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Rheo-optical two-dimensional (2D) near-infrared (NIR) correlation spectroscopy for probing strain-induced molecular chain deformation of annealed and quenched Nylon 6 films

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ABSTRACT

A rheo-optical characterization technique based on the combination of a near-infrared (NIR) spectrometer and a tensile testing machine is presented here. In the rheo-optical NIR spectroscopy, tensile deformations are applied to polymers to induce displacement of ordered or disordered molecular chains. The molecular-level variation of the sample occurring on short time scales is readily captured as a form of strain-dependent NIR spectra by taking an advantage of an acousto-optic tunable filter (AOTF) equipped with the NIR spectrometer. In addition, the utilization of NIR with much less intense absorption makes it possible to measure transmittance spectra of relatively thick samples which are often required for conventional tensile testing. An illustrative example of the rheo-optical technique is given with annealed and quenched Nylon 6 samples to show how this technique can be utilized to derive more penetrating insight even from the seemingly simple polymers. The analysis of the sets of strain-dependent NIR spectra suggests the presence of polymer structures undergoing different variations during the tensile elongation. For instance, the tensile deformation of the semi-crystalline Nylon 6 involves a separate step of elongation of the rubbery amorphous chains and subsequent disintegration of the rigid crystalline structure. Excess amount of crystalline phase in Nylon 6, however, results in the retardation of the elastic deformation mainly achieved by the amorphous structure, which eventually leads to the simultaneous orientation of both amorphous and crystalline structures.

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1. Introduction

This article provides an illustrative application example of a near-infrared (NIR) characterization technique for studying molecular-level deformation of polymer samples. When external physical forces, such as tensile deformations are applied to semi-crystalline polymers, it substantially induces displacement of ordered or disordered molecular chains, as well as disintegration of lamellar crystals. Consequently, crystalline and amorphous structures respond to mechanical perturbations in a different manner, showing different deformation behaviors. A spectroscopic study of a semicrystalline polymer sample under well-controlled mechanical perturbation thus may provide useful information to derive in-depth understanding of system at the molecular level [1–5].

We have so far developed a rheo-optical characterization technique based on the combination of NIR spectrometer and tensile testing machine to measure strain-dependent NIR spectra as well as tensile stress of polymer sample (Fig. 1) [6–8]. This technique utilizes an acousto-optic tunable filter (AOTF) NIR spectrometer coupled with a tensile testing machine as an excitation device to collect sets of NIR spectra of polymer samples undergoing mechanical deformation. AOTF works as a small size electronically tunable bandpass filter with no moving parts [9–11], eventually making it possible to collect single spectrum within approximately 10 s. This offers a definite advantage over the conventional grating-monochromator or interferometer based approach in terms of high speed data acquisition, especially when the variation of the system occurs in relatively short time scale. In fact, many dynamic phenomena of major importance in tensile testing essentially occur at time scales in the range of seconds, or even longer [4–6]. Thus, by carrying out such rapid scan based on NIR light, it should be able to capture sets of transmittance spectra of relatively thick samples, which are often required for mechanical integrity during the deformation.

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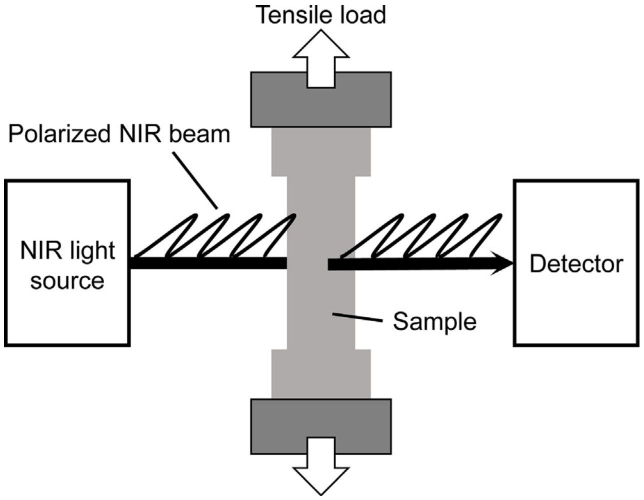

Fig. 1. A schematic illustration of rheo-optical characterization technique based on the combination of NIR spectrometer and tensile testing machine.

Application of the rheo-optical characterization technique is extended to semicrystalline Nylon 6 polymers. The systems studied are films of Nylon 6 polymer having different crystalline contents. Namely, quenched and fully annealed Nylon 6 samples were examined to show how the rheo-optical NIR spectra can be analyzed to sort out physically meaningful information. Nylon 6 possess polymer structure consisting of folded-crystalline lamellae embedded in amorphous matrix [12]. Change in polymer structure usually results in noticeable variations of NIR spectra [13,14]. By studying such spectral changes monitored during tensile deformation, it may provide penetrating insight on the structural and morphological deformation of the semicrystalline polymer.

2. Experimental

2.1. Sample preparation

A commercial Nylon 6 was supplied by Sigma-Aldrich. Total 5 g sample was hot-pressed at 230 °C for 10 min. A sample was then press-molded with a Teflon® spacer of 1 mm thickness by applying 10 MPa pressure and quenched in the ice water. Another sheet was prepared by applying an annealing process (e.g. 100 °C for 180 min) to cause additional development of the crystalline structure of Nylon 6. The sheets were cut into 4 × 4 cm samples to undergo the rheo-optical NIR measurements. The thicknesses of the samples were approximately 500 μm.

2.2. Rheo-optical NIR measurement

A portable AOTF-NIR spectrometer (Systems Engineering Inc., Tokyo) was equipped with a tensile testing machine MX2-2500N (Imada Co. Ltd., Aichi). Each polymer sample was fixed by clumps and the upper clamp was moved upward to apply a tensile stress to the sample while being probed with NIR beam polarized perpendicular to the given deformation direction. The sample films were stretched at the speed of 0.5 mm/min. Sets of NIR spectra were collected every 4 s by co-adding 32 scans over the 1300–2400 nm region and the corresponding stress and strain were also recorded simultaneously.

3. Result and discussions

3.1. Tensile test

Fig. 2(A) represents stress-strain curves of the Nylon 6 samples obtained by the rho-optical NIR measurements. The quenched sample shows obvious increase in stress at the onset of the tensile test, indicating the elastic deformation of the sample. The stress then increases loosely to indicate so-called plastic deformation and the sample finally ends up with breaking. Such deformation behavior, in fact, is very typical to the viscoelastic polymer where rubbery amorphous and rigid crystalline structures coexist. The annealed sample, on the other hand, exhibits a steep increase followed by sudden break, while its maximum stress is apparently increased. Fig. 2(B) represents energy-to-break toughness of the Nylon 6 samples. The toughness was calculated as the area under a tensile stress-strain curve. Difference in the energy-to-break toughness between the samples indicates that the additional development of the crystalline content in the polymer system is obviously associated with ductile properties of the sample. Such response suggests the possible onset of a very different type of deformations depending on the polymer structure.

Apparently, the variation of the deformation behavior observed

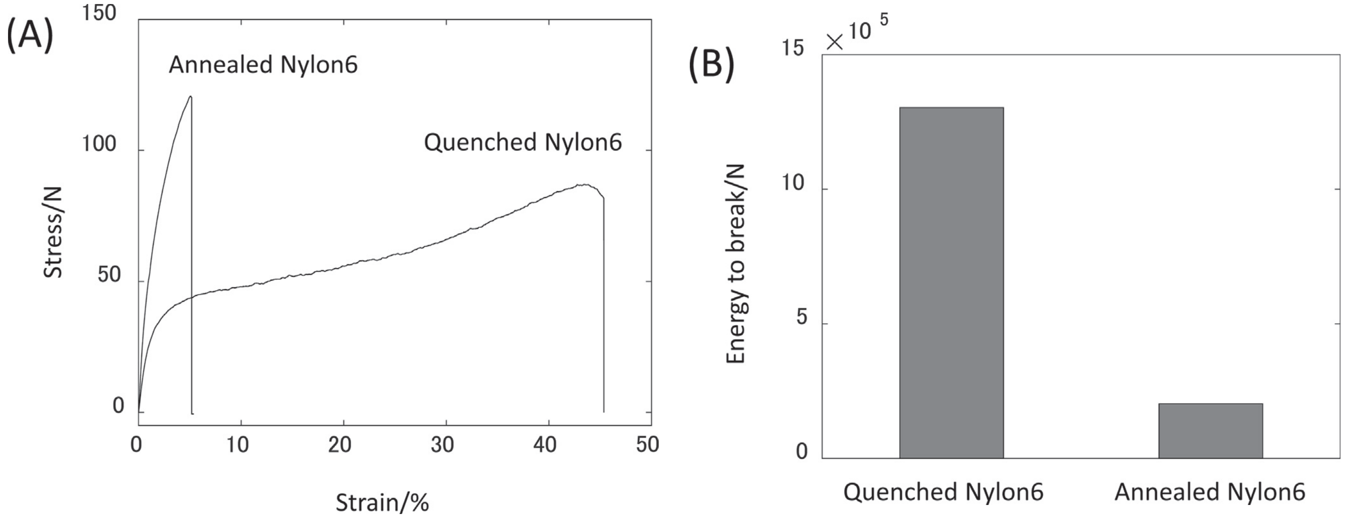

Fig. 2. (A) stress-strain curves and (B) energy-to-break toughness of Nylon 6 samples.

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