

# Transmission Spectrum of PDMS in 4-7 $\mu$ m Mid-IR Range for Characterization of Protein Structure

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## ABSTRACT

Infrared spectroscopy has been an important tool to characterize secondary structure of proteins for decades. Recent advances in the miniaturization of devices for biochemical assays have embraced poly(dimethylsiloxane) as material. However, the Infrared transmission characteristics of PDMS, especially in the form of sub-mm film, are not well understood. This hampers utilization of microdevices for protein optical identification.

This paper characterizes mid-infrared transmission of Dow Corning Sylgard 184 using Fourier transform infrared spectrometer. Effects of various fabrication parameters are considered, particularly the mixing ratio of base to curing agent of the pre-polymer. For typical mixing ratio of 10:1, spectral results showed two viable transmission bands with transmittance above 50%: 2500-2194  $\text{cm}^{-1}$  and 2122-1980  $\text{cm}^{-1}$ , where the former band exhibits higher and near-constant transmittance. The transmittance is found to depend strongly on the mixing ratio; lower mixing ratio results in higher transmittance. Maximum transmittance of about 95% is found between 2490-2231  $\text{cm}^{-1}$  with mixing ratio of 8:1. This wavenumbers range appears promising to characterize IR properties of suitable biomolecules using PDMS-based microdevices.

**Keywords:** PDMS (polydimethylsiloxane), transmission spectrum, Fourier transform-infrared (FT-IR) spectroscopy, protein secondary structures, protein characterization

## 1 INTRODUCTION

Micro total analysis system has emerged as a technology platform to shrink analysis tools from a conventional laboratory onto an integrated microfabricated device. The fabrication material of choice is predominantly the elastomer PDMS[1]. Some advantages of PDMS include rapid prototyping, bio-compatibility, non-toxic, and low autofluorescence under laser irradiation[2] and used as sorbent for solid-phase microextraction[3]. PDMS has also been used to be the coating of fiber sensor[4].

Infrared (IR) spectroscopy has been applied in characterizing PDMS properties, such as crystallization[5], Si-H formation in microwave plasma modification[6], chain length[7], and surface properties after surface treatment[8] and even in quantifying PDMS in foods[9].

Mid-infrared (mid-IR) region is of high interest, since absorption peaks of most protein secondary structures lie in this range[10]. Hence, the transmission spectrum of PDMS over this range is required prior to usage of PDMS fabricated microdevices in spectroscopic characterization of proteins. In this regard, specific application determines which spectral range to be studied and transmittance, rather than conventional absorbance, should take preference.

The mid-IR spectra of Dow Corning Sylgard 184, a predominant kind of poly(dimethylsiloxane) in making microfluidic chip, were demonstrated[8, 11], while other kinds of PDMS are also measured[3, 5, 6, 9]. Results in the literature thus far are not sufficient to provide decisive information required for spectroscopic characterization of proteins. Regarding the physical state and composition of PDMS, some are in fluid phase, some in solid mixture, such as fabric and filter paper, and the other from various brands. Commercial secret often hinders exposure of precise chemical composition necessary for progress. These factors aggravated the difficulty to compare among states and products, especially in an attempt to conduct quantitative analysis. Hence, generalization of prior art is limited.

This paper aims to characterize mid-IR transmission of PDMS using FT-IR spectroscopy, with the goal of identifying viable wavelength regions for protein characterization. Various fabrication factors are considered, particularly the mixing ratio of base to curing agent the polymer. Results of this work should be useful in application of PDMS-based microdevices in spectroscopic characterization of proteins.

## 2 EXPERIMENT

This section covers experiment setup and the design of experiment. It begins with IR transmission spectroscopy configuration and ends with experimental factors and levels for each factor we selected.

### 2.1 Spectral Measurement

Experiments were conducted using PDMS film due to its wide acceptance as material in microfluidic devices. Standard procedure[12] for preparation was adopted. The film was mounting on a paperboard with a hole, letting the IR beam pass through then analyzed by an IR spectrometer (Nicolet Nexus 870). Spectrometers use various principles

to do analysis, such as FT-IR, Raman, attenuated internal reflection. Among them, FT-IR transmission spectroscopy has the simplest configuration, as shown in Fig. 1 (a). Broadband IR beam transmits through the PDMS film in a detector. Fig. 1 (b) shows the photo of PDMS film on a paperboard covering the hole on the board, mounted in the spectrometer. The band location of amide I band of protein secondary structures ( $1700-1620\text{ cm}^{-1}$ )[10] is the main focus in determining measurement range, covering  $2500-1500\text{ cm}^{-1}$ . Since water is the dominant source of interference, the cover was kept closed during measurement and dry air was directed into the instrument in order to purge the water vapor.

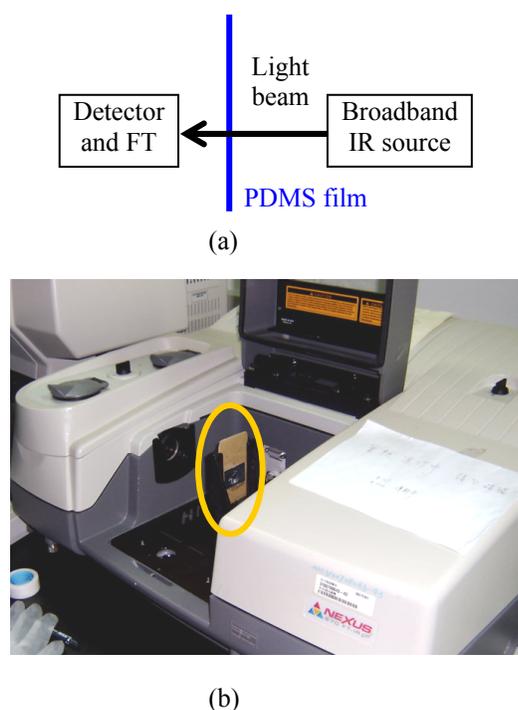


Figure 1: Experimental setup. (a) Configuration of transmission spectroscopy. (b) The transmission spectrum of PDMS was measured by Nicolet Nexus 870 FT-IR spectrometer. The PDMS film was located as indicated.

## 2.2 Experimental Variables

Two design factors are selected in the fabrication process of PDMS film, including the mixing ratio of the two parts in Sylgard 184, and the rotation rate of spin coating. The mixing ratio of two parts causes the composition of PDMS to change. The spin rate of spin coating determines the thickness of PDMS thickness. Actually, both the mixing ratio and angular frequency of spin affects the film thickness, which is assumed to be one of the major factors on transmittance. The thickness decreases as mixing ratio goes down and spin rate goes up.

Regarding spectral measurement, there are three design factors: purge time, number of scan, and resolution of spectrum. Purge time is critical to reduce the affect of water vapor. Both number of scan and resolution can be adjusted in the software to control Nexus 870, related to the quality of spectra.

All five factors are summarized in Table 1. Each factors has two levels besides mid-level. If we need to go through all the combinations, there are  $2^7=128$  cases to be studied! To restrict total experiment number within twenty,  $2^{7-4}$  fractional factorial design[13] is adapted to gauge the effects of factors. This technique ensures us to make the most of the experimental results and to find the optimal experimental settings efficiently.

Variables	Unit	Range (high, mid, low)
• The mixing ratio of base to curing agent		12, 10, 8
• The angular frequency of spin coating	RPM	1500, 1000, 500
• Purge time	Min.	20, 15, 10
• Number of scan		192, 128, 64
• Resolution of spectrum		8, 4, 1

Table 1: Experimental factors– the first two fabrication parameters and last three measurement parameters.

The maximum transmittance of each spectrum is the response. A spectrum is reduced to one representing parameter. The final part of next section is to link key factors to the maximum transmittance by a regression model.

## 3 RESULTS AND DISCUSSION

Results are discussed in two aspects: (1) PDMS transmission spectra over various experimental factors and (2) the relationship between maximum transmittance and the factors. The first part includes spectra, comparison to previous works, and interpretation of the transmission valley, where strong absorption occurs. The second part reports the regression model linking maximum transmittance and mixing ratio.

### 3.1 Spectra

Figure 2 presents representative results of transmission spectra for different mixing ratio of base to curing agent tested. Although other factors are varied, mixing ratio is proved to be the only significant factor on the spectral response. Two viable transmission bands exist with transmittance above 50%:  $2500-2194\text{ cm}^{-1}$  and  $2122-1980\text{ cm}^{-1}$ . The former band exhibits more desirable characteristics; the maximum transmittance occurs in this

band with a near-constant transmittance. Within this band – from 2490 to 2231  $\text{cm}^{-1}$  – the transmittance is 62% for typical mixing ratio of 10:1, and over 95% for mixing ratio of 8:1.

The overall trend of the spectra results agrees with the literature. Previous works[3, 5, 6, 9, 11] exhibit similar qualitative dependence of spectral characteristics on wavenumbers. Fig. 2, however, is in better agreement with some[3, 5] than others.

In the application of PDMS as the wall material for spectroscopic measurement, IR beam needs to pass through PDMS wall twice. Preferably, transmittance greater than 70% will be needed ( $0.7^2 \approx 0.5$ ). Hence, Fig. 2 suggests that Sylgard 184 appears inappropriate for amide I band (1700-1620  $\text{cm}^{-1}$ )[10] in spectra of Sylgard 184. However, the transmission band 2490-2231  $\text{cm}^{-1}$  is ready for other applications.

The increase in transmittance with decreasing mixing ratio might be due to change in Young's modulus. Since fabrication with lower mixing ratio results in a PDMS with higher Young's modulus, Fig. 2 seems to suggest that Young's modulus plays a vital role here. This is further supported by the fact that over the range of mixing ratio from 8:1 to 12:1, the Young's modulus changes by about 35-40% where the density changes by only 1%[14]. Further investigation, particularly on the structural detail, is needed to quantify this effect.

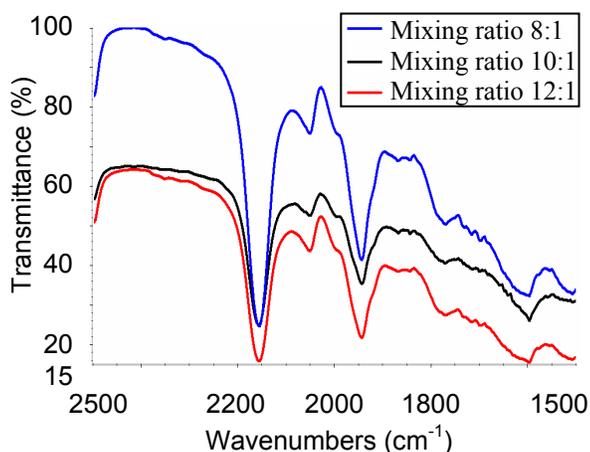


Figure 2: The mid-IR transmission spectra of the PDMS (Dow Corning Sylgard 184) for 3 mixing ratios. The wavenumbers range of 2500-2194  $\text{cm}^{-1}$  spectrum exhibits more desirable characteristics; the maximum transmittance occurs in this band with a near-constant transmittance.

### 3.2 Comparison with Other Works

Some measured spectra of PDMS in the form of fluid[9] or solid film from Gaboury '91[6], Merschman '98[3], Bokobza '00[5], and Mata '05[11]. The last four are used to compare with the present result, in the 'Chen' column

(Table 2). Most of the previous works demonstrated absorption spectra, and absorption peak is corresponding to valley in transmission spectra. One thing to be noticed is that the absorption here is more band-like, instead of sharp peaks in atomic absorption spectroscopy.

In all the five cases listed below, there are common bands in 2160-2150  $\text{cm}^{-1}$ , 1950-1942  $\text{cm}^{-1}$ , and around 1600  $\text{cm}^{-1}$ . For bands not in individual works, there are 1510-1500  $\text{cm}^{-1}$  appears in both Gaboury and Chen, along with 2025  $\text{cm}^{-1}$  and 1850  $\text{cm}^{-1}$  in Gaboury. The variation in band center wavenumbers in each band can be due to either the different formulas of different PDMS products or misinterpreting the peak locations of previous works, from their spectra often spanning wider than 2500-1500  $\text{cm}^{-1}$ . The former causes the wavenumber shift greater than 10  $\text{cm}^{-1}$ [15], the latter a few  $\text{cm}^{-1}$ .

	Gaboury	Merschman	Bokobza	Mata	Chen
2160				★	
2156					★
2050		★	★		
2025	★				
1950		★	★	★	
1942					★
1850	★				
1600		★	★	★	
1599					★
1509					★
1500	★				

Table 2: Comparison of IR wavenumbers ( $\text{cm}^{-1}$ ) studied by various authors.

### 3.3 Bands Assignments

PDMS has Si-Methyl (SiMe) group and siloxane (SiOSi). Hence, we expect to see the correspondent absorption bands. Within the measured spectral range, there are none of the bands of these two structures[15], while the intense valley with center frequency 2156  $\text{cm}^{-1}$  is observed. This valley is the sign of SiH[15]. This band was found in plasma treated PDMS[6]. The 2156  $\text{cm}^{-1}$  isn't expected for the PDMS in this work has not been plasma treated. Along with Mata's result[11], it seems that Sylgard 184 has SiH group. For the rest bands centered at 1942, 1599, and 1509  $\text{cm}^{-1}$ , it is not clear which chemical structures account for them. Finally, we focus to evaluate PDMS as a window material for protein identification in amide I band region, instead of characterizing PDMS, so the bands of SiMe and SiOSi, out of the range of the measurement range, are ignored.

### 3.4 Maximum Transmittance

The maximum transmittance has strong dependence, among other factors as shown in the Table 1, on the mixing ratio of the base to the curing agent of PDMS pre-polymer. Surprisingly, thickness of film, controlled by spin rate of coating, doesn't have much effect on transmittance. Thus, a regression model with mixing ratio is sufficient to predict the amount of maximum transmittance in each spectrum.

Figure 3 shows that the maximum transmittance of PDMS is between 66.0% and 96.5% with mixing ratio of the two parts varied from 8:1 to 12:1. The regression model is noted in legend, where M is maximum transmittance, R mixing ratio of the base to the curing agent of PDMS pre-polymer. All the quantities above are dimensionless.

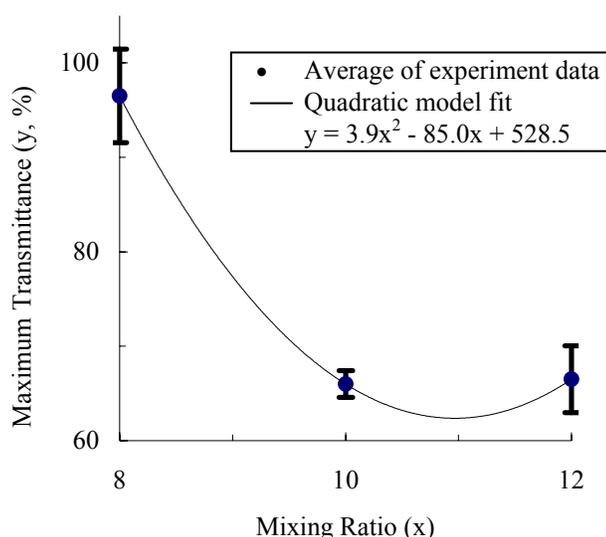


Figure 3: The effect of mixing ratio of base to curing agent on maximum transmission rate. Quadratic regression model is used. Results show maximum transmission rate is strongly dependent on the mixing ratio. (Note that for each mixing ratio, there are two data points)

The transmittance is comparative when mixing ratio is ten or twelve, but at mixing ratio eight, transmittance is about 1.5 times as that at other two mixing ratio. The variation of maximum transmittance is the lowest among the three mixing ratio. This suggests conventional mixing ratio produces the most stable spectroscopic properties.

Figure 3 demonstrates that polymeric composition plays an important role in mid-IR transmission characteristic. Hence, PDMS material can be tuned to provide necessary characteristic of window material in the wavenumbers range of 2490-2231  $\text{cm}^{-1}$ . This transmission band might be used to identify certain biomolecules.

### 4 CONCLUSION

The Dow Corning Sylgard 184 film with typical mixing ratio, there are two viable transmission bands with transmittance over 50%: 2500-2194  $\text{cm}^{-1}$  and 2122-1980  $\text{cm}^{-1}$ . The former band exhibits higher and near-constant transmittance. The transmittance is found to depend strongly on the mixing ratio; lower mixing ratio results in higher transmittance. This dependence is believed to be linked to the difference in Young's modulus. Maximum transmittance of about 95% is found between 2490-2231  $\text{cm}^{-1}$  with mixing ratio of 8:1. This wavenumbers range appears promising to characterize IR properties of suitable biomolecules using PDMS-based microdevices.

### ACKNOWLEDGEMENT

The financial help of the National Science Council of the Republic of China is gratefully appreciated.

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