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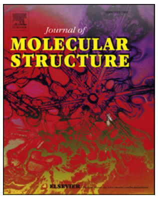

Analysis of molecular interaction using a pulse-induced ring-down compression ATR-DIRLD step-scan time resolved spectroscopy/2D-IR[☆]

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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. The improved method is used to analyze molecular interactions in cellulose acetate propionate (CAP) films including tricresyl-phosphate (TCP), as compared with cellulose triacetate (CTA) films with the TCP case. The result suggests that the existence of molecular interaction among propionyl groups in the CAP, the TCP's Methyl, and phenyl rings, which is not observed in the CTA-TCP system.

1. Introduction

Major concern in our laboratory for many years has been to detect molecular interactions in polymeric materials. Our specific interest is to find out which molecular groups; i.e. backbones, side-chains, or other functional groups originated from some additives, are related to molecular interactions. Dynamic infrared linear dichroism (DIRLD) method published in Applied Spectroscopy [1] has inspired us to pursue our current research activities.

Stress- or strain-induced molecular orientation is one of the most significant factors determining the microscopic properties of polymeric materials. Noda and his co-workers developed the infrared (IR) spectral measurement method of dynamic orientation change under a sinusoidal strain perturbation, i.e., DIRLD [2], more than a decade ago. The DIRLD spectroscopy can also be combined with two-dimensional correlation analysis to yield detailed information about the dynamic behavior of polymers [3], and has been applied to various polymeric materials including isotactic polypropylene [4], polyethylene [5], polyurethane [6–8], poly(ethylene terephthalate) (PET) [9,10].

The DIRLD had been traditionally used with transmission mode. However, transmission mode frequently suffered from strong absorption problem especially in the mid IR regions [11–13]. One of the solutions for the problem is the use of near-infrared (NIR) region with much less intense absorption [14]. The use of NIR region, however, lacks well-established spectral information, as compared with mid IR fingerprint regions. Thus, it becomes very difficult to assign unknown peaks, except for relatively well known absorption bands, such as overtone bands of H_2O 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 our ATR DIRLD system, dynamic compression stress is applied instead of stretching.

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

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low 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, very little works has 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 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 [16–21]. 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 [22]. By inserting a tungsten - carbide block with different massive weights between a film sample and a piezoelectric multilayer actuator, a ring-down response to a 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 [23,24].

In the present study, we have used the improved system to detect molecular interactions in cellulose ester films with a plasticizer. Cellulose esters, one of the biomass-derived materials, are useful optical materials and have been used in many applications for many decades by virtue of their excellent transparency and high degree of heat resistance [25–27]. For the same reason, currently, cellulose esters are being actively studied as a potential material for optical films such as polarizer protective films and retardation films in liquid crystal display (LCD) application. Cellulose ester films, including cellulose acetate propionate (CAP), and cellulose triacetate (CTA) are normally used with some plasticizers, such as tricresylphosphate (TCP), to attain mechanical, optical, and thermal stability. Better understanding of molecular interactions among them is crucial for providing excellent transparency and high degree of heat resistance [28,29].

In the present paper, analysis of molecular interactions in a CAP film including TCP, which acts as a plasticizer, as compared with a CTA film with TCP case, is demonstrated using a pulse-induced ring-down compression ATR-DIRLD step-scan time resolved spectroscopy (TRS)/2D-IR. The result suggests that the existence of molecular interaction between propionyl groups in the CAP and the TCP's phenyl rings, which is not observed in the CTA-TCP cases. 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 Ge hemisphere crystal (14 mm in diameter) is firmly fixed with a tungsten carbide material, and equipped on a carbon steel S45C mount holder. In order to generate ring down compression signals, we inserted additional blocks with massive weight from 96 g to 4 g between a film sample and the PZT, as shown in Fig. 1a. 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.

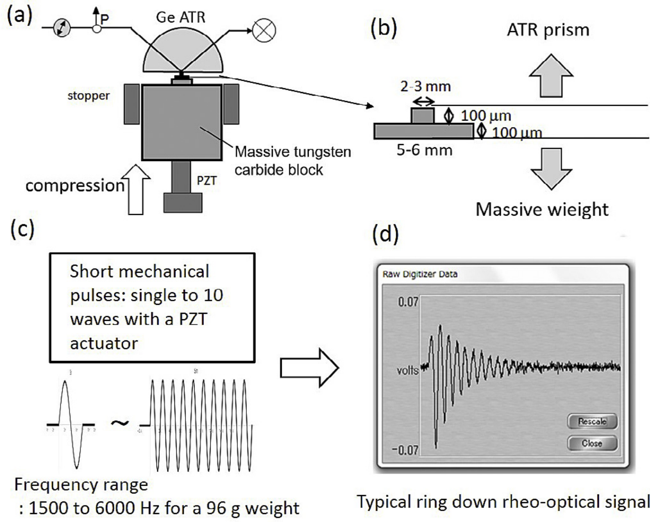

Fig. 1. Schematic outlines of the pulse-induced ring down compression ATR-based rheo-optics by using a massive tungsten carbide block; (a) optical layout of a ATR prism, a mussibve weight, and a PZT actuator, (b) sampling layout of two layered films, (c) conditions of input sinusoidal waves with a massive weight; (d) an example of resulting pulse-induced ring down signal waveform.

In order to obtain good compression signals, two layered films were prepared. One is very small (about 2–3 mm square), which is attached directly to ATR prism side, and the other has lager size (about 5–6 mm square) which is attached to massive weight surface (Fig. 1b). The film sample kept contact firmly with the crystal. 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, as shown in Fig. 1 c and d. Actually, pulse-induced ring down basic resonance frequencies are varied from 1500 to 6000 Hz for the 96 g massive weight, more than 6000 Hz to less than 10 kHz for the 48 or 31 g weight, and more than 10 kHz for the 9.6 or 4 g weight due to film thicknesses and visco-elastic properties of polymeric samples. The ring down pulse responses were traced by using a step-scan time-resolved FT-IR system.

2.2. Pulse ring-down based dynamic compression ATR time resolved FT-IR system

A Nicolet iS50R FT-IR spectrometer from Thermo Fisher Scientific Inc. (Madison, WI) was used to obtain the pulse-induced ring down compression step-scan time-resolved ATR spectra. A piezo-driver (model M-26107, Mess-Tech Inc.) was connected to the PZT

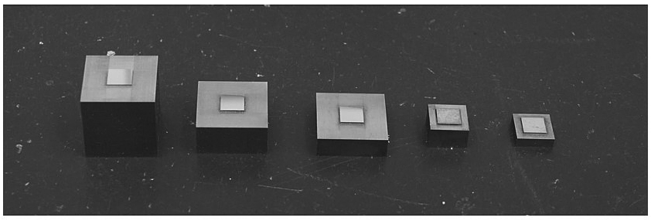

Fig. 2. A photograph of tungsten carbite weights.