

Original method for studying the tensile drawing behaviour of polymers by Infrared Spectroscopy at high-strain rates

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Summary

This communication deals with the description and experimentation of an original method for studying the molecular processes of deformation in polymers by means of infrared spectroscopy under high-speed drawing conditions. The equipment is based on the model of an industrial drawing bench which involves the pulling of a continuous tape or yarn between two sets of feed rolls and draw rolls, in combination with a Fourier Transform Infrared spectrometer.

Preliminary light-polarized measurements concerned with a linear low density polyethylene have been undertaken. Well-resolved infrared spectra are reported for a sample drawn at a take up velocity $V_d=39\text{m/min}$, with a draw ratio $\lambda=7.8$.

Introduction

The dynamic structural analysis of the deformation in semi-crystalline polymers has been a matter of numerous studies based on birefringence (1,2), small-angle light scattering (1), X-ray diffraction (1,3), optical microscopy (4) and most of all infrared spectroscopy (5-15) which provides a deep insight into the elementary molecular processes on a scale of a few atoms. These investigations relied on either an oscillating tensile deformation or a continuous drawing. The studies of the first kind allowed to scrutinize the time dependency of the reversible structural changes in the elastic range of strain, chiefly the orientation motions of the crystal axes. The second kind of investigations aimed at characterizing the plastic deformation processes and accompanying relaxation phenomena. In this later case, low deformation rates were generally used because of recording time constraints imposed by the transient nature of the experiment.

However, the drawing of polymers on an industrial scale is usually performed at high speeds (16,17) which cannot be investigated by means of the conventional drawing machines developed up to now. So, in order to contribute to the study of the molecular orientation and relaxation phenomena during high-speed drawing, we have contrived a stationary drawing device especially fitted for infrared spectroscopic measurements. This equipment is based on the principle of the industrial continuous drawing process which involves two sets of feed rolls and draw rolls operated at different rotation rates (16). Moreover, the rolls have been designed for driving long strips which are more appropriate than yarns for spectrometric measurements. The main advantage of this stationary drawing technic is to be free of time constraints as regards the recording of the infrared spectra.

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Experimental part

The various devices already used for infrared spectrometric studies of the transient drawing of polymers were very small machines designed to be inserted inside the sample compartment of the spectrometer (see for instance ref.7,9,14). Oppositely, the development of a device affording a high speed stationary drawing based on the principle of the industrial continuous drawing required a heavy equipment that should be placed outside the spectrometer.

Fig.1 shows a schematic view of the 3m long drawing bench and its combination with the spectrometer. The polymer strip is delivered from the feed bobbin through the feed roll set at a feed velocity, V_f , then wound onto the take up bobbin through the draw roll set at a draw velocity, V_d , greater than V_f . The feed and draw roll sets consist of four pulleys which are driven by two 0.9KW engines by means of cogged belts. The pulleys are coated with a polyurethane layer in order to prevent the slipping of the strip under tension. The draw ratio applied to the strip is determined from the relation $\lambda = V_d/V_f$ owing to the measurement of the rotation rates of the engines. The actual draw ratio can be controlled after the drawing experiment by measuring the width and thickness of the drawn strip.

The 0.6m long oven consists of two parallel hot plates held together by means of transverse stems which also ensure the vertical stability of the sample. A slight bending of the plates allows the sample to rub against one of them for a better heat transfer. The sample temperature is determined by means of an infrared camera focused on the sample at the oven exit. The heating power of the oven is adjusted in order that the sample temperature compares closely with the chosen drawing temperature. In the case of non-homogeneous drawing, the oven can be moved longitudinally on rails in order to displace the neck of the sample in front of the windows of the infrared spectrometer. The vertical hot plates are provided with several openings which allow the infrared beam to transverse the sample at various positions along the oven.

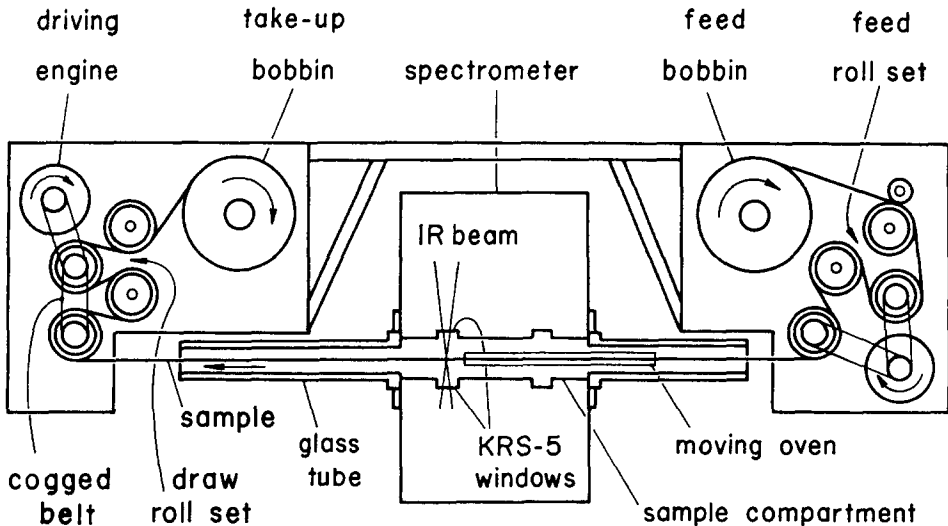


Figure 1. Continuous drawing bench for dynamic infrared measurements.

The infrared apparatus is a IFS 113V BRUCKER Fourier Transform spectrometer operated under vacuum. The sample compartment is composed of an insulated vacuum-proof metallic tube equipped with temperature-proof windows made of KRS-5 thallium iodobromide. A germanium wire grid polarizer is used for performing the dichroic measurements. The width of the infrared beam on the sample is about 4mm.

This original device allows infrared studies of polymer drawing in stationary regime which eliminates the recording time constraints characteristic of the transient drawing. Moreover, it makes possible high speed drawing experiments. However, in this later case, the method is highly sample-consuming.

Application to polyethylene

We have used our apparatus for studying the drawing behaviour of a linear low density polyethylene having a crystal weight fraction $\alpha_c^w = 0.6$ in the isotropic state (18,19). The strips were cut out from blown films supplied by C.d.F.Chimie. The strip dimensions were 200m in length, 16mm in width and 200 μm in thickness. The polymer under investigation gave rise to a neck for draw ratios $\lambda > 1.8$, even when raising the temperature close to the melting point. At the drawing temperature $T_d = 110^\circ\text{C}$, the tapes exhibited a stable neck at the exit of the oven as shown in Fig.2.

Drawing experiments have been conducted by fixing the feed velocity at the value $V_f = 5\text{m/min}$ and varying the draw velocity, V_d , from 5 to 50m/min. Infrared spectra have been obtained by storing 64 interferograms of 2cm^{-1} resolution, for an acquisition time of 48s. Fig.3 displays infrared spectra recorded with the infrared beam polarized parallel and perpendicular to the draw direction, for draw ratios below ($\lambda = 1.5$) and beyond ($\lambda = 7.8$) the neck formation. In the second case the infrared measurements were performed from the end of the neck, according to Fig.2. The spectra of Fig.3 clearly exhibit the dichroic effect due to chain orientation, even for the low intensity bands in the $900\text{--}1100\text{cm}^{-1}$ region. It is worth to mention that the spectra are free of perturbing modulations usually found with FTIR spectroscopy as a result of multiple reflexions on the thin sample surfaces. This can be explained by the slight fluctuation in sample thickness which blurs the multiple reflexion effect as several meter long sections of tape are fed for the recording of every spectrum.

A detailed dynamic study of the LLPE orientational behaviour will be

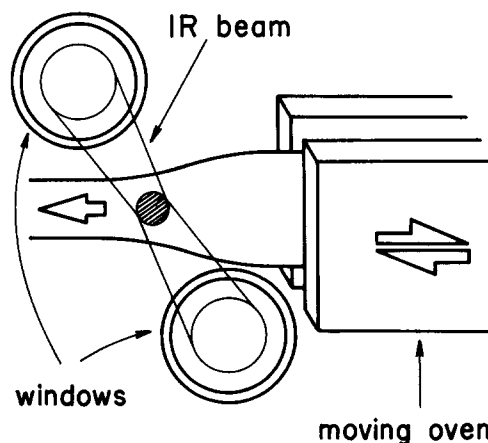


Figure 2. Sketch of a LLDPE strip necking down at the exit of the oven. Visualisation is given of the infrared beam and its trace on the sample.

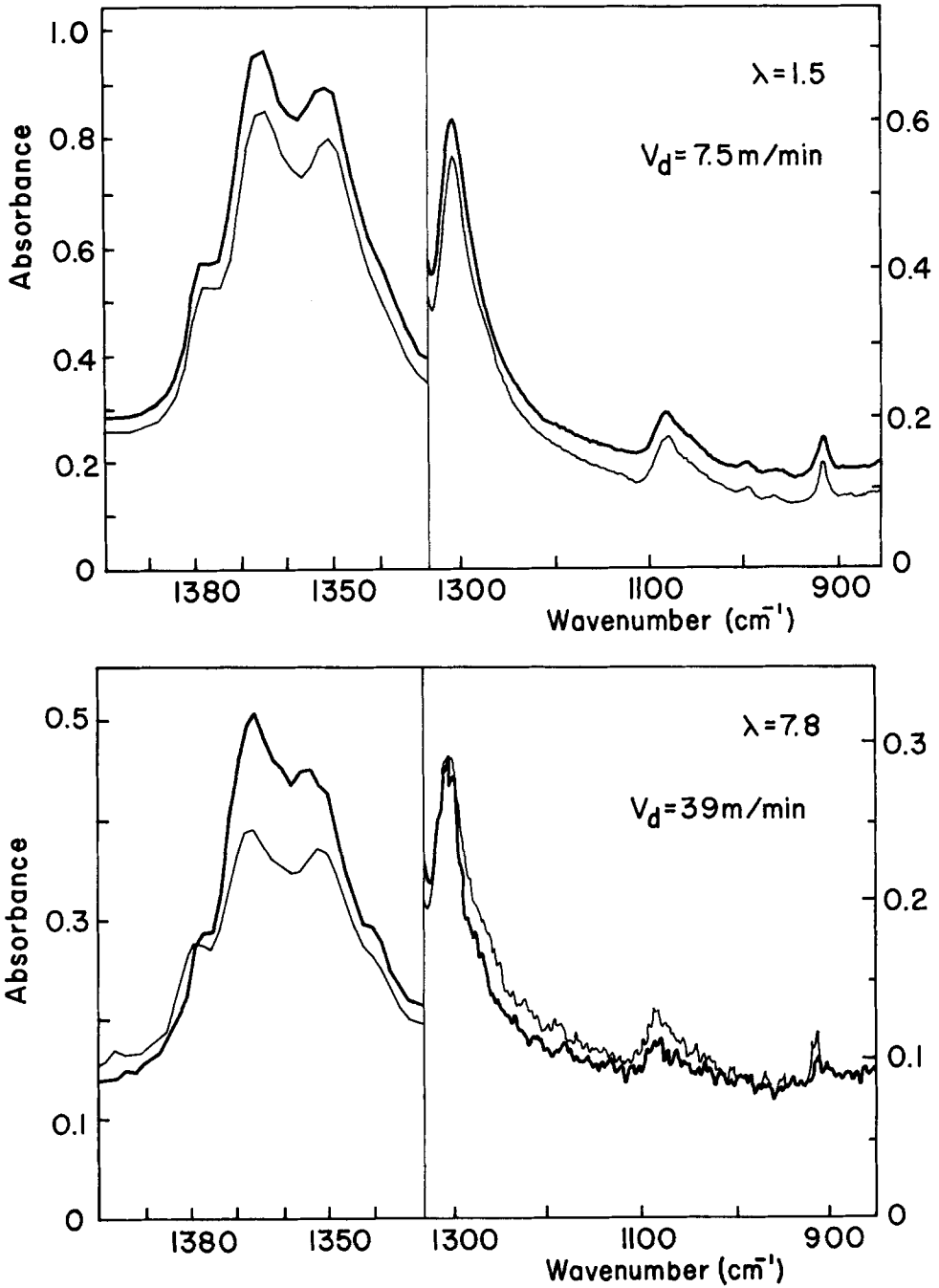


Figure 3. Infrared spectra of LLDPE tapes drawn at $T_d=110^\circ\text{C}$, for draw ratios $\lambda=1.5$ and 7.8 . Polarization parallel (---) and perpendicular (- - -) to the draw direction.

reported elsewhere (20) together with some evidence of fast relaxation effects in the time scale of a few milliseconds.

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