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Research Paper

Time-domain transient fluorescence spectroscopy for thermal characterization of polymers

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ABSTRACT

In this work, a time-domain fluorescence spectroscopy technique is developed to characterize thermophysical properties of polymers. The method is based on fluorescence thermometry of materials under periodic pulse heating. In the characterization, a continuous laser (405 nm) is modulated with adjustable periodic heating and fluorescence excitation. The temperature rise at sample surface due to laser heating is probed from simultaneous fluorescence spectrum. Thermal diffusivity can be determined from the relationship between normalized temperature rise and the duration of laser heating. To verify this technique, thermal diffusivity of a polymer material (PVC) is characterized as 1.031×10^{-7} m^2/s, agreeing well with reference data. Meanwhile, thermal conductivity can be obtained by the hot plate method. Then, both steady and unsteady thermophysical properties are available. Quenching effect of fluorescence signal in our measurement can be ignored, as validated by longtime laser heating experiments. The uncertainty induced by uniformity of laser heating is negligible as analyzed through numerical simulations. This non-destructive fluorescence-based technique does not require exact value about laser absorption and calibration experiment for temperature coefficient of fluorescence signals. Considering that most polymers can excite sound fluorescence signal, this method can be well applied to thermal characterization of polymer-based film or bulk materials.

1. Introduction

In recent years, polymer-based materials have been studied extensively [1–4], and have shown great potentials in biomedical [5], photovoltaic solar cells [6], supercapacitors [7], LEDs [8] and so on [9]. Thermal conductivity and thermal diffusivity are important thermophysical parameters which determine steady and unsteady thermal transport performance. Thus, accurate measurement of these parameters is the key to the successful thermal design of polymer-based heat dissipation applications. Most polymer materials are poor in thermal transport, and thus extremely thin structures are usually used in electronics, not many techniques are available for thermal characterization. To date, a few works have been reported for successful characterization of polymers. Kim et al. used differential 3ω method to measure thermal conductivity of an amorphous-structured polymer as 1.5 W/m K [10]. In Lee et al.'s work, a modified hot wire method was employed to explore the thermal conductivity enhancement of polymer composites filled with hybrid filler [11].

The above referenced techniques are joule heating-based methods. Meanwhile, various optical techniques have been applied to polymer's characterizations. Song et al. studied thermal conductivity of an epoxy-graphene composites as 1.53 W/m K by laser flash method [12,13]. In another work, Wang et al. used time-domain thermoreflectance (TDTR) method to measure thermal conductivity of polymer fibers [14]. The TDTR method coupled with ultra-fast laser offers a superior temporal resolution, however, has drawbacks on the complexity in system operation and data analysis. As a spectroscopy method, Raman spectrum has been widely used for temperature probing and thermal characterization in recent years [15–18]. Generally, Raman thermometry is for steady state thermal measurement, e.g., the first report of superior thermal conductivity of graphene [19]. Recently, Raman thermometry has been successfully extended to transient measurement based on periodic laser heating and Raman excitation. The characterized thermal parameter is not limited to thermal conductivity but also thermal diffusivity [15,16,20]. However, when it comes to polymers, Raman scattering is not as significant as other crystalline structures. Thus, it is

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not a good option to use Raman thermometry on characterization of polymers.

Fluorescence is another commonly used spectroscopy technique which also possess strong temperature dependent property. Moreover, fluorescence signal can be easily detected from polymers [21–24]. With high sensitivity and short response time ($< 10^{-9}$ s) [25], fluorescence thermometry has been used in thermal imaging and temperature probing [26–29]. Here are some examples: Ivan et al. measured the temperature of glass-ceramic material based on its fluorescence emission [30]. Donner et al. used green fluorescent proteins as the thermal probe for intracellular temperature mapping [31]. Yarimaga et al. employed conjugated polymers as temperature sensor in an integrated circuit chip [32]. Recently, our group developed a steady-state electrical-heating fluorescence-sensing (SEF) technique for thermal conductivity measurement of materials [33], showing that fluorescence signal can be well applied to thermal characterizations. In this paper, we extend above technique to the transient thermal measurement, and establish a novel technique termed time-domain transient fluorescence spectroscopy to characterize thermal diffusivity of materials.

2. Physical model and experimental principle

As shown in Fig. 1(a), the sample is heated and excited by multiple laser pulses (or a continuous laser with modulated mode). The fluorescence signal is collected during the laser heating period. The sample is placed on a heat sink in a vacuum chamber to eliminate convection heat loss. The schematic of thermal transport is presented in Fig. 1(b). If the heating pulse is very short compared with heat diffusion time of the sample, the thermal transport is only confined within a very thin layer near sample surface. A semi-infinite model is applicable to describe the temperature evolution during laser heating, and the temperature rise at sample surface can be derived as:

$$T(t) = \frac{2q_0\sqrt{\alpha t/\pi}}{k}\exp(-x^2/4\alpha t) - \frac{q_0 x}{k}erfc(x/2\sqrt{\alpha t}) + T_0 \quad (1)$$

where α is thermal diffusivity, k is thermal conductivity, q_0 is heat flux density induced by laser heating, T_0 is room temperature, x is the distance from any cross section to the surface, *erfc* is the complementary error function. The sample is thick enough to ensure that the bottom of the sample stays at room temperature. It is shown in this model that α can be obtained from temperature rise against heating time.

Fluorescence signal is temperature dependent in terms of photon density (signal intensity), photon frequency (wavelength), photon decay (lifetime). Among various temperature indicators, fluorescence intensity is strong and features high sensitivity for temperature probing. Thus, based on excited fluorescence intensity, the temperature of sample surface can be obtained under pulse laser heating. As shown in Fig. 2(a), the pulse laser consists of an excitation period (t_e) followed by a relaxation period (t_r). Under laser heating, rising temperature of the sample causes the decrease of fluorescence intensity. During the off-duty period (much longer time), the sample is fully cooled down to room temperature. Fig. 2(b) shows selected laser pulses under various excitation periods. The temperature rise under different laser heating period can be obtained by accumulating fluorescence signal exited from all pulses. The fluorescence spectrum in one period of heating-cooling cycle is shown in Fig. 2(c). As excitation times (t_e) is increased, fluorescence intensity is decreased. Fig. 2(d) shows significant decrease in fluorescence intensity for sample temperature from 30 °C to 70 °C.

The heating power is always required in most characterization techniques. In this measurement, the heat source q_0 (laser absorption) is yet hard to define and characterize, especially for an unknown material. To avoid such uncertainty, a normalized temperature rise: $T(t)^* = [T(t) - T_0]/(T_m - T_0)$ is defined, where T_0 is room temperature and T_m is the maximum temperature rise. Meanwhile, the temperature coefficient is not necessary for thermal diffusivity measurement. By defining $F(t) = 2\sqrt{\alpha t/\pi}\exp(-x^2/4\alpha t) - x\cdot erfc(x/2\sqrt{\alpha t})$, the normalized temperature rise is derived as: $T(t)^* = [t_m\cdot\int_0^x\int_0^t F(t)]/[t\cdot\int_0^x\int_0^{t_m} F(t)]$, where t_m is the maximum heating time. α can be obtained from the normalized temperature rise against heating time. To test this model, a polymer material (poly vinyl chloride, PVC) with known thermal properties is employed for verification. PVC is one of the most widely produced synthetic polymers [34]. Its thermal conductivity is around 0.16 W/m K [35]. Most importantly, PVC can excite strong fluorescence signal with desirable temperature dependence, as shown in Fig. 2(c) and (d).

3. Results and discussion

3.1. Experimental verification and results analysis

In the measurement, the PVC is placed in a vacuum chamber to eliminate convection heat loss. The PVC bottom is attached on a copper heat sink. A continuous semiconductor laser (150 mW) with 405 nm wavelength is modulated with adjustable pulse duration. Different from other measurements with two-laser configurations, only one laser in the measurement is employed as the heating and fluorescence excitation source. Excitation spectra are collected by a fluorescence spectrometer (HR2000+, Ocean Optics). The fluorescence signals between 450 nm

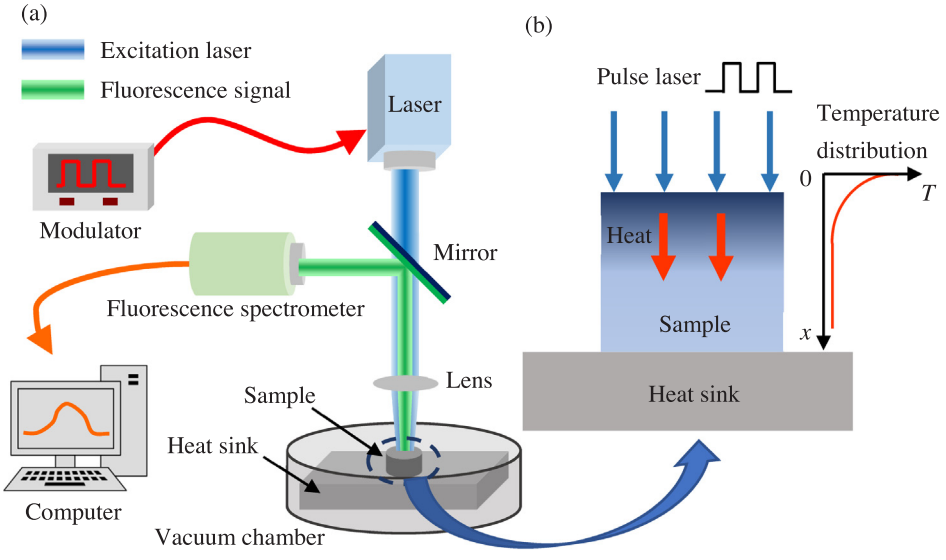

Fig. 1. (a) The schematic of time-domain transient fluorescent technique. A continuous laser is modulated by an electric-optical modulator to generate variable square pulse. The laser beam is focused on the sample for both photon heating and fluorescence excitation. Fluorescence signal is collected by a spectrometer for temperature measurement. (b) The schematic of thermal transport in polymers. For a short period of laser heating, thermal transport is confined within a layer close to the sample surface. The heat sink with large heat capacity ensures that the bottom of the sample keeps at room temperature. The vacuum condition of the sample eliminates the heat convection effect.