Wettability and surface energy of parylene F

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Abstract

Parylenes are barrier materials employed as protective layers. However, many parylenes are unsuitable for applications under harsh conditions. A new material, parylene F, demonstrates considerable potential for a wide range of applications due to its high temperature and UV resistance. For the first time, the wettability and surface energy of parylene F were investigated to determine the feasibility of parylene F as an alternative to the commonly employed parylene C. The results show that parylene F has a hydrophobic surface with a water contact angle of 109.63 ± 0.85°. We found that 3.5 µl probe liquid is an optimal value for the contact angle measurement of parylene F. Moreover, we found that the Owens–Wendt–Kaelble and the Lifshitz–van der Waals/acid–base approaches are unsuitable for determining the surface energy of parylene
F, whereas an approach based on the limitless liquid–solid interface wetting system is compatible. Furthermore, the results show that parylene F has a surface energy of 39.05 ± 3.94 mJ/m². Considering the improved resistance, relatively low cost, and the desirable properties, parylene F can replace parylene C for applications under harsh conditions.

Keywords:
Parylene F; Contact angle; Surface energy; Interface; Surface

1. Introduction

Parylene has been widely used as a superior protection layer in a variety of applications, including printed circuit boards (PCBs), electronic components, micro-electro-mechanical systems (MEMS), sensors, implanted electronic devices (IEDs), and medical devices [1-7]. There are five members in the parylene family, namely, parylene C, parylene D, parylene N, parylene F (PF), and parylene HT [8]. Among these, parylene C is widely used; however, parylene C (as well as parylene D and parylene N) cannot be used in high temperature environments and show poor ultraviolet (UV) resistance, indicating it cannot be used in some fields. For example, parylene C cannot endure traditional high temperature and UV disinfection procedures in medical applications. New materials, such as PF and parylene HT overcome the above shortcomings, exhibiting high temperature and UV resistance [8]. Of these two materials, PF is significantly cheaper than parylene HT. Therefore, PF is a promising barrier material for the future because it has high temperature and UV resistance, and is a low-cost material. For practical applications, wettability and surface energy of barrier materials are crucial factors [9-11].

To our knowledge, no literature has reported on the wettability and surface energy of PF; therefore, it is essential that these two parameters be investigated.
Chandraprakash Chindam et al. [9] determined the surface energy of parylene C by applying the Li–Neumann theory [12], which was consequently questioned by M. Golda-Cepa et al. [13] In their comments, they recommend the Owens–Wendt–Kaelble approach [14] for calculating the surface energy of crystalline–amorphous composites [15], such as parylene C. In this study, the surface energy of PF was initially calculated via the Owens–Wendt–Kaelble approach, as PF is a similar material to parylene C. Thereafter, it was calculated by the Lifshitz–van der Waals/acid–base approach [16] and the approach based on the limitless liquid–solid interface wetting system [17, 18]. Because wettability and surface energy are determined by contact angle measurements [19, 20] and questions persist about the optimal drop size [9, 13, 21], the effect of the drop size of probe liquids on the contact angle was considered. For this study, PF was coated on a polydimethylsiloxane (PDMS) substrate through the chemical vapor deposition (CVD) method (Fig. 1a), and the contact angles were measured by the custom-designed contact angle measuring system (Fig. 1b). The effect of the drop size on the contact angle can provide a comparative parameter, thus contributing new information to the literature. Furthermore, the wettability and surface energy of PF are expected to provide a reference for determining its potential applications.

Fig. 1. Schematic illustration of (a) the coating process in which PF is deposited on a PDMS substrate through the CVD method, and (b) the custom-designed contact angle measuring system.
2. Materials and methods

2.1 Preparation of PDMS substrate

Firstly, 1 g curing agent was added to 10 g silicone (Dow Corning® 184, Dow Inc., USA) under mechanical agitation for 2 h at 500 rpm. Subsequently, the mixture was placed in a vacuum chamber for defoaming until no bubbles overflowed completely. The mixture was then poured into a custom-designed acrylic mold (groove depth :1 mm) and cured at room temperature for 48 h to obtain a PDMS substrate with 1 mm thickness.

2.2 Deposition of PF

The PF dimer (Suzhou Parylene Materials Co., LTD., China) was placed in the vaporizer of the parylene coating equipment (DYL4570, Paihua Coating Co., LTD., China) at 150 °C, forming the dimer gas. Next, the dimer gas was converted to monomer gas in the pyrolysis chamber at 650 °C. Finally, the PDMS substrate was coated in the deposition chamber at room temperature, and the thickness of the PF coating was controlled at 5 μm.

2.3 Characterization

Raman spectra of the samples were measured by a Raman spectrometer (2500i, Princeton Instrument, USA) with a He-Ne laser with 632.8 nm wavelength. Surface topography and roughness were determined by atomic force microscopy (AFM, Cypher ES, Oxford Instruments, UK).

2.4 Contact angle measurement

For contact angle measurements, the PF samples were treated with ultrasonic cleaning for 10 min, then the samples were dried and measured. Deionized (DI) water and α-bromonaphthalene (Wuxi Zhangwang Chemical Co., LTD., China) were selected as probe liquids to study the effect of drop size on the contact angle. In further studies, contact
angles of the PF samples were also analyzed with glycerol (Tianjin Zhiyuan Chemical Co., LTD., China). All measurements were performed under a custom-designed contact angle measuring system, as reported by Lei Jiang et al. [22], and each sample was measured in triplicate to minimize experimental error. The images of the contact angles were analyzed by ImageJ software (V1.47, Wayne S. Rasband, USA) with a drop analysis plugin, through the LBADSA method [23].

3. Results and discussion

Raman spectroscopy was performed to identify the chemical composition of the PDMS and PF surfaces. The black curve in Fig. 2a indicates that it is a typical Raman spectrum of PDMS [24]. The Raman spectrum of PF (red line) shows three new peaks (marked with arrows), which are the aliphatic C–C stretch (999 cm\(^{-1}\)), C–F stretching (1341 cm\(^{-1}\)), and the aromatic C–C stretch (1656 cm\(^{-1}\)). These results indicate that PF was successfully deposited on the PDMS surface. Surface topography and roughness of PF are shown in Fig. 2b. It is evident that PF features an undulant surface, and the roughness, \(R_q\), is 14.71 ± 1.92 nm. This roughness can increase the contact angle of PF, as a rough surface can trap more air than a flat surface [25, 26].

![Raman spectra of PDMS and PF. (b) AFM measurement results of PF.](image-url)
DI water and α-bromonaphthalene were employed to show the effect of drop size on the contact angle of PF. The results in Fig. 3a reveal that the PF surface exhibits hydrophobicity, and the contact angle increases with the drop volume of DI water. In contrast, the contact angle decreases with the drop volume of α-bromonaphthalene. These trends can be explained by the line tension effect [27]. Because the drop volume affects contact angles significantly, obtaining an optimal value is necessary. The mean values of the contact angles for DI water and α-bromonaphthalene are 109.1° and 42.67°, respectively, according to Figs. 3a and 3b. In addition, the contact angle values with 3.5 μl of probe liquids are the closest to the mean value for the data. Therefore, 3.5 μl of probe liquid is an optimal value for the contact angle measurement of PF.

![Graph](image)

**Fig. 3.** Effect of drop size on contact angle with (a) DI water, and (b) α-bromonaphthalene.

In the Owens–Wendt–Kaelble approach for estimation of surface energy, the equations are as follows:

\[ \gamma_{sv} = \gamma_{lv}^d + \gamma_{lv}^h \]  
(1)

\[ \gamma_{lv} (1 + \cos \theta) = 2 \sqrt{\gamma_{sv}^d \gamma_{lv}^d} + 2 \sqrt{\gamma_{sv}^h \gamma_{lv}^h} \]  
(2)

where \( \gamma_{lv} \) and \( \gamma_{sv} \) represent surface energies of the liquid and solid, and superscripts \( d \) and \( h \) refer to the dispersion force components and hydrogen bonding, respectively; \( \theta \) is the
According to equation (2), two liquids are necessary to calculate the surface energy of a solid. The $\gamma_l$, $\gamma_{lv}^d$, and $\gamma_{lv}^a$ of DI water and $\alpha$-bromonaphthalene can be obtained from the literature [28]. The mean contact angle values of DI water and $\alpha$-bromonaphthalene with droplets of 3.5 $\mu$l are 109.63° and 43.19°, respectively. These values were substituted in equation (2), obtaining two equations with two unknowns. However, we found that the two equations have no solution, thus indicating that the Owens–Wendt–Kaelble approach is unsuitable for calculating the surface energy of PF.

Further, the Lifshitz–van der Waals/acid–base approach was employed to calculate the surface energy of PF. This approach involves the following equations:

$$\gamma_{sv} = \gamma_{lv}^{ LW} + 2\sqrt{\gamma_{sv}^+ \gamma_{sv}^-}$$  \hspace{1cm} (3)$$

$$\gamma_{lv} (1 + \cos \theta) = 2(\sqrt{\gamma_{sv}^{ LW} \gamma_{lv}^{ LW}} + \sqrt{\gamma_{sv}^+ \gamma_{sv}^+} + \sqrt{\gamma_{sv}^- \gamma_{sv}^-})$$  \hspace{1cm} (4)$$

where $\gamma_{lv}$ and $\gamma_{sv}$ represent surface energies of the liquid and solid, respectively; $\gamma_{sv}^{ LW}$ is the Lifshitz–van der Waals component; and $\gamma_{sv}^+$ and $\gamma_{sv}^-$ are the components of the electron-acceptor and the electron-donor, respectively.

Thus, if the $\gamma_{lv}^{ LW}$, $\gamma_{lv}^+$, and $\gamma_{lv}^-$ of three different liquids (of which two must be polar) were known, the $\gamma_{sv}^{ LW}$, $\gamma_{sv}^+$, and $\gamma_{sv}^-$ of a solid can be determined. In our measurement, three probe liquids were employed, and two of them are polar (Table 1). Employing the values of $\gamma_{lv}^{ LW}$, $\gamma_{lv}^+$, $\gamma_{lv}^-$, [28] and the mean contact angle of the three liquids (Table 1), the surface energy of PF was calculated. However, as we found that the three equations have no solutions, we determined that this approach is incompatible for surface energy estimation of PF.

Table 1. Contact angle results for probe liquids with a drop volume of 3.5 $\mu$l.
Since both the Owens–Wendt–Kaelble and the Lifshitz–van der Waals/acid–base approaches are empirical formulas, obtaining the above erroneous results is to be expected [29]. To achieve accurate results, different semi-empirical approaches based on physical basis were developed (e.g., the Berthelot rule [29, 30]). A physics-based approach was proposed by Dingyi Zhu et al. on the basis of the limitless liquid-solid interface wetting system [17, 18], and involves the following equations:

\[
\gamma_{sl} = \frac{\gamma_{lg}}{2} (\sqrt{1 + \sin^2 \theta} - \cos \theta) \\
\gamma_{sg} = \frac{\gamma_{lg}}{2} (\sqrt{1 + \sin^2 \theta} + \cos \theta)
\]

(5) \hspace{1cm} (6)

where \(\gamma_{lg}\) and \(\gamma_{sg}\) are the surface tensions (surface energies) of the liquid and solid, respectively; \(\gamma_{sl}\) is the surface tension of solid–liquid interface; \(\theta\) is the contact angle.

According to the above equations, \(\gamma_{sg}\) and \(\gamma_{sl}\) can be obtained by using only one liquid. Employing the values of \(\gamma_{lg}\) [28] and the mean contact angle of each liquid, three sets of data were obtained (Table 2). The resulting surface energies were 37.78 mJ/m\(^2\) (DI water), 43.48 mJ/m\(^2\) (\(\alpha\)-bromonaphthalene), and 35.91 mJ/m\(^2\) (glycerol). Therefore, the surface energy of PF was determined to be 39.05 \(\pm\) 3.94 mJ/m\(^2\), which is similar to the surface energy of parylene C [13].

Table 2. Crucial data from the literature [28] and the present study.

| Probe liquid       | Liquid type | Contact angle (degrees) |
|--------------------|-------------|-------------------------|
| DI water           | Polar       | 109.63 ± 0.85           |
| \(\alpha\)-bromonaphthalene | Non-polar   | 43.19 ± 3.04            |
| Glycerol           | Polar       | 105.46 ± 0.22           |
|                | 109.63 | 72.8  | 37.78 |
|----------------|--------|-------|-------|
| α-bromonaphthalene | 43.19  | 44.8  | 43.48 |
| Glycerol        | 105.46 | 64    | 35.91 |

4. Conclusions

Based on this study, we recommend using 3.5 μl of drop volume for contact angle measurement of PF. PF exhibits a hydrophobic surface with a water contact angle of 109.63 ± 0.85°. Moreover, the Owens–Wendt–Kaelble and the Lifshitz–van der Waals/acid–base approaches are unsuitable for determining the surface energy of PF, whereas the formula based on the limitless liquid–solid interface wetting system is compatible with this type of material. The results show that the PF coating has a surface energy of 39.05 ± 3.94 mJ/m², which is similar to the surface energy of parylene C. In addition, PF exhibits high temperature and UV resistance. These properties indicate that PF can replace parylene C for applications in harsh environments.

Declaration of interest

None.

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