-necking regions exhibit high local strain. This mirrors the W-shaped distribution of crystallinity that was observed in the structural analysis of the neck using Raman microscopy. High local strain hence triggers melting of polypropylene. The melted polymer in turn (partially) recrystallizes at the center of the neck where local strain is low.

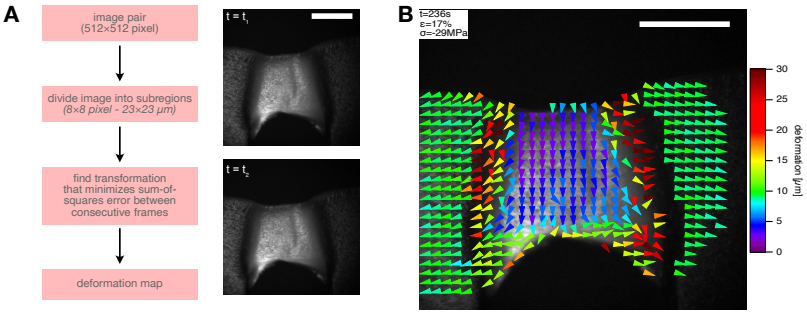

Fig. 3 Optical flow deformation maps: (A) Outline of the algorithm and (B) deformation map of the stretched sample at 17% strain. The scale bar is 500 µm.

Fig. 4 shows a comparison of structural changes (top), morphology (center), and deformation (bottom) during uniaxial stretching. A neural-network classifier was used to enhance contrast of the Raman mappings [1]. Strain-induced structural changes propagate upwards from the incision point. Once the yield point is reached, local strain becomes heterogeneous and regions of high local strain trigger melting of the polymer.

4. Discussion

Combining optical and Raman microscopy reveals that the deformation of polypropylene during stretching is a dynamic and highly local process involving strain-induced melting in regions of high strain followed by recrystallization. We anticipate that the techniques discussed in this work will find application in the investigation of a wide variety of samples undergoing deformation.

5. References

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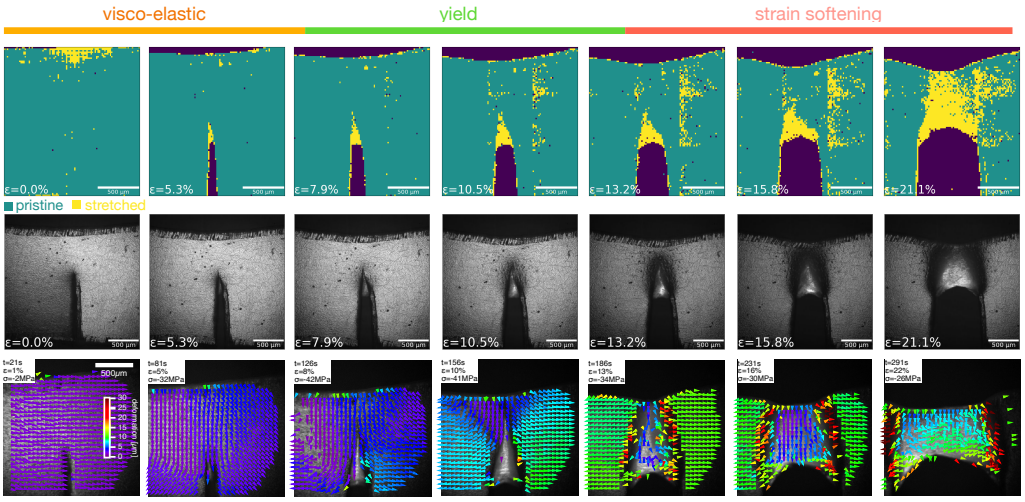

Fig. 4 Deformation mechanism of polypropylene. Comparison of chemical structure obtained from Raman mapping (top), video imaging (center) and deformation maps (bottom) at different stages of uniaxial stretching.