



Analysis of molecular interactions in polymer systems by using a pulsed compression time-resolved FT-IR/2D-IR spectroscopy. Generation of ring down compression pulses[☆]



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ABSTRACT

A rheo-optical method; based on pulsed compression ATR dynamic infrared linear dichroism (DIRLD) step scan time-resolved-FT-IR/2D-IR spectroscopy; is further improved. By inserting a tungsten carbide block with massive weight between a film sample and a piezo electric actuator; a ring-down response was successfully generated according to the inertial effect. As a result; it became possible to generate the multiplexed compression stress; which has a broad frequency distribution according to the viscoelasticity characteristic of polymer films. For crystallized poly (ethylene terephthalate); dynamic response differences among C=O; C—C—O stretching; and trans CH₂ wagging vibration region was found at 45.5 kHz Fourier frequency. In the case of poly(3-hydroxybutyrate-co-3-hydroxy-hexanoate); C=O stretching vibration regions also show different dynamic feature with increasing Fourier frequencies.

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1. Introduction

Elucidation of inter- or intra- molecular interactions in polymer-polymer or polymer-additive systems, as well as their mechanical properties, is of great importance especially for functional polymers, such as semi-conductive, biodegradable, and optically functional polymers.

Vibrational spectra contain vast amounts of molecular or microscopic information in polymeric materials. Geometric and steric isomerism, molecular orientation, conformational regularity, crystallinity, and the local microscopic environment of specific functional groups of polymeric materials can be elucidated with vibrational spectroscopic analysis.

Dynamic infrared linear dichroism (DIRLD) spectroscopy is an infrared-based rheo-optical technique for characterizing polymeric samples under a small-amplitude sinusoidal mechanical strain, traditionally operated in transmission mode [1,2]. The technique is widely used for the characterization of polymeric materials [3–8].

DIRLD spectroscopy can also be combined with two-dimensional correlation analysis to yield detailed information about the dynamic behavior of Polymers [9,10].

Such rheo-optical study of solid polymeric materials has been challenged by the strong absorption in the mid IR region [11–13]. The use of IR light often faces a serious obstacle in analysis where substantially thick samples are required for mechanical integrity during the deformation. One of the solution for the difficulty is the use of near-infrared (NIR) region with much less intense absorption [14]. The use of NIR region, however, lacks spectral information, as compared with mid IR fingerprint regions. Thus, it becomes very difficult to assign unknown peaks, except for relatively well defined absorption bands, such as overtone bands of H₂O and OH.

On the other hand, an attenuated total reflection (ATR) based Fourier transform infrared (FT-IR) spectroscopic method is basically free from the strong absorption problems in the mid IR region. However, only little work has been reported on dynamic compressive deformation coupled with ATR [15], which can be easily applied to thick real-world specimen.

In the conventional DIRLD, a fixed very low frequency (~20 Hz) sinusoidal deformation has been applied. For better understanding the mechanism involved in polymer deformation, the low

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frequency sinusoidal deformation is available. However, possible existence of various short- or long-range complex interactions, including strong-, and weak- hydrogen bonding, and van der Waals force should be taken into account. In order to elucidate the detailed inter- or intra molecular interactions, adoption of broader range of frequency responses, including relatively high frequency responses, will be needed. Again, almost no works have been reported by using a higher frequency mechanical deformation on rheo-optical spectroscopy.

By moving away from the fixed low frequency sinusoidal experiment, and adopting multiple frequency sinusoidal pulses, expanded opportunity for probing inter- or intra molecular interactions in polymer systems will be achieved. We have previously reported the attempt to multiplex the time domain information of the detailed viscoelastic responses of polymer systems by moving away from a fixed frequency sinusoidal experiment [16–23]. But their signal-to-noise ratio, repeatability, and accuracy are not adequate for probing detailed molecular interactions.

A major improvement in the previously reported rheo-optical method, based on pulsed compression ATR dynamic infrared linear dichroism (DIRLD) step scan time-resolved-FT-IR, spectroscopy coupled with 2D correlation analysis, has been reported [8]. Furthermore, by inserting a tungsten – carbide block with different massive weights between a film sample and a piezoelectric multilayer actuator, a ring-down pulsed compression was successfully generated according to the inertial effect. As a result, it became possible to generate the multiplexed compression stress, which gains higher and broader frequency distributions (including up to over-tone bands about 60 kHz, by using a smaller mass weight) according to the viscoelastic characteristic of polymer films.

We have further entertained the idea of using a variant form of 2D-IR spectroscopy different from the conventional generalized 2D correlation spectroscopy [24,25], combined with Pareto scaling [26] which utilizes data rescaled by square root of standard deviation. The Pareto scaled method makes it easier to obtain phase information for relatively small signals. Applying the double Fourier transformation of the data along the relaxation time axis and interferogram time axis, we have successfully produced contour map representations of wavenumber vs. Fourier frequencies of dynamic deformation, i.e., a new class of 2D-IR spectra with a given Fourier frequency (referred to as co-spectra and quad-spectra).

In the present paper, further detailed study about this method with some different mass of weights has been studied. For the crystallized poly(ethylene terephthalate), dynamic response differences in C=O, C—C—O stretching, and CH₂ wagging vibration regions were found with 20 kHz ring-down experiments including much higher Fourier frequencies (about 45 kHz). In the case of poly(3-hydroxybutyrate-co-3-hydroxy-hexanoate), C=O stretching vibration regions also show different dynamic feature with increasing Fourier frequencies. The present method provides us a powerful way to visualize the differences in dynamic molecular interactions of polymer systems.

2. Experimental and theoretical method

2.1. Generation of ring down compression signals

A Si hemisphere crystal (14 mm in diameter) is firmly fixed with a tungsten carbide material, and equipped on a carbon steel S45C mount holder. In previous experiments, a polymer film cut out minimum size (about 2–3 mm square) was inserted between the crystal and a piezo actuator (PZT), and the film sample kept contact firmly with the crystal.

In order to generate ring down compression signals, we inserted additional blocks with massive weight from 96 g to 9.6 g between a film sample and the PZT, as shown in Fig. 1. The blocks were made from tungsten carbide (V30) which has a higher specific gravity and hardness with the size from 20 × 20 × 20 to 10 × 10 × 3.5 mm. An example of the massive weights are shown in Fig. 2.

Ring down pulse compression signals were successfully generated due to resonance effects created from the inertial effects of the massive weights and visco-elastic properties of polymer film samples. An initial excitation pulse with one cycle sinusoidal wave with frequencies of 4400–25 kHz was generated from a signal generator. The ring down pulse responses were traced by using a step-scan time-resolved FT-IR system.

2.2. Ring down-pulse based dynamic compression ATR time resolved FT-IR system

A Nicolet is 50R FT-IR spectrometer from Thermo Fisher Scientific Inc. (Madison, WI) was used to obtain the ring down-pulse compression step-scan time-resolved ATR spectra. A piezo-driver (model M-26107, Mess-Tech Inc.) was connected to the PZT (NEC-Tokin, model AE0505D08 or noliac, model NAC2013-H10-A01) generating an initial excitation pulse to create ring down pulse compressions. Frequencies of the initial excitation pulses were set from 4400 to 20 kHz. A single reflection Harrick Seagull ATR accessory equipped with a wire-grid polarizer was used to measure the ring down-pulse induced compression ATR spectra. Incident angle of 40° was used. A narrow-band MCT detector was used. The MCT detector signals were then introduced to a high-speed digitizer board; 100 MHz, Gage Applied Tech., model cs1422.

2.3. Timing chart of TRS experiment

A timing chart of a ring down-pulse compression experiment is shown in Fig. 3 (in the case of 4400 Hz excitation). A pulse generator created one cycle excitation pulse signals and sent them to the piezo driver. The piezo driver amplified the signal to 0–90 V and applied it to the PZT to drive the compressive motion, and then created the ring down compression pulses according to the massive weight (96–9.6 g) and viscoelasticity of the polymeric film samples, as shown in Fig. 3. The maximum displacement of the PZT was set to about 5.4 μm. At each step, about one thousand data points, with time slices of 5.0–2.0 μs were sampled and recorded over about 2.0-μs period, and 100 data points were averaged at each sampling point. When data collection at a given retardation was completed, the interferometer mirror was stepped to the next retardation. Total measuring time was about 1 h and 55 min. After all interferograms were obtained, they were Fourier transformed to single-beam spectra. The first six single-beam spectra were averaged, and used as background single-beam spectra. Additional experimental conditions and data manipulations for dynamic compression TRS spectra were described in detail in the previous papers, except for generation of ring down pulses [21–23].

2.4. Fourier transformation of the ring down-pulse dynamic compression TRS data along the relaxation time axis

Obtained dynamic compression absorbance difference TRS series data were divided into the total of one thousand binary absorbance spectra. The binary spectra were then further converted to the total of 1000 csv text files by using a Microsoft Excel macro program. The obtained numerical text data were rearranged and Fourier transformed by using a Mathematica 8 for 64bit Windows 7 operating system. The definition of Fourier

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