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Spectroscopic determination of the optical constants and radiative properties of black PMMA for pyrolysis modeling

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ABSTRACT

In-depth radiation absorption significantly affects the ignition time and burning rate of flammable translucent materials. To improve the accuracy of flammability predictions by pyrolysis models, the spectral dependency of radiation sources and the depth of the computational cell in the sample should be considered. This paper provides the absorption spectra of black Poly(methyl methacrylate) (PMMA) in a wide spectral range of 0.25 to 25 μm by measuring the high-resolution spectral transmissivity of thin samples. Compared to clear PMMA, black PMMA has a higher spectral absorption coefficient in the UV–Vis–NIR region (<2.3 μm). We extracted the complex index of refraction of black PMMA from the spectral absorption coefficient by applying the Kramers–Kronig transform (KK-transform). Furthermore, to investigate the effect of PMMA temperature on its absorption, the absorbance of the sample was measured with FTIR-ATR for the temperature up to the polymer’s melting temperature. The results showed that the radiation absorption of PMMA may increase for higher material temperature. Implementing the measured optical constants, simulated temperature profiles in a layer of PMMA subjected to the heat flux of 15 and 28 kW/m² are obtained, showing good agreement with the experimental data. Finally, a set of data for the effective absorption coefficient as a function of source temperature and depth is proposed for the black PMMA to improve the gray modeling of radiation for pyrolysis simulations.

1. Introduction

Black PMMA is commonly used in fire research due to its beneficial characteristics such as non-charring thermal decomposition, absence of melting flow, and swelling. In-depth radiation absorption is an essential mechanism in the prediction of ignition time of black PMMA, especially at high heat fluxes (i.e., higher than 70 kW/m²) [1,2]. The experimental data for transmissivity of black PMMA [3] showed that about two-thirds of radiative energy is attenuated within the first 0.33 mm of the material. Though, this may suggest the surface absorption assumption (i.e., κ → ∞) to estimate the thermal radiation in pyrolysis models [4], the validity of this assumption was questioned by other studies [1,5]. For instance, the experimental study of radiative transfer in clear PMMA exposed to cone heater and tungsten lamp [5] and numerical study on the ignition time of black PMMA [1] proved the importance of in-depth radiation in pyrolysis modeling.

A previous study [6] showed that changing the absorption coefficient in a pyrolysis model may alter the calculated ignition time of black PMMA with a factor of 2 for low heat fluxes. This variation for high heat fluxes might be up to a factor of 11 [6]. In the past studies, mostly the kinetic and thermophysical parameters of black PMMA were determined either through experiments (e.g., TGA and DSC) [7,8] or optimization [9,10], but the spectral radiative properties of black PMMA have rarely been measured. Most experimental studies of the in-depth radiation absorption have reported spectrally averaged, i.e. mean absorption coefficient. Jiang et al. [11] measured the total transmissivity of black PMMA samples with thicknesses of 1.06 to 3.82 mm using the infrared heaters with source temperature between 1050 to 1650 K causing various heat flux levels. Assuming a linear change of ln(τtot) with the sample thickness, they reported a constant value for the mean absorption coefficient. Linteris et al. [3] applied broadband technique using National Institute of Standards and Technology (NIST) gasification device (GD) together with a broadband thermal detector and spectral technique using integrating-sphere system. Their measurements revealed the non-linear behavior of ln(τtot) with the thickness of the material that was in contrast to the reported data by Jiang et al. [11]. Although the experimental study of Linteris et al. [3] showed that the spectral calculation of radiative heat transfer might be necessary for accurate prediction of the black PMMA’s flammability characteristics, it is common in literature to apply Beer’s law assuming a constant value for absorption coefficient and skipping the effect
of materials self-emission in calculation of the penetrated radiative heat transfer within pyrolysis models without solving radiative transfer equation (RTE) [12,13]. For doing such a spectral radiation modeling, the spectral radiative properties needs to be measured beforehand. Most of the studies for radiative properties in literature have been done for clear PMMA. Wallner et al. [14] measured the averaged solar optical and radiative properties of PMMA for the samples with thicknesses from 50 to 125 μm within the wavelength region of 2.5 to 55.5 μm. The refractive index of PMMA was measured by Kasarove et al. [15] for the finite points in the wavelength region of 0.43 to 1.05 μm. Using the measured values of refractive index, they proposed a correlation for this parameter by applying the modified Cauchy’s approximation. Blümel et al. [16] extended the experimental data of refractive index by measuring this parameter for the wavelength region of 1.25 to 3.33 μm. They proposed a more accurate correlation for the refractive index compared to the previous correlations. For the wide wavelength range of 0.5 to 77 μm, spectral absorption coefficient and refractive index of clear PMMA have been reported by Boulet et al. [17] using measured spectral transmissivity for samples with thicknesses of 0.37 and 14.79 mm and reflectivity for samples with thicknesses of 1.7 and 96.8 mm. Due to the large thicknesses used in their experiments, transmissivity for wavenumbers less than 6000 cm⁻¹ was zero. Hence, they used reflectivity measurements to extract the optical indices for low wavenumbers. Experiments of [16,17] were done using different devices and sample shapes. Using two different methods for calculation of the refractive index, they have reported fairly similar values for the refractive index. For black PMMA, the optical indices have not been reported in literature yet.

The flammability of fuels is experimentally characterized for various levels of heat flux irradiated to their surface. However, the radiating source used in different experiments may have different temperatures to cause the same heat flux at the sample surface. Experimental observation of Bal et al. [5] with cone heater and infrared (IR) lamps proved the important role of the heater type. IR lamps and cone heater showed different irradiation spectra to provide the same heat flux at the sample surface [18] that is mainly due to the higher source temperatures in the IR lamps. Hence, the mean absorption coefficient calculated from the broadband transmissivity measured in these two devices for the same heat flux might be different. Numerical results proved that using mean absorption coefficient (i.e., gray method) cannot accurately capture the heat source distribution within the condensed media [19]. Moreover, experimental results showed that the mean absorption coefficient varies with changing the thickness of black PMMA [3]. Therefore, applying a constant value for mean absorption coefficient cannot give an accurate estimation of the radiation penetration into the PMMA layer as it is dependent on the thickness and the source temperature.

In past studies [3,11], the radiative properties of black PMMA were measured when the sample was at room temperature. During thermal degradation in fire, the temperature of the various depth of the PMMA may reach higher temperatures. Effect of sample temperature on absorbance spectra has been investigated for some polymers [20,21]. It is reported that the strength and location of the peaks in absorbance spectra of polymers change with temperature. This analysis has not been done for black PMMA in literature.

Accordingly, the primary objective of the present research is to provide detailed high resolution information of spectral radiative properties and optical indexes of black PMMA which is not available in the literature. We measured the transmissivity of the ultrathin PMMA samples for a wide range of UV–Vis–NIR and FTIR spectroscopy. Then, spectral absorption coefficient and complex refractive index are calculated applying the transmissivity equation and KK-transform, respectively. The effect of temperature on the absorbance spectra of black PMMA is investigated using the ATR-FTIR measurements. Finally, using the measured high-resolution absorption spectra, we provide an effective mean absorption coefficient as a function of source temperature and the material thickness to improve the pyrolysis models that assume gray radiative heat transfer.

2. Experimental procedures

2.1. Sample preparation

We used the black PMMA samples manufactured by Evonic with tradename of ACRYLITE® cast black 9H01 GT in this research. This
material was provided by MaCFP working group to provide measurement data of black PMMA for the 2021 MaCFP Condensed Phase Workshop [22]. The thickness of the original sample was 6 mm. However, to measure spectral transmissivity with spectrometers, besides the thicker layers, some layers with four different thicknesses of $33 \pm 1$, $50 \pm 1.3$, $65 \pm 1.0$, and $73 \pm 1.5 \mu m$ were prepared using grinding process. Thickness values have been reported with standard deviation that was calculated from at least 10 thickness measurements of different sample points. In the preparation process, the ultrathin samples were fixed on the polishing holder using two-sided tapes. Liquid ethanol was used to dissolve the tape to detach the samples after polishing. For the Attenuated Total Reflectance (ATR) measurement at different temperatures, several samples were prepared from the 175$\mu m$ thick film cut into $2 \times 2$ mm$^2$.

### 2.2. Measurement devices

For the wavelength range of 0.25 to 2.5 $\mu m$ (i.e., UV–Vis–NIR region), the spectral transmissivity of the ultrathin PMMA samples was measured using the Cary 5000 UV–Vis–NIR spectrometer from Agilent Technologies [23]. For the same region, total and diffuse spectral reflectivities were measured for the original 6 mm thick sample. The difference between these spectral reflectivities is the spectral specular reflectivity at the air–PMMA interface used to extract the refractive index of PMMA. The spectral resolution of the spectrometer for both measurements is 1 nm. For the wavelength region of 2.5 to 25 $\mu m$ (i.e. Mid-Infrared region), transmissivity was measured using the Nicolet i50 FTIR spectrometer [24] with a resolution better than 0.09 cm$^{-1}$. Using the same spectrometer equipped with the accessory GladiATR with a diamond prism and heating stage capable of reaching 200 °C from Pyke technologies, ATR measurements were performed at various temperatures with resolution better than 0.09 cm$^{-1}$. Table 1 summarizes the information for different spectral measurements.

### 3. Calculation methods

#### 3.1. Spectral absorption coefficient

In spectrometers, a light beam is sent in nearly normal direction to a sample surface. The RTE for forward direction with neglecting the medium emission and scattering is written as:

$$\frac{dI^+_s}{dx} = -\kappa_s I^+_s$$

(1)

where $I^+_s(x)$ and $\kappa_s$ are forward radiation spectral intensity, distance from the sample surface, and spectral absorption coefficient, respectively. For the backward direction, the RTE is written in a similar way. The boundary condition for Eq. (1) is:

$$I^+_s(0) = (1 - \rho)I_{in} + \rho I^+_s(0)$$

(2)

where $\rho$ is the reflectivity and is assumed to be constant for all the interfaces. The boundary condition for the backward direction is:

$$I^-_s(L) = \rho I^-_s(L)$$

(3)

where $I^-_s$ and $L$ show the backward spectral radiation intensity and thickness of the sample. Detailed description of the geometry is shown in Fig. 1. Solving the above equations gives the following equation for the transmissivity:

$$t_s = (1 - \rho)^2 \exp(-\kappa_s L) \Rightarrow \ln(t_s) = -\kappa_s L - 2\ln(1 + \rho)$$

(4)

where $t_s = I_{out} / I_{in}$ is the transmissivity of the sample and $I_{in}$ and $I_{out}$ are the radiation intensity at front and back surfaces of the sample, respectively. Although neglecting the effect of multiple internal reflections due to their expected small effect, Eq. (4) gives an accurate value of the spectral transmissivity. However, strictly speaking, it is not exact. Performing spectroscopy, spectral transmissivity of samples with different thicknesses can be measured. Using the measured transmissivity for different thicknesses and using the linear regression for the measured points of $t_s$ and $L$, the spectral absorption coefficient is calculated using Eq. (4).

#### 3.2. Calculation of refractive index using reflectivity

Optical constants of materials are given in the form of complex index of refraction, $m_j = n_j - ik_j$, where $n_j$ and $k_j$ called refractive index and absorptive index, respectively. Using the measured spectral absorption coefficient, the absorptive index is readily calculated using:

$$k_j = \frac{k_j \lambda}{4\pi}$$

(5)

To extract the specular reflectivity at the interface from the measured specular reflectivity, multiple reflections should be considered as shown in Fig. 2. In this figure, $I_{in}$, $L$, and $\rho_{in}$ are incident intensity, sample thickness, and specular reflectivity. By including the multiple reflections, measured total specular reflectivity ($\rho_{in, tot}$) can be expressed by:

$$\rho_{in, tot} = \rho_{in} + \rho_{in}(1 - \rho_{in})^2 \exp(-2k_{in} L)$$

(6)

The first term in the right-hand side of the Eq. (6) is the direct reflection at the interface and the second term includes the effect of internal reflections within the sample. For the samples with strong absorptivity like most of the solids, the second term can be neglected. To avoid any probable error due to the simplification, specular reflectivity is calculated using Eq. (6).
Reflection is measured by spectroscopy by sending a ray with an incident angle of around 8°. Due to the higher refractive index for black PMMA, θ is always less than the incident angle. Therefore, an assumption of normal radiation incidence can be accurately made and applied to Eq. (6). Hence, at the interface of air as non-absorbing medium and black PMMA as absorbing medium, the specular reflectivity for the normal incidence is given by the Fresnel’s relation [25]:

$$\rho_{sl} = \frac{(n_1 - 1)^2 + k_1^2}{(n_1 + 1)^2 + k_1^2}$$

(7)

where the refractive index of air is assumed to be unity. Having the calculated spectral absorptive index of the measured spectral reflectivity, \(n_j\) is calculated by Eq. (7).

### 3.3. Calculation of the refractive index

According to KK-transform, the real and imaginary parts of the complex refractive index are connected through [26]

$$n_i = n_\infty + \frac{2}{\pi} \int_0^\infty \nu' \kappa_{s j} \nu' d\nu'$$

(8)

and

$$k_i = \frac{2}{\pi} \int_0^\infty \nu' n_{\infty} - n_\infty d\nu'$$

(9)

where \(n_\infty\) is the value of \(n\) for the wavenumber of infinity and \(P\) is the principal value of the integrals. Besides experimental uncertainties, two other sources of uncertainties in Eq. (8) are the value of \(n_\infty\) and the values of \(k_i\) for the part of the spectrum not included in our spectroscopy (i.e., <0.25 μm and >25 μm). To determine the value of \(n_\infty\) using Eq. (8), a known value of refractive index at a wavenumber is needed. For the black PMMA sample, this value is not known, hence minimizing the difference between the calculated refractive indexes from Eqs. (7) and (8) for the spectral range of the measured reflectivity gives the value of \(n_\infty\).

### 3.4. Monte Carlo method for radiative heat transfer simulation

To verify the application of the measured optical properties of black PMMA in radiative heat transfer simulations, we performed a Monte Carlo simulation for a one-dimensional slab of black PMMA exposed to an external radiative heat flux from cone calorimeter as shown in Fig. 3. The distance between the sample surface and the cone heater was considered to be 25 mm.

As Fig. 3 shows, thermal radiation is emitted from a certain angular span of the cone heater. This angular distribution of irradiation together with the change of direction and magnitude of radiation intensity at the interface of air–PMMA should be included in the radiative heat calculations within the sample [27]. In this paper, the shown geometry of the cone heater in Fig. 3 is only for giving an accurate boundary condition at the center of the sample (i.e., the photons directions). Monte Carlo simulation perfectly accounts for the directional and spectral details of irradiation entering the sample. By having the direction of the photons and spectral refractive index of the black PMMA, the penetration or reflection of any photon is determined by applying the Fresnel’s relation within the Monte Carlo simulation. By knowing the heat flux at the center of the sample for the cone calorimeter experiments, the absorbed in-depth radiative energy is determined using the fraction of absorbed photons coming from cone heater. A similar procedure is done for the material self-emission for absorbed radiative energy from other parts of the material. To do so for the considered one-dimensional problem, by dividing the whole thickness into \(N\) equal sublayers, the radiative heat source is [25]:

$$q''_{i\text{adi}} = -4k_p \sigma T_i^4 + q''_{i\text{em}} + \sum_{j=1}^N 4k_p \sigma T_j^4 F_{j\rightarrow i}$$

(10)

where \(T_i, F_{j\rightarrow i}, k_p, \Delta x_i, \text{and } F_{j\rightarrow i}\) are the temperature, radiative exchange factor from cone heater to \(i\)th sublayer, Planck-mean absorption coefficient of the \(i\)th sublayer, sublayer’s thickness, and the radiative exchange factor from sublayer \(j\) to sublayer \(i\), respectively. \(F_{j\rightarrow i}\) is calculated as the ratio of absorbed photons in \(i\)th sublayer to the whole photons coming from cone heater and \(F_{j\rightarrow i}\) is calculated as the ratio of the absorbed photons in \(i\)th sublayer to the whole photons coming from sublayer \(j\). The spectral modeling of radiation has been included in calculation of \(F_{j\rightarrow i}\) and \(F_{j\rightarrow i}\) by sampling a wavelength for each photon. Planck-mean absorption coefficient is given as:

$$\kappa_p = \frac{1}{I_b(T)} \int_0^\infty I_b(T) \kappa_s d\lambda$$

(11)

In Eq. (11), \(I_b\) and \(I_{b\lambda}\) are the total and spectral intensities of the blackbody. Due to considering very thin sublayers, their temperature can be assumed constant. Profile of spectral absorption coefficient of liquids and solids are usually smoother than gases, therefore, a lower number of photons can lead to good accuracy in Monte Carlo simulation of radiative heat transfer in condensed materials. To simulate the incident radiation from cone heater and medium emission from each sublayer, 10⁵ and 10³ photons are applied in the present Monte Carlo simulations, respectively.

To calculate the temperature profile within the sample, the energy conservation equation should be solved that is written in the following form assuming negligible gasification within the sample:

$$c_p \frac{dT}{dx} = \frac{dq}{dx} + q''_{i\text{adi}}$$

(12)

Temperature makes Eqs. (10) and (12) coupled, and therefore, they should be solved iteratively until the convergence criterion of \(\Delta T < 0.01\) K is met. To solve the Eq. (12), two boundary conditions and one initial condition are needed. The initial temperature of the sample at the beginning of the simulation is set to the ambient temperature (i.e., 297 K). The convective heat transfer and adiabatic boundary conditions are applied for upper and bottom surfaces, respectively.

The obtained numerical temperature profiles are compared with the experimental data reported in [28] for two radiative heat fluxes of 15 and 28 kW/m² at times of 40 and 20 s, respectively. The temperature profiles were measured using the advanced flammability measurements apparatus using a black carbon coating for the surface of black PMMA to make the experimental results similar to the experiments with cone calorimeter with a sample without coating [28]. They showed this similarity with measuring and comparing the ignition time of black PMMA applying the same heat fluxes on two experimental devices. In present research, in the absence of any other experimental data for temperature inside the sample in cone calorimeter experiment, the simulations are done for the cone calorimeter using the same temperature profiles reported in [28]. The other setting parameters of the simulations are summarized in Table 2 based on [1,7]:

### 3.5. Averaged values of the absorption coefficient

Surface absorption has been the simplest approach to model radiation heat transfer in pyrolysis modeling of solids and evaporation modeling of liquids. A more accurate modeling assumption is considering
Fig. 4. The measured spectral transmissivity of black PMMA samples in the UV–Vis–NIR range.

Fig. 5. The measured spectral transmissivity of black PMMA samples in the FTIR range.

Fig. 6. The measured total and diffuse reflectivity of black PMMA sample in UV–Vis–NIR range.

Fig. 7. The calculated spectral absorption coefficient of black PMMA by Eq. (4) and linear regression between the results of various thicknesses.

Fig. 8. Comparison of the spectral absorption coefficient of black and clear PMMA.

Fig. 9. Comparison of the calculated refractive index using the Fresnel’s relation and the KK-transform.
homogeneous global absorption within the thickness of the condensed materials assuming a gray absorption coefficient [11]. Higher fidelity models for including spectral variation of absorption in radiative heat transfer in condensed materials have been reported in our previous works [19,29]. Here we aim to account for spectral nature of the source and sample thickness in gray absorption coefficient used in gray radiation modeling. In present research, an effective mean absorption coefficient is suggested for gray modeling. It includes the effect of radiation source (source temperature) and the distance from material surface. Such an effective mean absorption coefficient can accurately represent the spectral changes of absorption of a sample weighted by the spectral intensity of a source. Using the measured data of spectral absorption coefficient, we obtained the mean effective absorption coefficient of PMMA as a function of distance from the material surface (x) and source temperature (T_s). To do so, total transmissivity is calculated using Eq. (13), then Eq. (14) gives the value of the effective absorption coefficient.

\[
\tau_{tot} = \frac{1}{I_b(T_s)} \int_0^\infty I_b(T_s) \exp(-\kappa_{eff}(x,T_s)x) d\lambda = \exp(-\kappa_{eff}(x,T_s)x) (13)
\]

\[
\kappa_{eff}(x,T_s) = -\frac{1}{x} \ln(\tau_{tot}) (14)
\]

In present research, a look-up table is provided for the effective absorption coefficient as a function of source temperature and depth. To apply the effective absorption coefficient within pyrolysis models, at each time step, a decent value for each computational cell is determined by doing interpolation through the look-up table with knowing source temperature and the distance of each cell from the surface.

4. Results and discussion

4.1. Spectroscopy measurements

The measured spectral transmissivity profiles for two of the ultra-thin samples by UV–Vis–NIR spectrometer are shown in Fig. 4. As seen, the samples were opaque for wavelengths less than 0.25 μm.

Results of transmissivity measurements for three different sample thicknesses using FTIR spectrometer are given in Fig. 5. These three thicknesses were selected after a series of careful measurements with samples of larger thicknesses between 100 and 200 μm. The thicker samples were opaque for a wide range of mid-IR spectrum suggesting the use of thinner samples for capturing transmissivity data for the whole mid-IR spectrum. However, even with the ultrathin samples, some small parts of the spectrum cannot be captured due to the opacity of the samples. The brittleness of black PMMA and current manufacturing restrictions prevented preparing thinner samples. The data of spectral transmissivity of different thicknesses are given in the data in brief paper.

Even with the thinner ultra-thin sample, the transmissivity of two narrow spectral regions of 5.72–5.85 μm and 8.3–8.85 μm cannot be captured. The thinner sample is still opaque in these regions suggesting that transmissivity can be assumed zero for these two regions.

Fig. 6 shows the spectral reflectivity of a 6 mm sample measured by UV–Vis–NIR spectrometer. The noisy results corresponding to the larger wavelengths of the working range of the spectrometer (>2.0 μm) were skipped and are not shown in the figure. For the measured wavelength region, the value of total reflectivity is around 4% and the value of diffuse reflectivity is less than 1 %.

This measurement has been done only for calculation of \( n_\infty \).
Fig. 12. The measured normalized absorbance of black PMMA at different temperatures using FTIR-ATR.

Fig. 13. Comparison of numerical and experimental temperature profiles for the heat fluxes of: (Left) 15 kW/m$^2$ at the time of 40 s and (right) 28 kW/m$^2$ at the time of 20 s.

Fig. 14. (Left) transmissivity and (right) radiative heat source calculated by the Monte Carlo model for a 3 mm layer of black PMMA subjected to various heat fluxes in the cone calorimeter.
Using the measured transmissivity data shown in Figs. 4 and 5, the spectral absorption coefficient of black PMMA was calculated by applying Eq. (4) and linear regression between the calculated spectral absorption coefficient of various thicknesses. The results are shown in Fig. 7. To complete the spectrum in the range of 0.25 to 25 μm, an extrapolation was used for the opaque regions. Assuming the 1 μm uncertainty for the sample thickness, 0.005 for the reflectivity, and assuming a 1% uncertainty for the transmissivity measurement, by applying the Taylor series expansion for the uncertainty propagation, the uncertainty of absorption coefficient (standard deviation) is estimated to be less than 5%.

To compare clear and black PMMA, profiles of the spectral absorption coefficient of these polymers are plotted in Fig. 8. Two polymers show a similar absorption coefficient for wavelengths larger than 2.23 μm, and the small differences can be due to the uncertainties of the two experiments. The main difference between two polymers exists for wavelengths shorter than 2.23 μm with higher absorption for black PMMA. Therefore, radiation absorption of black PMMA is larger due to the importance of short wavelengths in the emission of high-temperature flames in fires. This conclusion is consistent with the previously reported experimental observations [3,30].

### 4.2. Optical constants

Using the measured spectral absorption coefficient, the absorptive index is calculated using Eq. (5). The refractive index can be then calculated using the KK-transform (Eq. (8)). The \( n_{\infty} \) in Eq. (8) is calculated using the specular reflectivity and applying Eq. (7). To do so, the specular reflectivity is calculated as difference of total and diffuse reflectivity shown in Fig. 6. Then using Eqs. (6) and (7), the refractive index is calculated for the wavelength region of 0.5 to 2 μm. We then calculate the integral term in Eq. (8) for the same wavelength region. Now, \( n_{\infty} \) is calculated by minimizing the difference between the calculated refractive index using Eqs. (7) and (8). It leads to \( n_{\infty} = 1.47 \). The refractive indexes calculated by these two methods are compared in Fig. 9.

By using \( n_{\infty} = 1.47 \), the refractive index is calculated for the entire spectrum up to 25 μm. The extrapolation suggested in [26] was used to reduce truncation error related to the lack of measurement in the spectral regions beyond the spectral range of our devices. The calculated optical constants of black PMMA in the range of 0.25 to 25 μm are shown in Fig. 10.

### 4.3. Effect of sample temperature

To investigate the effect of sample temperature on absorbance spectra, ATR experiments were done at various temperatures up to the melting temperature of black PMMA (160 °C). The results for the temperatures of 50 and 150 °C are given in Fig. 11. Increasing the sample temperature increases the absorbance especially for the wavelengths of 6 to 13 μm. Considering the emission spectrum of a blackbody emitter at 1000 K, the mentioned wavelength region covers less than 22% of the radiation power. Due to the known experimental uncertainties in ATR measurements such as material softening at elevated temperature, it is difficult to use ATR-FTIR absorbance for quantitative calculations. To quantitatively address the effect of temperature on the absorption coefficient, the absorption of the black PMMA should be measured at higher material temperatures. In addition to the temperature effect, a band assignment based on [31,32] is given for different peaks of the measured absorbance spectra in Fig. 11.

We also observed that the temperature of the sample changes the locations of the peaks of the absorbing bands as shown in Fig. 12 for peak wavelengths of 5.8 and 8.8 μm. In each of the plots in Fig. 12, the measured absorbance has been normalized with the absorbance of the peaks. A similar effect of sample temperature was reported in the literature for other polymers [21]. This shape change is not expected to significantly effect in the simulation of radiative heat transfer within the sample where total radiation source term and heat flux are desired.

### 4.4. Monte Carlo simulation

The results of the Monte Carlo simulation of black PMMA subjected to heat fluxes of 15 kW/m² at the time of 40 s and 28 kW/m² at the time of 20 s are shown in Fig. 13. The calculated temperature capture the experimental results reported in [28]. To show the effect of in-depth radiation absorption, similar simulations have been done assuming surface absorption. The results of the simulations have been compared with the results of in-depth radiation absorption in Fig. 13. As seen, considering in-depth radiation greatly improved the accuracy of simulation especially in the first layers of the sample in which pyrolysis takes place.

The profiles of transmissivity and radiative heat source along a 3 mm layer of black PMMA have been calculated for different incident radiative heat fluxes from the cone heater by the Monte Carlo simulation. Assuming a view factor of 0.78 and emissivity of 0.91 for incident radiation from cone heater [33] and assuming gray radiation from cone [18], the applied heat fluxes of 10, 30, 50, and 100 kW/m² correspond to the heater temperatures of 706.0, 929.2, 1055.8, and 1255.5 K, respectively. According to the results in Fig. 14, most of the thermal radiation is absorbed within a skinny layer (i.e., less than 1 mm) just below the surface. Moreover, for the lower incident heat fluxes, the absorption is stronger. For example, 90% of the incident radiation is absorbed within a thickness less than 0.6 mm for heat flux of 10 kW/m², while this thickness for the heat flux of 100 kW/m² reaches 0.8 mm.

### 4.5. Effective absorption coefficient

The effective mean absorption coefficients (\( \kappa_{\text{eff}} \)) as explained in Section 3.5 are given as a function of distance from material surface at different source temperatures in Fig. 15. The \( \kappa_{\text{eff}} \) exhibits nonlinear behavior with depth. Due to the shape of the absorption coefficient spectrum, by increasing source temperature, \( \kappa_{\text{eff}} \) decreases, but the difference for higher temperatures is lower.

Gray method (i.e., using an averaged value of absorption coefficient) is the most common approach to solve spectral radiative heat transfer within PMMA. To improve the accuracy of pyrolysis models, at each source temperature, based on the distance from the material surface, different values of absorption coefficient is applied for different material cells in numerical simulations. Although applying of varying...
The spectral absorption coefficient is one of the most important parameters characterizing the radiative heat transfer in different media. This parameter together with the optical constants of black PMMA was determined using spectroscopy. The spectral absorption coefficient of black PMMA was determined by measuring the transmissivity of several thicknesses of the material for the wavelength region of 0.25 to 25 μm. The spectral absorption coefficient in most of the spectrum except the short wavelengths (<2.3 μm). By measuring the reflectivity and applying the combination of KK-transform and Fresnel’s relation, refractive index was determined for the same wavelength region. To investigate the sensitivity of the absorption coefficient to sample temperature, we performed the FTIR-ATR measurement for the temperatures up to the melting point. The results showed a small shape variation of the absorbance spectrum with temperature and higher absorption of the material at elevated temperatures. The quantitative determination of temperature effect on the absorption coefficient could be done in future research. To demonstrate the usage of the obtained spectral data in high fidelity calculations of radiative heat transfer in PMMA, a Monte Carlo simulation was performed and coupled with the energy conservation equation for the initial heating stage of the sample at the cone calorimeter experiment. The results of the simulations showed a good agreement with experimentally measured temperature profiles. To provide suitable gray absorption coefficient for the pyrolysis models, a concept of effective mean absorption coefficient as a function of source temperature and depth from the material surface was proposed and a dataset was provided for it.

5. Conclusion and remarks

The spectral absorption coefficient is one of the most important parameters characterizing the radiative heat transfer in different media. This parameter together with the optical constants of black PMMA was determined using spectroscopy. The spectral absorption coefficient of black PMMA was determined by measuring the transmissivity of several thicknesses of the material for the wavelength region of 0.25 to 25 μm. A comparison between clear and black PMMA showed similar values for the spectral absorption coefficient in most of the spectrum except the short wavelengths (<2.3 μm). By measuring the reflectivity and applying the combination of KK-transform and Fresnel’s relation, refractive index was determined for the same wavelength region. To investigate the sensitivity of the absorption coefficient to sample temperature, we performed the FTIR-ATR measurement for the temperatures up to the melting point. The results showed a small shape variation of the absorbance spectrum with temperature and higher absorption of the material at elevated temperatures. The quantitative determination of temperature effect on the absorption coefficient could be done in future research. To demonstrate the usage of the obtained spectral data in high fidelity calculations of radiative heat transfer in PMMA, a Monte Carlo simulation was performed and coupled with the energy conservation equation for the initial heating stage of the sample at the cone calorimeter experiment. The results of the simulations showed a good agreement with experimentally measured temperature profiles. To provide suitable gray absorption coefficient for the pyrolysis models, a concept of effective mean absorption coefficient as a function of source temperature and depth from the material surface was proposed and a dataset was provided for it.

Data availability

Data will be made available on request.

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