Measuring the adhesion strength of a thin film to a substrate by centrifugation

Liang Wu, Hui Feng, Dameng Guo and Bo Zheng*

This paper describes a centrifugation-based method of quantifying the adhesion strength of a thin film to a substrate. Normally thin films possess extremely small mass, and the centrifugal force cannot dislodge the thin films from the substrates even with the most powerful centrifuge. To solve this problem, we synthesized hydrogel particles on top of the thin film. The hydrogel particle was bound to the thin film through covalent bonds. The centrifugal force was therefore substantially increased, and the thin film could be dislodged from the substrate together with the hydrogel particles in a tabletop centrifuge. We validated this method by measuring the adhesion strength of adhesive tape to Teflon and made comparison with the pull-off test result. We applied this method to measuring the adhesion strength of polydopamine (PDA) thin film to Teflon, which has not yet been characterized. The measurement of the PDA adhesion strength would help study the mechanism of PDA adhesion and develop stronger PDA adhesive. The centrifugation-based method is simple and applicable to a broad range of thin films and substrates.

Introduction

Various methods have been developed to measure the adhesion strength of a film to a substrate, such as pull-off tests, acoustic imaging, laser techniques, and scratch tests.[1, 2] These methods require specialized and often costly equipments. Pull-off tests use adhesive to adhere a pull stub to the film and the substrate, respectively, and then measure the force of pulling off the film.[3, 4] But the measurement result suffers from uneven adhesive and adhesive failure.[5] In addition, the adhesive or solvent may penetrate the thin film and affect the film-substrate interface[1]. Acoustic imaging utilizes an acoustic plane wave to obtain a micrograph of adhesion surface to study the adhesion. This method is a semi-quantitative characterization method.[6, 7] Laser techniques utilize laser impingement onto the film or substrate to detect or produce dislodgment, a nondestructive method.[8, 9] The main limitation here is the film's thickness, which needs to be in micrometers to millimeters.[1, 10, 11] Typically the pulsed laser with the duration of a few nanoseconds can vaporize a thin film of less than 1 micron of thickness.[10] So this method is not applicable for the thin film in nanometers thickness. Scratch test is the most popular method for measuring the adhesion strength and is widely used for the adhesion strength measurement of hard PVD and CVD films on steels and cemented carbides.[1, 12-14] However, the scratch test is easily affected by factors including film thickness, surface roughness, film hardness, friction between the film and the indenter. Normally micrometers' thickness of the film is needed in the scratch test.[1, 14-17] These factors indicate that scratch test is not suitable for measuring the adhesion strength of soft thin film with nanometers' thickness.

Herein, we developed a simple method to measure the adhesion strength of a thin film to a substrate. The method is based on the principle for measuring cell adhesion strength on substrates.[18] In the method, substrate together with the thin film is placed in a centrifuge, and the substrate and the thin film are parallel to the centrifugal axis. In the centrifugal field, the thin film will be dislodged from the substrate when the centrifugal force is equal to the adhesion strength. By calculating the centrifugal force when the thin film was dislodged, we can get the adhesion strength of the thin film to the substrate. However, different from measuring cell adhesion strength, the thin film with an extremely small mass cannot generate large enough centrifugal force. To overcome this difficulty, we synthesized hydrogel particles to covalently bind the thin film to increase the centrifugal force. As a result, the thin film with the hydrogel particle can generate sufficient centrifugal force leading to dislodgment in a tabletop centrifuge.

In this work, first we measured the adhesion strength of adhesive tape to Teflon by adhering iron sheet to adhesive tape to increase the centrifugal force. Comparison with the pull-off test validated this centrifugation-based method. Then we applied this centrifugation-based method to measuring the adhesion strength of polydopamine (PDA) thin film to Teflon, which hasn't been characterized yet. PDA is a unique material which can adhere strongly to many different types of substrates.[19] The polymerization process of dopamine involves the oxidation of dopamine to 5,6-dihydroxyindole (DHI), followed by sequential formation of covalent bonds between DHI and dopamine monomers. Self-assembly of dopamine and DHI through hydrogen bond and π-stacking also takes place in the polymerization process.[20] The detailed binding mechanism of PDA is still under investigation. The adhesion strength of PDA to various substrates is also uncharacterized. PDA thin film deposited on Teflon substrate is soft[21] and thin, only in several nanometers.[19] The common methods mentioned above are not applicable for measuring the adhesion strength of such thin PDA film to Teflon. Herein, we synthesized polyacrylamide hydrogel to covalently bind PDA thin film[22] and successfully measured the adhesion strength of PDA thin film to Teflon by centrifugation.

Experimental

Materials: Dopamine hydrochloride (Sigma- Aldrich), fluorinated ethylene propylene (FEP) substrates (Shanghai Yuyisong Plastic Products), N,N'-methylene bis(acrylamide) (NMBA) and acrylamide (Farco International), N,N,N',N'- tetramethylethylenediamine (TEMED) (Acros Organics), ammonium peroxodisulfate (APS) (Beyotime), tris hydrochloride (International Laboratory USA).

Preparation of PDA and hydrogel particle array: In the experiment, 2 mg/mL dopamine in Tris buffer (pH=8.5)[19] was used to deposit spots array of PDA thin film on the FEP substrate. Each spot of PDA thin film was generated by depositing 10 μL dopamine solution on the FEP substrate for 1.5 h. After removing the rest of dopamine solution and washing FEP substrates with DI water, we flowed the hydrogel precursor over the surface of the FEP substrate. The precursor contained acrylamide (0.75 g/mL), NMBA (22.5 mg/mL) and APS (7.5 mg/mL) in DI water. The precursor formed droplets only on the PDA thin films. The hydrogel particles were formed in 30 s after the addition of TEMED into the precursor.

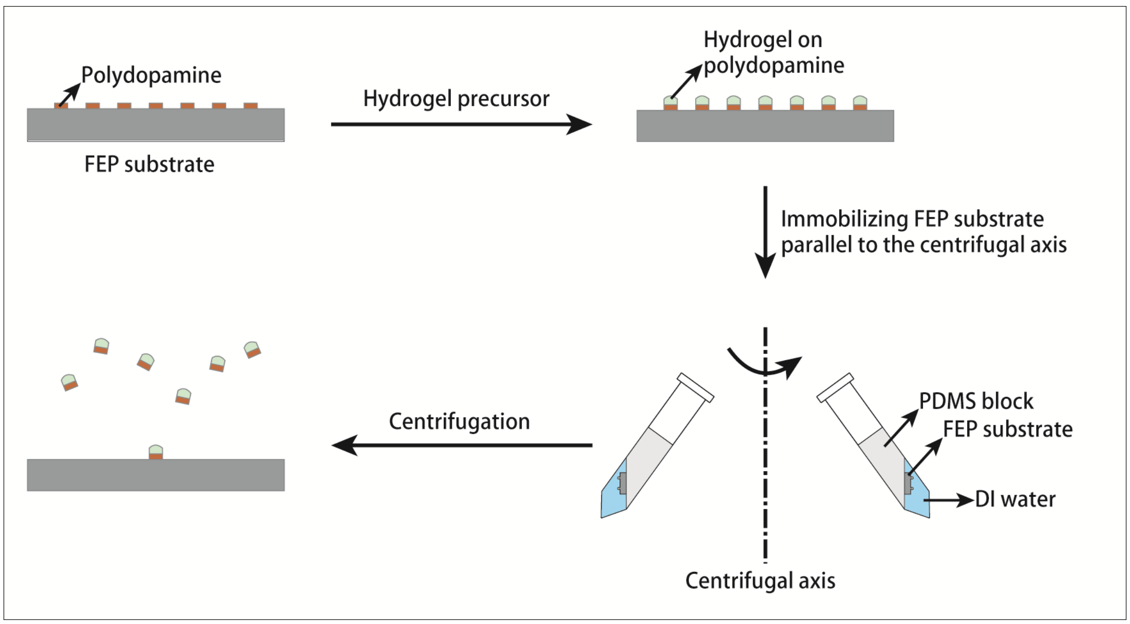

Fig. 1 Scheme of the adhesion strength measurement process.

Centrifugation measurement: The adhesion strength measurement process was shown in Fig. 1. After the preparation of PDA film and hydrogel particle array, the FEP substrate was immobilized on a PDMS block. The PDMS block would keep the FEP substrate parallel to the centrifugal axis when loaded into a centrifuge tube and then into a centrifuge. The centrifuge tube was filled with DI water and underwent centrifugation to dislodge PDA from the FEP substrate. The fabrication of the PDMS block was as follows. Angle β between centrifuge tube in the centrifuge and the horizontal plane was measured first. The centrifuge tube containing uncured PDMS, i.e., mixture of Sylgard 184 (Dow Corning) at the base-to-curing agent ratio of 10:1, was then put into the 65°C oven in a tilt angle 90^{o}-β for two hours and the PDMS block was formed. When we loaded the PDMS block inversely in a new centrifuge tube and then into the centrifuge, the bottom surface of the PDMS block would be parallel to the centrifugal axis (Fig. 1). In the validation experiment of measuring the adhesive tape on the FEP substrate, the adhesive tape had round shape with the diameter of 6.1 mm. Iron sheet with the mass 0.2616 g was attached to each tape. After immobilizing the FEP substrate on the PDMS block, centrifugation measurement was carried out in the centrifuge tube filled with air.

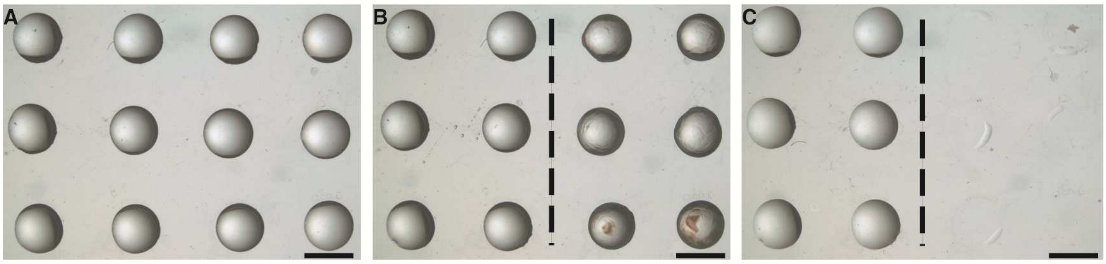

Fig. 2 Spots array of PDA thin film formed on the FEP substrate and dislodged from the FEP substrate. (A) Water droplets formed on the spots array of PDA thin film on the FEP substrate. (B) Hydrogel particles were synthesized on the right half of the spots array of PDA thin film on the FEP substrate while water droplets deposited on the left half. The two halves were separated by the black dashed line. (C) With the dislodging of hydrogel particles after centrifugation, no water droplets formed on the right half of the FEP substrate, indicating the dislodging of PDA thin films from the FEP substrate on the right half. Scale bars, 3 mm.

Results and discussion

The centrifugation-based method was first validated by measuring the adhesion strength of double-sided adhesive tape to the FEP substrate. Most adhesive tapes were dislodged from the FEP substrate in the range from 1300 rpm to 1500 rpm (Fig. S1). The adhesion strength is calculated as follows: [18]

$$F_D = m \times \mathrm{RCF} \quad (1)$$

$$\mathrm{RCF} = 1.118 \times 10^{-5} \times n^2 \times r_{ac} \quad (2)$$

In the equations, F_D is the dislodgment force of each adhesive tape, RCF is the relative centrifugal force, and n is the centrifugal speed in rpm. r_{ac} is the average centrifugal radius from the adhesive tape to the centrifugal axis. m is the total mass of the adhesive tape and the iron sheet. Using the two boundary centrifugation values 1300 rpm and 1500 rpm, the adhesion strength of adhesive tape to the FEP substrate was determined to be in the range from 12.8 kPa to 17.0 kPa. This result was well consistent with the result from the pull-off test, which was 14.8±1.4 kPa (Fig. S2).

The effect of the hydrogel particles on the PDA thin films were tested (Fig. 2). First we confirmed the formation of spots array of PDA thin film on the FEP substrate. The deposited PDA thin film was measured by ellipsometry (SC600, Shanghai Sanco Instrument) to be 6.5 nm in thickness and difficult to observe under optical microscope. Here we flowed excess water over the FEP substrate to produce water droplets array on the FEP substrate (Fig. 2A), indicating the successful formation of spots array of PDA thin film on the FEP substrate. Next we identified the role of the hydrogel particles in dislodging of the PDA thin films from the FEP substrate. We synthesized hydrogel particles on the right half of the spots array of PDA thin film on the FEP substrate while no hydrogel particles were on the left half (Fig. 2B). After centrifugation, hydrogel particles were dislodged. To prove the dislodging of the PDA thin films on the right half together with hydrogel particles, we flowed again excess water over the whole FEP substrate. There were no water droplets forming on the right half of the FEP substrate (Fig. 2C), indicating the dislodging of the PDA thin films together with the hydrogel particles from the FEP substrate. In the meanwhile, there were water droplets forming on the left half of the FEP substrate (Fig. 2C), indicating spots array of PDA thin film remained on the left half of the FEP substrate after centrifugation. These results show that the hydrogel particles are essential to the dislodging of PDA thin films from the FEP substrate.

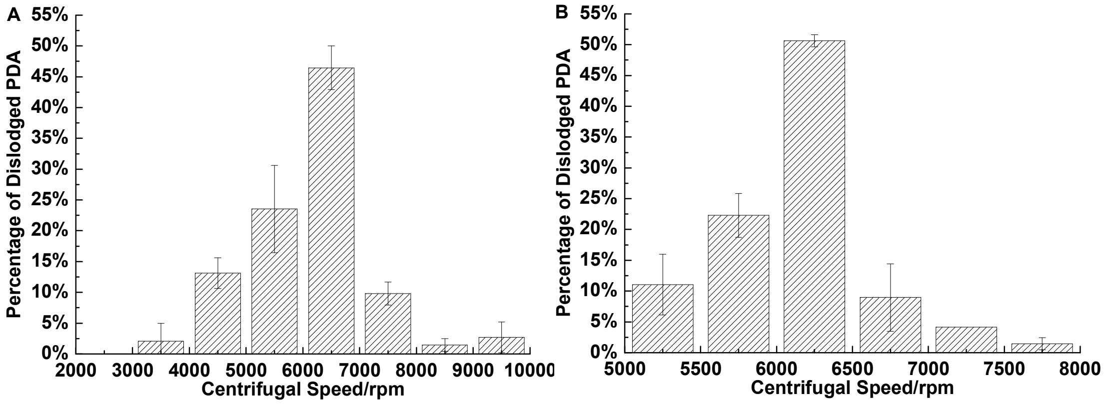

Fig. 3 Statistic curve showing the number of dislodged spots of PDA thin film at different centrifugal speed. (A) Centrifugation underwent 1000 rpm step-increase; (B) Centrifugation underwent 500 rpm step-increase. Each bar here represents the amount of dislodged spots of PDA thin film in percentage within the specified centrifugal speed range.

The number of the dislodged spots of PDA thin film at different centrifugal speed was shown in Fig. 3. Initially we tested a large range of centrifugal speed from 3000 rpm to 10000 rpm, with 1000 rpm step-increase (Fig. 3A). The dislodged spots of PDA thin film were counted from the remaining spots in the substrate, excluding the dislodged spots before. Most spots of PDA thin film were dislodged when centrifugal speed exceeded 5000 rpm. In order to get a more accurate result, we shortened the centrifugal speed range, beginning from 5500 rpm, with 500 rpm step-increase (Fig. 3B). Most spots of PDA thin film, more than 50%, were dislodged when centrifugal speed was 6500 rpm. This result indicates the adhesion strength of PDA to Teflon is in the range from 6000 rpm to 6500 rpm. The adhesion strength of PDA to Teflon is calculated according the Equation (2) and the following Equation (3):[18]

$$F_D = |\rho_{gel} - \rho_{water}| \times V_{gel} \times \mathrm{RCF} \quad (3)$$

In the equation, F_D is the dislodgment force of each spot of PDA thin film. The average centrifugal radius (r_{ac}) from the PDA array to the centrifugal axis is 7.67 cm. The hydrogel particle density (ρ_{gel}) is 1.101 g/cm^3. ρ_{gel} was measured by putting the hydrogel particle into a series of sodium chloride solutions with different concentrations. ρ_{gel} equals to the density of a sodium chloride solution when the hydrogel particle suspends immediately. Because the thickness of PDA film was only several nanometers, PDA's mass and volume were negligible compared to those of the hydrogel particles. We directly used the hydrogel particle's volume to calculate the dislodgment force. The volume of each hydrogel particle (V_{gel}) on each spot of PDA thin film is 4.5±0.1 mm^3. V_{gel} was determined by the mass of the hydrogel particle. We collected 40 hydrogel particles and measured their mass each time. The diameter of deposited spot of PDA thin film (d_{PDA}) on the FEP substrate was 3.00 mm. The adhesion strength was calculated from the dislodgment force divided by surface-to-surface area. Using two boundary values 6000 rpm and 6500 rpm, the adhesion strength was determined to be in the range from 1.9 kPa to 2.3 kPa. This range is in the same order of magnitude as other non-covalent binding strength.[23]

In the centrifugation method, the RCF was inversely proportional to the diameter of deposited spot of PDA thin film, d_{PDA}. This relationship sets a limit of the minimum diameter of deposited spot of PDA thin film, below which the PDA thin film cannot be dislodged even with the hydrogel. The limit is 1.27 mm under our experimental conditions. The limit can be lowered by using more powerful centrifuge or hydrogel with higher density.

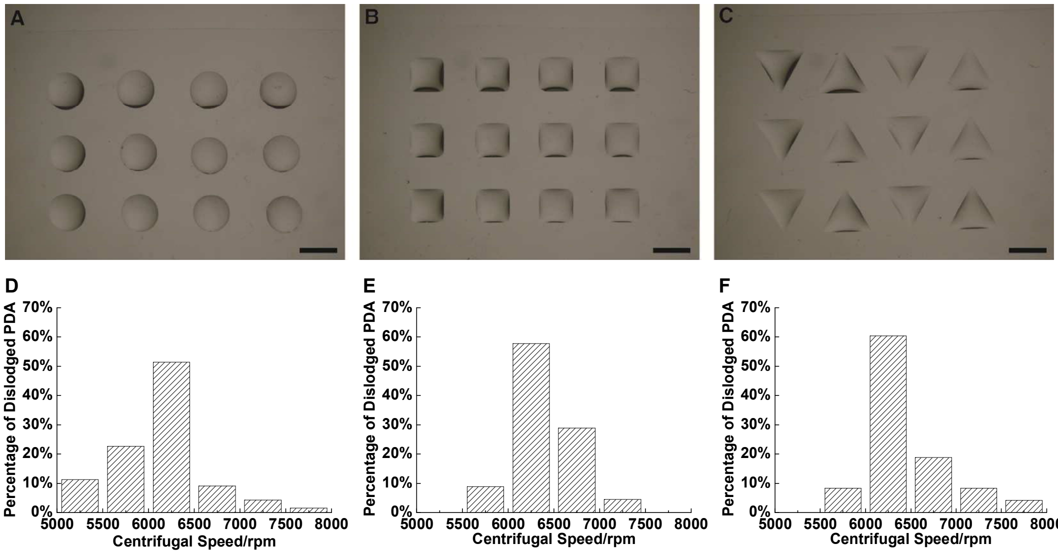

Fig. 4 Arrays of three different shapes of PDA thin film and the corresponding histogram of the dislodgment of the PDA thin film at different centrifugal speed. (A) and (D) Round shape; (B) and (E) Square shape; (C) and (F) Triangle shape. Scale bars: 3 mm.

We tested the effect of several factors, including the shape, the thickness, and the diameter of PDA thin film, and the crosslink density of the hydrogels on the measured adhesion strength. Square and triangle PDA thin film arrays were deposited along with round PDA thin film on the FEP substrate and then underwent centrifugation measurement (Fig. 4). All the PDA thin film arrays with different shapes had the same area. The same dislodgment range from 6000 rpm to 6500 rpm was observed for the three shapes, indicating the centrifugation measurement was not affected by the shape of the PDA thin film. We also found that the centrifugation measurement was unaffected by the PDA film thickness and diameter, and crosslink density of the hydrogel (Fig. S3-S5).

Conclusions

In conclusion, we developed a simple method of measuring the adhesion strength of PDA to Teflon with a tabletop centrifuge. Knowing the adhesion strength could help gain insight of the PDA binding mechanism and help us further develop PDA-based multi-functional coating materials. This method of measuring the adhesion strength of thin films to substrates is compatible with non-uniform film thickness and with soft substrates. This method is especially advantageous to the film in nanometers' thickness.

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Notes and References

Department of Chemistry, The Chinese University of Hong Kong, Hong Kong, China. Fax: 852-2603-5057; Tel: 852-3943-6261; E-mail: bozheng@cuhk.edu.hk

Electronic Supplementary Information (ESI) available: Histograms of the dislodgment of PDA thin film with different PDA thickness, diameter, and different hydrogel crosslink density within the specified centrifugal speed range; Histograms of the dislodgment of double-sided adhesive tape within the specified centrifugal speed range; Scheme of the pull-off test experiment.

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