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Analysis of Thermal Radiation Properties of Polyimide and Polymeric Materials Based on ATR-IR spectroscopy

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A facile and non-distractive method for estimating thermal emissivity of solid polymers based on ATR-FT-IR method was newly developed. This method is applicable to thick and non-transparent samples without using blackbody furnace. The thermal emissivity estimated by this method are consistent with the reference values obtained using blackbody furnace. The ATR-IR method enables to estimate thermal emissivity of polymer materials having arbitrary shapes not only bulk and films but also forms and fabrics.

Keywords: Polyimide / thermal emissivity / polymer / ATR

1. Introduction

Thermal transfer phenomenon is crucial for cooling/heating and thermal insulation of materials. Three types of thermal transfer are well-known; thermal conduction, thermal convection, and thermal radiation. Compared with the former two types, fewer studies have been conducted on the thermal radiation coefficients of polymeric materials. The thermal radiation property is quantified by thermal emissivity ε. For example, materials having large and small ε can be used for thermal radiator and heat insulator, respectively.

In general, thermal emissivity is measured by comparing radiation between blackbody furnace and material, though blackbody furnace is not versatile for material scientists. In addition, thermal emissivity is sometimes measured in the UV-Vis and near-infrared (IR) regions, although the maximum radiation wavelength is located in the mid-infrared region at room temperature.[1]

According to Kirchhoff's law, thermal emissivity is equivalent to the absorption at equilibrium state Sasamori [2] has developed a method to evaluate thermal emissivity of solids by measuring reflectance and transmittance in the IR region. However, this method is applicable only to transparent and thin film samples, where impurity and inhomogeneity inducing light scattering should be removed. One possible solution for the problems is a use of attenuated total reflection (ATR)-IR method which is non-destructive and enables to estimate absorption of materials. In this study, a novel method for evaluating thermal emissivity of solids is developed based on ATR-IR, and the thermal emissivities of various polymeric materials are compared.

2. Theory

2.1. *Kirchhoff's law and Plank's law*

The absorption per unit thickness $\alpha(\lambda)$ can be obtained from the reflectance $R(\lambda)$ and transmittance $T(\lambda)$ as $\alpha(\lambda) = 1 + R(\lambda) + T(\lambda)$. Here, λ represents a wavelength. The absorbed and radiated energy of a material should be equivalent at the equilibrium state (Kirchhoff's law); therefore, thermal emissivity $\varepsilon(\lambda)$ is equal to $\alpha(\lambda)$ as

$$\varepsilon(\lambda) = \alpha(\lambda). \qquad (1)$$

The blackbody with $\varepsilon(\lambda) = 1$ emits electromagnetic radiation called blackbody radiation $B(\lambda)$ in accordance with Planck's law as

$$B(\lambda) = \frac{2hc^2}{\lambda^5}\frac{1}{e^{hc/\lambda k_B T} - 1} \qquad (2)$$

Here, h, c, k_B, and T represent Planck's constant, velocity of light in vacuum, Boltzmann constant, and absolute temperature of material, respectively. The thermal emissivity of material can be estimated from the equation below by comparing the radiations of blackbody and the sample.

$$\varepsilon = \frac{\int B(\lambda)\alpha(\lambda)d\lambda}{\int B(\lambda)d\lambda} \tag{3}$$

2.2. *Evaluation of thermal emissivity via polarized transmission measurement.*

Transmission measurement was performed using *p*-polarized IR beam with an incident angle of Brewster's angle, where reflectance *R* becomes null (eq. 4) and multiple reflection is eliminated.

$$R = \left(\frac{n\cos\theta - n_0\cos\theta_t}{n_0\cos\theta_t + n\cos\theta}\right)^2 \tag{4}$$

Here, n_0, n, θ, and θ_t represent refractive indices of air and material, incident angle, and refraction angle ($\sin\theta_t = n_0/n \sin\theta$), respectively. The absorbance $A(\lambda)$ is normalized by the light-path length l estimated from thickness d as $d/(\cos\theta_t)$. Thus, the unit thermal emissivity $\varepsilon_{\text{tans}}$ is obtained as

$$\varepsilon_{\text{trans}} = \frac{\int (B(\lambda)A(\lambda)\cos\theta_t/d)d\lambda}{\int B(\lambda)d\lambda} \tag{5}$$

It should be noted that anisotropy in refractive index, i.e. birefringence and wavelength dispersion of refractive index are not taken into account.

2.3. *Evaluation of thermal emissivity via ATR-IR measurement.*

ATR method is based on 'total internal reflection' resulting in an evanescent wave. Observed absorbance $A(\lambda)$ can be analyzed by extinction coefficient $k(\lambda)$ [3,4] as

$$A(\lambda) = \frac{(\alpha+\beta+\gamma)k(\lambda)}{\ln 10} \tag{6}$$

where α, β, and γ are defined as follows.

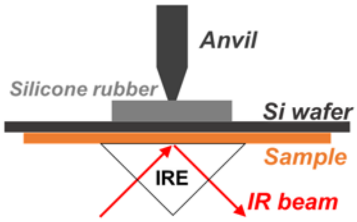
$$\alpha = \frac{4n^2}{X\left(1-\frac{n^2}{{n_p}^2}\right)} \tag{7}$$

$$\beta = \frac{4n^2(1-n^2\sin^2\theta)}{X\left(1-\frac{n^2}{{n_p}^2}\sin^2\theta + \frac{n^4}{{n_p}^4}\cot^2\theta\right)} \tag{8}$$

$$\gamma = \frac{4n^2}{X\left(1-\frac{n^2}{{n_p}^2}\sin^2\theta + \frac{n^4}{{n_p}^4}\cot^2\theta\right)} \tag{9}$$

$$X = {n_p}^2\sqrt{\tan\theta\left(1-\frac{n^2\sin^2\theta}{{n_p}^2}\right)} \tag{10}$$

Here, n, n_p, and θ represent refractive indices of material and prism, and incident angle, respectively. The unit absorption coefficient $\alpha_0(\lambda)$ is obtainable based on the following equation.



Scheme 1. Schematic diagram of ATR apparatus.

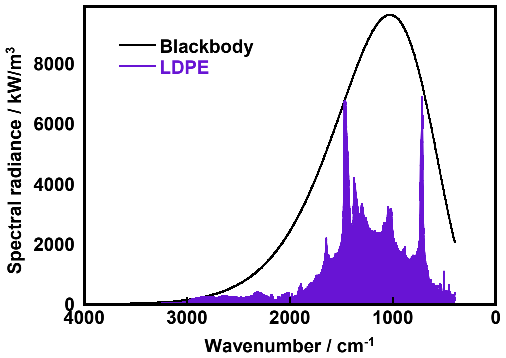


Fig.1 Calculated radiation spectra of blackbody and low-density polyethylene film (r.t., 100 μm thick).

$$\alpha_0(\lambda) = 4\pi k(\lambda)\tilde{\nu} \tag{11}$$

where $\tilde{\nu}$ represents the wavenumber of light. Finally, ε_{ATR} can be estimated by eq. 3 using an equation: $\alpha(\lambda) = 1 - \exp(-\alpha_0(\lambda))$. According to eq. 2, the calculated radiation spectra of blackbody and low-density polyethylene (LDPE) at 298 K are presented in Fig. 1 as an example.

3. Experimental

3.1. *Materials*

Pellets of low-density polyethylene (LDPE, Showa Denko Co.), high-density polyethylene (HDPE, Showa Denko Co.), nylon 6 (Toray Co.), polyethylene terephthalate films (PET, Toray Co.), and polyethylene foam (PE, Asahi Kasei Co.), and nylon 6 fabric (Toray Co.) were obtained from the Society of Polymer Science Japan. Polyimide (Kapton-V) film was kindly supplied by DuPont-Toray Co., Ltd.

3.2. *Measurements*

Transmission IR absorption spectra were collected with a Jasco FT/IR-4200 spectrometer with 32 scans per spectrum at a 4 cm^{-1} resolution. Spectra were collected using a *p*-polarized incident beam at Brewster's angle (~58°). A Jasco PL-82 wire-grid polarizer was used to polarize the incident beam. Refractive indices of the polymers ($n = 1.4 \sim 1.7$) indicate that the reflectance should be less than 0.16% according to eq. 4.

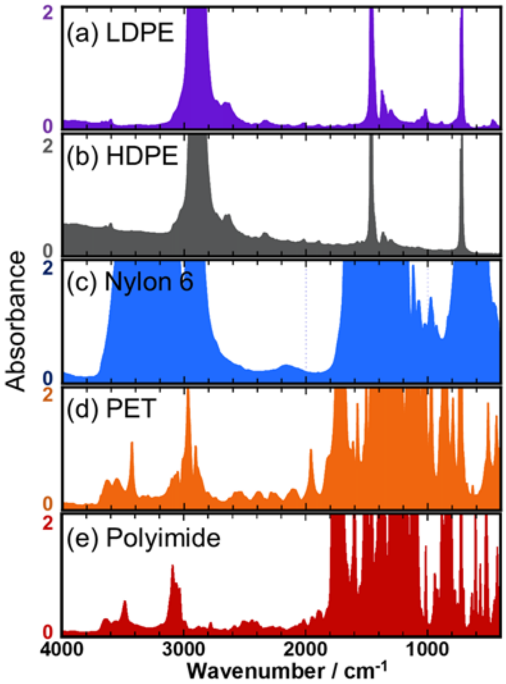


Fig.2 Absorption spectra (transmission) of polymers.

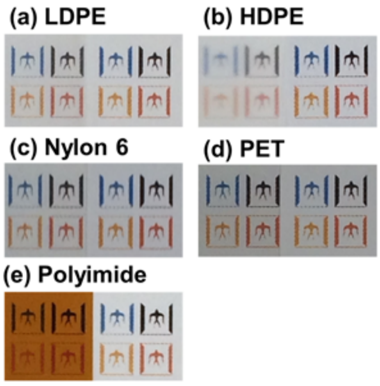


Fig.3 Photo-images of polymer films.

A robust single-reflection ATR accessory (ATR Pro-one, JASCO) with a diamond internal reflection element (IRE) (n = 2.4195, incidence angle: 45.0°) were used for ATR-FT-Mid-IR measurements. The samples were pressed contacting onto the IRE using a stainless anvil having a special mechanism providing a preset pressure. Silicon wafer and silicone rubber sheet with ca. 1 mm thickness were placed between the sample and the anvil to ensure the uniformity of pressure at the contact surface (Scheme 1). IR spectra were recorded with a Jasco FT/IR-4200 spectrometer with 32 scans per spectrum at a 4 cm^{-1} resolution.

4. Results and Discussion

4.1. *Transmission FT-IR spectra and calculated radiation spectra of polymer films*

The absorption spectra of polymer films are presented in Fig. 2. Their thickness, refractive indices[5], and calculated thermal emissivity are presented in Table 1. Here, thermal emissivity are calculated by assuming a 100 μm thick film to eliminate the thickness dependence [6].

Table 1. Thickness d, refractive index n, and thermal emissivity $\varepsilon_{\mathrm{trans}}$ of polymer films.

Sample	Thickness d (μm)	Refractive index n [5]	Emissivity $\varepsilon_{\mathrm{trans}}$ (/100 μm)
LDPE	110	1.471	0.23
HDPE	95	1.471	0.30
Nylon 6	100	1.542	0.85
PET	100	1.542	0.82
PI	50	1.642	0.74

As seen in Fig. 2, the absorption peaks are apparently saturated because all the sample films are thicker than 50 μm. In other words, transmission method is hardly applicable for thick films and bulk samples. Moreover, in Fig. 2b, HDPE exhibits very broad extinctions from 4000 to 400 cm^{-1}, originating from light scattering due to the semi-crystalline nature as evidenced by its opaque appearance (photo-image of Fig.3b). The optical extinction in Fig. 2b, which is significantly influenced by scattering, overestimates the absorption.

4.2. *ATR-FT-IR spectra and calculated radiation spectra of polymer films*

The ATR-IR absorption spectra of polymer films are presented in Fig. 4. Obviously, these peaks are not saturated, in contrast with the transmission method. In addition, ATR method is applicable to non-transparent or diffusible samples such as polymer foams or fabrics. The absorption spectra of PE foam and Nylon 6 fabric are also investigated in Fig. 5.

The thermal emissivity ($\varepsilon_{\mathrm{ATR}}$) of polymers at 298 K were calculated based on eqs. 3 and 6. Evanescent light intensity decays in an exponential manner with a distance from the incident point at the ATR prism. The penetration depth of total reflection, d_{p}, where the beam intensity is decreased by 1/e of initial intensity, is defined as

$$d_p = \frac{\lambda}{2\pi n_p} \frac{1}{\sqrt{\sin^2\theta - n^2/{n_p}^2}} \qquad (12)$$

The values of $\varepsilon_{\mathrm{ATR}}$ and d_{p} of polymer samples thus estimated are listed in Table 2. The d_{p} values (0.5~5.5 μm) are small enough compared with the sample thickness, which enables quantitative evaluation of absorption. It should be noted that the refractive indices of samples should be smaller than 1.711, otherwise the total reflection condition does

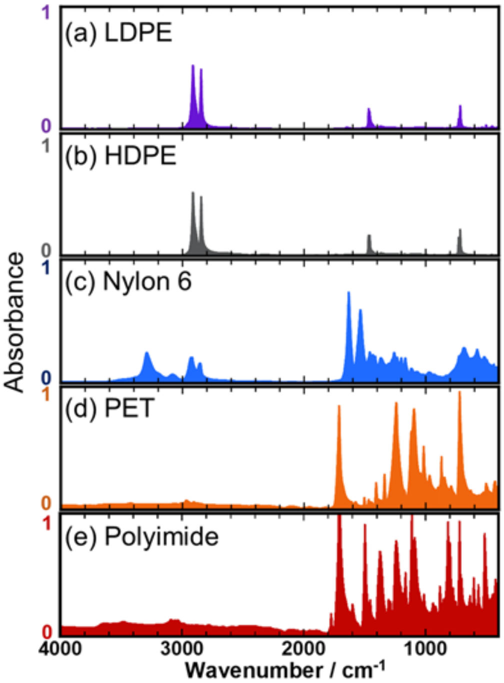


Fig.4 Absorbance of polymer films (ATR method).

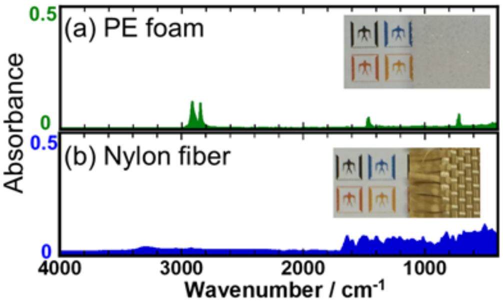


Fig.5 Absorption spectra by ATR and photo-images (inlet) of (a) PE foam and (b) nylon fabric.

not met at diamond prism. Germanium (Ge) prism is useful to measure materials with high refractive indices because of its high refractive index ($n_p = 4$). However, we should be careful that the high n_p significantly reduces d_p, which enlarges the experimental errors of absorption.

The thermal emissivity of 100 μm thick films of PE, nylon 6, and PET have been reported as ca. 0.30, 0.75, and 0.80, respectively [6]. The ε_{ATR} values of PE, nylon 6, and PET films in Table 2 are close to the reference, indicating the validity of the present method. In this experiment, PE samples were compressed and deformed by an anvil. In particular for the PE foam, significant densification should be induced by compression. Nylon 6 fabric exhibited a smaller ε_{ATR} than nylon 6 film because voids between fibers lowers apparent absorption.

The estimated ε_{ATR} values of PE samples are smaller than the other polymers because of the simple –CH$_2$– sequences with reduce number of vibration modes. On the other hand, polyamide (nylon 6), PET, and polyimide exhibit large ε_{ATR} values because these polymers consist of different functional groups such as carbonyl, ester, and imide moieties. Consequently, the incorporation of various functional groups is effective to endow high ε_{ATR} with polymer materials.

Table 2. Thermal emissivity ε_{ATR}, ε from reference, and penetration depth d_p of polymer samples

Sample	Emissivity ε_{ATR} (/100 μm)	Emissivity ε [6] (/100 μm)	Penetration depth d_p (μm)
LDPE	0.27	≈ 0.30	0.5~3.1
HDPE	0.28	≈ 0.30	0.5~3.1
Nylon 6	0.73	≈ 0.75	0.5~3.6
PET	0.81	≈ 0.80	0.5~3.6
PI	0.83	–	0.8~5.5
PE foam	0.23	–	0.5~3.1
Nylon fiber	0.61	–	0.5~3.6

For estimating thermal emissivity at high temperatures, the blackbody radiation spectrum changes according to eq. 2. However, even at 600 K, the radiation spectrum shows the peak around 2000 cm^{-1} and therefore the absorption $\varepsilon(\lambda)$ in the infrared region is still dominant for polymer materials. Thereby, the IR absorption strength is not drastically influenced with increasing the temperature, and the ATR method is facile and versatile for predicting thermal emissivity at different temperatures.

5. Conclusion

A facile method to estimate thermal emissivity of non-transparent and thick polymeric samples was newly developed based on ATR-IR method. The thermal emissivities thus estimated agree well with the reference values obtained using blackbody furnace. ATR-IR method enables to estimate the thermal emissivity of polymer materials quantitatively even for foam and fabric samples.

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