# Fabrication and Hydrophobic Properties of Diamond-Like Carbon Films on Polyester Surfaces (Post-print)

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## Abstract

Using linear ion beam technology, diamond-like carbon (DLC) films were deposited on PET substrates to analyze the evolution of film structure and properties with ion beam current and investigate the relationship between wetting characteristics and surface morphology, structure, and surface energy. Results demonstrate that DLC films deposited on PET surfaces exhibit typical structural characteristics of amorphous carbon films; with increasing ion beam current, the $sp^2/sp^3$ ratio increases from 0.774 to 1.622, indicating enhanced surface graphitization; the contact angle of modified PET material increases from 63.51° to 103.7°. Further analysis reveals that improved hydrophobic performance is attributed to reduced surface energy, with enhanced surface graphitization and formation of micro-nano structures being the fundamental causes of this reduction. Additionally, the hydrophobic PET material demonstrates anti-reflective properties in the 500–760 nm visible light range, achieving transmittance exceeding 88.5%. Linear ion beam deposition of carbon films combined with etching techniques can produce appropriate micro-morphology and surface chemical structure, thereby improving the hydrophobic performance of PET flexible polymer materials while maintaining substrate transparency.

## Full Text

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### Preparation and Hydrophobic Properties of Diamond-like Carbon Films on PET Substrates

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## Abstract

Diamond-like carbon (DLC) films were deposited on PET substrates using linear ion beam (LIS) technology with varying ion beam current to achieve hydrophobic properties and improved wear resistance. The microstructure, morphology, and wettability were analyzed, and the relationship between wetting behavior and surface morphology, microstructure, and surface energy was investigated. The results show that the deposited DLC film exhibits typical amorphous carbon structure, with its $sp^2/sp^3$ ratio increasing from 0.774 to 1.622 as the LIS current increases, indicating enhanced graphitization. Meanwhile, the water contact angle of PET increased from 63.51° to 103.7°. Further analysis revealed that the improved hydrophobicity can be attributed to enhanced graphitization and the formation of micro-nano structures, which lead to decreased surface energy. In addition, the transmissivity of PET in the visible light range could reach over 88.5%, showing an enhanced effect within the 500–760 nm wavelength range. Therefore, controlling proper surface morphology and low surface energy through plasma modification technology can effectively improve the hydrophobic properties of flexible polymer materials while maintaining the transparency of PET.

**KEY WORDS** organic polymer materials, hydrophobicity, diamond-like carbon, surface morphology, surface energy

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## Introduction

PET materials offer excellent ductility, low density, high strength, and fatigue resistance, making them widely used in electronics, textiles, biomedicine, and other fields [1,2]. However, the terminal hydroxyl groups in PET make it prone to moisture absorption and poor wear resistance [3], limiting its applications in many areas. With the increasing use of transparent polymer devices in aerospace, marine environments, electronic displays, and biomedical applications, the demand for controlling the surface hydrophobic properties of PET materials has become more urgent, particularly for applications such as biofouling prevention, anti-adhesion in microelectronic system components, and inner walls of micro-syringe needles [4-6].

Surface functional modification of PET through physical or chemical methods represents an effective approach. However, chemical methods involve cumbersome processes and can cause environmental pollution. Among physical methods, plasma surface modification is a simple, convenient, and environmentally friendly technology. Low-temperature plasma treatment can achieve functional control of materials without affecting their intrinsic properties [7]. Current research on hydrophobic polymer materials has focused primarily on organic silicon and fluorine compounds, which are not only expensive but often compromise the mechanical properties of polymers [8,9]. Diamond-like carbon (DLC) films offer high hardness, low friction coefficient, excellent wear and corrosion resistance, broad optical transparency, and superior biocompatibility [10], and can be prepared using various environmentally friendly PVD low-temperature deposition techniques. Therefore, applying DLC modification to PET surfaces can significantly improve wear resistance, biocompatibility, and expand the functional applications of PET materials.

Numerous studies have investigated DLC film deposition on polymer surfaces. Rahmawan et al. [11] prepared three-dimensional DLC hydrophobic surfaces with matrix micropillars on PDMS substrates using templating and RF PACVD, achieving static contact angles of 160° when the micropillar duty ratio was less than 4. Shin et al. [12] treated PET fiber surfaces with O plasma using RF PECVD to create nanohair structures, then deposited SiOx-C:H films. These high aspect-ratio nanohair structures endowed PET fibers with superhydrophobic properties that were maintained even after liquid and oil immersion. Pandiyaraj et al. [13] prepared DLC on PET surfaces using RF technology with varying deposition bias voltages, and the DLC-coated PET surfaces exhibited hydrophilic characteristics (contact angles of 62.35°-71.17°). These results demonstrate that preparing hydrophobic DLC on polymer surfaces remains challenging.

This study employs linear ion source (LIS) technology to prepare DLC films with different structures on PET bulk surfaces through simultaneous Ar plasma etching and DLC co-deposition, investigating the relationship between film hydrophobicity and surface morphology/chemical structure.

### 1.1 Film Preparation

We employed linear ion source (LIS) technology, which offers high ionization rates, low-temperature operation without hot filaments, independent control of ion energy, and excellent large-area uniformity, to simultaneously perform plasma etching and DLC film deposition on PET surfaces. The etching gas was high-purity Ar, and the carbon source gas was high-purity CH . Prior to deposition, substrates were sequentially cleaned with alcohol and acetone in an ultrasonic bath, dried, and placed in the vacuum chamber. Deposition began when the vacuum pressure reached $3.0\times10^{3}$ Pa. During deposition, Ar gas was first introduced, and the substrate was etched with the ion beam for 10 minutes to remove surface oxide layers and contaminants. Then CH /Ar mixture gas was introduced to allow simultaneous DLC film deposition and Ar ion etching. The effect of DLC films on PET properties was investigated by varying the ion beam current, with a deposition time of 10 minutes. The specific deposition parameters are listed in Table 1 .

### 1.2 Film Characterization

A Raman spectrometer (Ar  laser wavelength 532 nm) was used to characterize the carbon atomic bonding structure in the films, with 0.5 mW laser power for non-destructive testing. An X-ray photoelectron spectrometer (XPS, ESCALAB 250, Thermo) with Al K  excitation source (1486.8 eV) was used to characterize chemical composition and elemental binding states, with binding energy accuracy of 1 eV for survey scans and 0.1 eV for narrow scans. Surface morphology was characterized using an S-4800 field emission scanning electron microscope (FESEM). Film thickness and surface roughness were measured using an Alpha-step IQ surface profiler, with test lengths of 500  m and 1500  m, and each sample was tested three times. A UV/Vis/NIR spectrophotometer (Lambda 950) was used to measure film transmittance in the visible light range from 250–850 nm. Contact angles were measured using an OCA20 contact angle goniometer, with each sample tested five times. The Owens two-liquid method [14] was employed to calculate surface energy using deionized water and glycerol as test liquids. The calculation formula is:

$$(1 + \cos\ ) = 2(\quad) \cdot\ + 2(\quad) \cdot$$

where  is the contact angle of different liquids on the solid surface,  and  are the dispersive and polar components of the liquid' s surface energy (mJ/m$^2$),  is the total surface energy (sum of dispersive and polar components), and  and  are the dispersive and polar components of the solid' s surface energy (mJ/m$^2$). The contact angles with deionized water and glycerol were measured to calculate the film surface energy. For deionized water, the polar component  is 51.0 mJ/m$^2$ and the dispersive component  is 21.8 mJ/m$^2$. For glycerol, the polar component  is 30.0 mJ/m$^2$ and the dispersive component  is 34.0 mJ/m$^2$.

## 2 Results and Discussion

### 2.1 Contact Angle

Figure 1 [Figure 1: see original paper] shows the variation of film contact angles under different deposition parameters. Compared with the PET substrate (sample 1#) contact angle of 78.92°, sample 2# decreased to 63.51°. However, as the ion beam current increased, the contact angle gradually increased, reaching a maximum of 103.7°. Surfaces with water contact angles greater than 90° are typically considered hydrophobic, while those below 90° are hydrophilic [15]. Thus, the PET surface transformed from hydrophilic to hydrophobic after DLC deposition combined with Ar ion etching modification.

### 2.2 Surface Energy

The degree of hydrophilicity/hydrophobicity on solid surfaces is closely related to the free energy at the solid-liquid interface; higher surface free energy corresponds to more hydrophilic surfaces, and vice versa [16]. The surface energy and its components for each sample, calculated using the Owens two-liquid method, are shown in Figure 2 [Figure 2: see original paper]. The surface energy initially increased then decreased, with sample 4# exhibiting the lowest dispersive and polar components at 14.76 mJ/m$^2$ and 2.62 mJ/m$^2$, respectively. Comparing Figures 1 and 2 reveals an inverse relationship between surface energy and contact angle, consistent with the wetting behavior principle that lower surface energy yields larger contact angles, while higher surface energy produces smaller contact angles [17].

### 2.3 Raman Structure of DLC Films

Under constant testing conditions, surface chemical structure and microscale geometry are the primary factors influencing contact angles [18,19]. Raman spectroscopy is a non-destructive method for characterizing carbon structures and can qualitatively determine sp$^3$ and sp$^2$ carbon hybridization content in amorphous carbon films. DLC Raman spectra exhibit two peaks: the G (Graphite) peak at approximately 1580 cm $^1$ and the D (Disorder) peak at approximately 1360 cm $^1$. The G peak corresponds to layered sp$^2$ cluster structures from C-C bond stretching vibrations in graphite structures, while the D peak corresponds to disordered microcrystalline graphite structures from six-membered carbon ring "breathing" vibrations. The carbon bonding characteristics can be determined from the G peak position, D peak position, G peak full width at half maximum, and the integrated intensity ratio ID/IG. For hydrogenated DLC films, the G peak position relates to sp$^2$ cluster size, while the ID/IG ratio reflects sp$^2$/sp$^3$ changes [20,21].

Figure 3 [Figure 3: see original paper] presents Raman spectra for samples under different deposition conditions. The modified PET samples (2#, 3#, and 4#) all show broadened peaks between 1100-1800 cm $^1$, indicating typical amorphous carbon film structures. Peak fitting revealed ID/IG values of approximately 0.98±0.066 for all three samples, with G peak positions maintained at (1529.9±11.01) cm $^1$. These results indicate no significant change in sp$^2$/sp$^3$ carbon bonding structure when ion beam current increased from 0.1 A to 0.2 A. Because the DLC films were relatively thin due to the combined effects of

DLC deposition and Ar etching, the Raman peaks were weak, making detailed analysis of surface chemical structure changes difficult.

### 2.4 XPS Structure of DLC Films

XPS analysis was performed on modified PET samples. Figure 4 [Figure 4: see original paper] shows elemental composition changes, XPS C 1s binding energy spectra, and fitted decomposition for the substrate and samples under different deposition conditions. Figure 4a demonstrates that carbon content increased significantly while oxygen content decreased after carbon film deposition, confirming successful carbon film formation on the PET surface. Detailed C 1s peak analysis is shown in Figure 4b. The PET C 1s XPS spectrum can be deconvoluted into three peaks corresponding to C-C bonds (284.6 eV), C-O bonds (286.2 eV), and carboxyl O-C=O bonds (288.6 eV) in the PET structure, confirming the pristine nature of the substrate. However, significant structural changes occurred after DLC film deposition (Figures 4c–4e). The C 1s spectra for samples 2#, 3#, and 4# can each be fitted with four peaks near 284, 285, 286, and 288 eV, corresponding to $sp^2$-hybridized carbon, $sp^3$-hybridized carbon, C-O, and C=O bonds. The $sp^2/sp^3$ ratio can be determined from the area ratio of $sp^2$ to $sp^3$ peaks.

As shown in Figure 4f, the $sp^2/sp^3$ ratio on the film surface gradually increased with ion beam current. This occurs because increased ion beam current raises the energy of incident carbon ions, promoting graphitization. The $sp^2/sp^3$ ratio increased significantly from 0.774 to 1.43 when ion beam current increased from 0.1 A to 0.15 A, then increased slowly from 1.43 to 1.622 when current further increased from 0.15 A to 0.2 A. This trend correlates with contact angle changes, as the hydrophobic properties of carbon films are related to the surface $sp^2/sp^3$ ratio [22]. Research has shown that $sp^2$-rich surfaces exhibit larger contact angles than $sp^3$-rich surfaces because intrinsic graphite has fewer dangling bonds and lower surface free energy, resulting in better hydrophobicity [23]. Therefore, increasing $sp^2$ bond content reduces surface energy, and the $sp^2/sp^3$ variation trend matches the contact angle changes, consistent with results shown in Figures 1 and 2.

### 2.5 Surface Properties

Solid surface wettability is determined by both surface chemical composition and microscale geometric structure. Surface roughness variations measured by surface profiler are shown in Figure 5 [Figure 5: see original paper]. The surface roughness Ra values for samples 1#–4# were 6.15 nm, 4.15 nm, 5.43 nm, and 7.56 nm, respectively, showing a trend of initial decrease followed by increase that correlates with contact angle changes. This indicates that surface roughness of DLC-modified films contributes to hydrophobic effects to some extent.

SEM surface morphologies of the PET substrate and DLC-coated PET are shown in Figure 6 [Figure 6: see original paper]. The PET substrate surface was relatively smooth. Sample 2# exhibited significantly altered surface morphology with ridge-like protrusions (width 120–180 nm) and grooves (width 100–200 nm), primarily because the lower ion beam current made etching dominant over DLC deposition during the combined process. As ion beam current increased, DLC deposition became more effective, and sample 3# showed smoother morphology with worm-like microstructures. Further increasing ion beam current caused the worm-like structures on sample 4# to become more numerous with sparse holes, though the overall morphology was similar to sample 3#. This demonstrates that optimal hydrophobicity can be achieved when PET surface morphology is controlled at the micro-nanoscale.

Cassie et al. [24] proposed that when surface roughness reaches a certain level, liquids cannot completely penetrate the grooves between micro-nanostructures, trapping air and forming a composite "solid-liquid-air" contact state known as the Cassie hydrophobic state. According to this theory, the micro-nano structures formed on samples 3# and 4# can trap substantial air during solid-liquid contact. Since water droplets cannot penetrate the air gaps, the contact area between water droplets and the material surface is reduced, increasing the contact angle. In contrast, the ridge-like structures on sample 2# are interconnected with large gaps between rough features, preventing effective air trapping and allowing water droplets to penetrate more easily, increasing contact area and significantly reducing contact angle [25].

### 2.6 Visible Light Transmittance of Hydrophobic PET

Thickness variations of PET after DLC deposition were measured, with results shown in Figure 7 [Figure 7: see original paper]. All treated PET surfaces were lower than the substrate height because the Ar gas flow rate exceeded the CH flow rate, making etching dominant. However, the height difference between samples and substrate gradually decreased with increasing ion beam current because higher current enhanced DLC deposition efficiency, shifting Ar ion etching from the PET substrate to both PET and hard DLC film, thereby reducing etch rate. These results are consistent with the morphological evolution shown in Figure 6.

To evaluate changes in visible light transmittance after DLC deposition, the transmittance of hydrophobic samples 3# and 4# was characterized in the visible range. As shown in Figure 8 [Figure 8: see original paper], compared with pristine PET, the DLC-modified hydrophobic PET surfaces not only maintained transparency but also exhibited enhanced transmission in the 500–760 nm wavelength range, with transmittance exceeding 88.5%. Sample 4# showed slightly lower transmittance than sample 3#, possibly because sample 4# contained less $sp^3$ bonding and had a thicker DLC film, leading to slightly increased light absorption.

## 3 Conclusions

(1) DLC films with typical amorphous carbon structure can be prepared on PET substrates using linear ion beam deposition combined with Ar ion etching. The $sp^2/sp^3$ ratio increases from 0.774 to 1.622 with increasing ion beam current.

(2) The contact angle of PET materials increased from 63.51° to 103.7° with increasing ion beam current, transforming the PET surface from hydrophilic to hydrophobic after DLC deposition.

(3) The hydrophobic PET samples prepared by plasma modification technology maintained the transparent properties of the substrate material, particularly showing enhanced transmission in the 500–760 nm visible range with transmittance above 88.5%.

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