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Effects of Polyurethane Substrate Pre-Treatment on Pulsed Cathodic Arc Deposited DLC Films

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Abstract: Diamond-like carbon (DLC) films were deposited by means of pulsed cathodic arc deposition on pretreated polyurethane (PU) rubber substrates. Tetrachloroethylene was chosen as a dissolution method to remove the plasticizer added in the PU substrates. Scanning electron microscopy (SEM) and Raman spectroscopy were applied to observe and characterize the surface morphologies and compositions of the deposited films, respectively. The tribological behaviours of uncoated and coated rubbers were investigated with ring-on-disc tribo experiments under dry sliding conditions. The coefficients of friction (COFs) of the coated rubbers were 40% lower than those of uncoated rubber and the COFs of different samples decreased first and then increased slightly with the increase in temperature and the time of ultrasonic treatment under dry friction. Based on the above experiments, ultrasonic treatment with tetrachloroethylene contributes to the increase in the wear resistance of DLC films deposited on PU rubbers. The most suitable temperature and time of ultrasonic treatment with tetrachloroethylene is 50 °C for 15 min.

Keywords: DLC; polyurethane rubber; wear resistance; tetrachloroethylene

1. Introduction

As a metastable form of amorphous carbon film, diamond-like carbon (DLC) film has received continuous interest and research regarding innovations and applications in the field of tribology, due to the unique properties of the DLC films, including self-lubrication, high hardness, and excellent wear resistance [1–5]. At first, DLC film is considered to be a surface protection coating deposited on metal materials and ceramic surfaces exclusively. Extensive reviews of DLC films deposited on metals exist in the literature [6–8]. However, a few studies have focused on rubber materials with problematic friction resistance, which are used extensively in engineering applications [9]. Pioneering research regarding the deposition of DLC onto rubber substrates was carried out in 2004 [10].

After that, significant efforts have been made to extend the applications of DLC films on rubber materials. Typical deposition technologies of DLC films can be divided into two categories: physical vapour deposition (PVD) and chemical vapour deposition (CVD) [11–15]. Furthermore, the research objects are mostly concentrated on butyl rubber and nitrile rubber. Aoki and Ohtake [11] deposited DLC films onto butyl rubber and aluminium substrates using RF-plasma CVD at a bias voltage of 2300 V with CH₄ gas as a precursor. The results showed that the film COFs were between 0.1 and 0.2 during 9000 cycles at loads of 0.98 to 1.96 N. At higher loads of 2.94 and 4.9 N, higher COFs (0.2–0.3) were observed after 200 cycles. Bui et al. [12,13] deposited DLC films on both Hydrogenated acrylonitrile

butadiene rubber (HNBR) and Si wafer substrates using closed-filed unbalanced magnetron sputtering with C_2H_2 gas as a carbon source, and reported that the film COFs are between 0.18 and 0.2.

Commonly, the polyurethane rubber performs well as a dynamic seal, owing to its good strength, elasticity, oil resistance, and thermal aging property [14]. Under dynamic friction conditions, the high COF of the seal element leads to intense surface wear and significantly reduces its working life. Ultimately, severe wear of the seal element causes oil leakage and even system failure [15,16]. Therefore, the study of DLC films on polyurethane rubber to enhance its wear resistance is of great significance for engineering applications, such as hydraulic seals, pneumatic seals, buffer rings, and piston seals.

Polyurethane rubber is prone to deformation after being heated. Therefore, the surface temperature should be kept as low as possible during the deposition. The conventional cathodic arc deposition technique involves an electric arc striking a cathode target and vaporizing the target material [17]. Then, the target material condenses onto a substrate forming a thin film. The pulsed cathodic arc deposition uses pulsed arc discharge instead of stable arc discharge in order to allow the generated heat to be transmitted in time by circulating cooling water at the target position within a time interval of the pulse. In this way, a low deposition temperature can be achieved and the fluctuation of the target temperature can be effectively controlled within 5 °C.

Another major difficulty in the preparation of the DLC film on polyurethane rubber is plasticizing additives in the rubber. Due to friction heating, the plasticizer will melt and precipitate out gradually, resulting in a sudden stress concentration between the film and the substrate. Then the high stress causes the film to crack and peel off [18]. It is of significance for avoiding the precipitation of the plasticizer, improving the binding ability between the DLC film and polyurethane rubber in the process of friction. In order to achieve this, an additional pre-treatment and after-treatment can be applied, which are common techniques in the coating industry [19,20].

In this paper, the pulsed cathodic arc method was used to deposit DLC films onto polyurethane rubber substrates. The rubber samples were sunk in tetrachloroethylene with an ultrasonic cleaning process to remove the plasticizer. The effects of the temperature and time of the ultrasonic pre-treatment in tetrachloroethylene on the morphology and friction properties of DLC films were studied.

2. Experimental Methods

The polyurethane rubber sheets were used as substrates with a size of 124 mm × 90 mm × 2 mm. The substrates were first ultrasonically cleaned with absolute ethanol and then rinsed in deionized water. In order to remove the plasticizer from the samples, tetrachloroethylene was chosen as the solvent in the ultrasonic treatment. The temperature and time of the ultrasonic treatment for different substrates are listed in Table 1.

Table 1. Parameters of the specimen pre-treatment.

No.	Solvents	Temperature/°C	Time/min
1	absolute ethyl alcohol	25	15
2	tetrachloroethylene	25	15
3	tetrachloroethylene	25	30
4	tetrachloroethylene	50	15
5	tetrachloroethylene	50	30

After the cleaning process, the PU rubber substrates were dried in an oven at 150 °C for 1 h. Then, the substrates were mounted onto sample holders and placed into a vacuum chamber. The DLC films were deposited on the cleaned substrates via the pulsed cathodic arc method with a voltage of 280 V and a pulse frequency of 3 Hz. The chamber pressure was kept at 0.05 Pa during the deposition time (6000 pulses).

As shown in Table 1, five substrates were chosen for different pre-treatments. The first sample was cleaned in ethyl alcohol for 15 min at 25 °C. Samples 2 and 3 were cleaned in tetrachloroethylene for 15 and 30 min at 25 °C. Samples 4 and 5 were cleaned in tetrachloroethylene for 15 and 30 min at 50 °C.

The un-coated polyurethane rubber samples and as-deposited samples were examined using a scanning electron microscope (INSPECT S50) to analyse the surface morphology of the DLC films. Raman spectroscopy was employed to study the microstructure of the deposited films.

The tribological tests were carried out by a ring-on-disc tribometer (MTT-1M) under dry sliding conditions at room temperature. The un-coated and coated samples were cut into a round shape with a diameter of 50 mm to fit in the test equipment. An annular chrome steel disk was used as the friction pair and a load of 50 N was applied to the specimen with a speed of 6.28 cm/s. The samples before and after the friction test were weighed using a precision electronic balance with a measurement accuracy of 0.0001 g. The wear track of the specimens after the tribological tests was analysed by optical microscopy.

3. Results and Discussion

3.1. Surface Morphology

The morphology of the rubber samples after different ultrasound treatments is shown in Figure 1a,e, corresponding to the samples after pre-treatments 1–5, respectively. Figure 1a shows the sample surface cleaned in ethyl alcohol for 15 min at 25 °C. Figure 1b,c show the specimens' surface morphology after pre-treatment in tetrachloroethylene for 15 and 30 min at 25 °C. Figure 1d,e are SEM images of sample surfaces cleaned in tetrachloroethylene for 15 and 30 min at 50 °C. Comparing with Figure 1a, more small fibers can be observed on the sample surfaces that were cleaned in tetrachloroethylene. This is a result of rubber plasticizer being washed out and bringing internal fiber reinforcements to the sample surface [21,22].

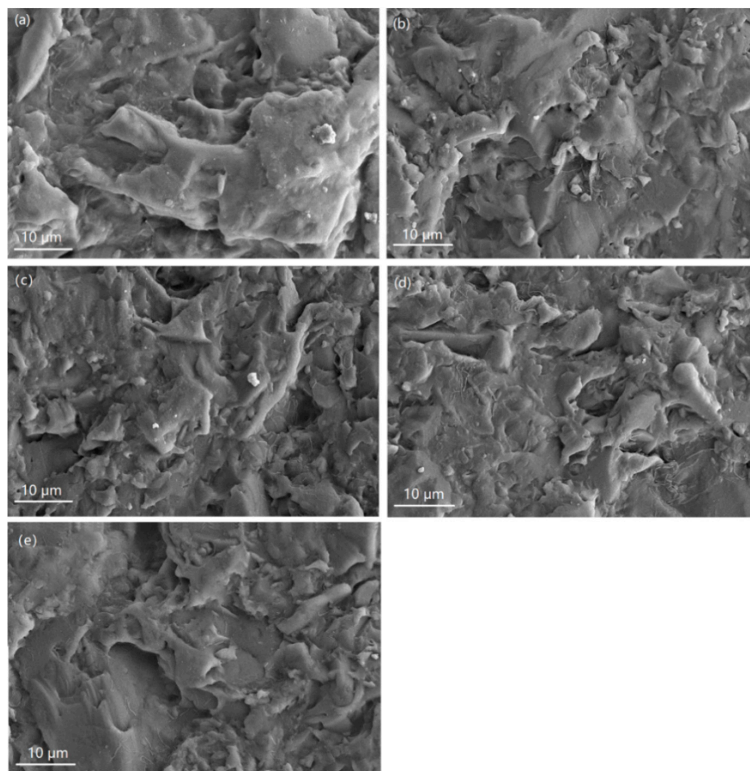


Figure 1. SEM micrographs of the specimens after pre-treatment. (a) Specimen 1; (b) Specimen 2; (c) Specimen 3; (d) Specimen 4; (e) Specimen 5.

SEM images of films deposited on rubber substrates with different pre-treatments are shown in Figure 2. All the films are characterized by crack networks, which are due to thermal mismatch stress during film growing. This feature is consistent with other DLC films deposited on rubber in the literature [23–25].

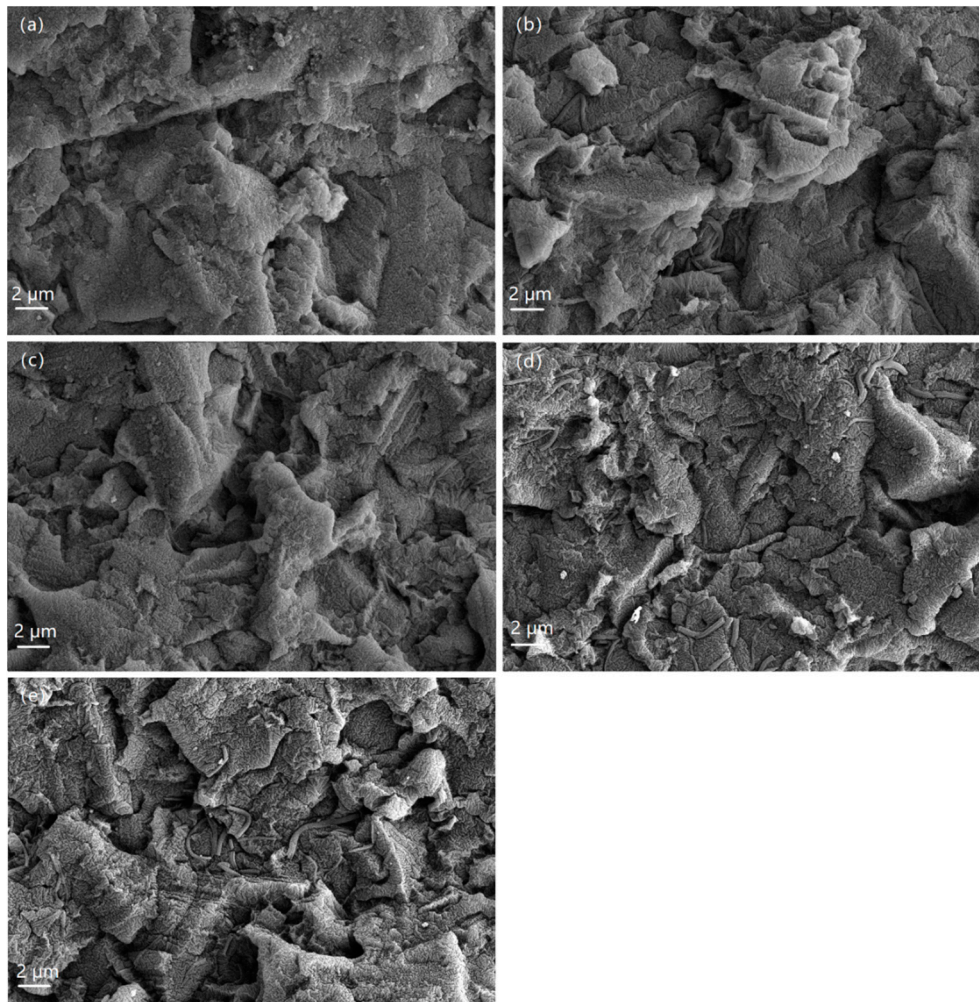


Figure 2. SEM micrographs of the films deposited on substrates. (a) Specimen 1; (b) Specimen 2; (c) Specimen 3; (d) Specimen 4; (e) Specimen 5.

3.2. Raman Spectroscopy

Raman spectroscopy is a fast and non-destructive characterization method, which is commonly used for studying the chemical bonding and structure of DLC films. In Raman spectroscopy, all carbon materials show common features in the $800\text{--}2000\text{ cm}^{-1}$ region, namely G and D peaks (at approximately 1590 and 1340 cm^{-1}). The Raman spectroscopies of all deposited films are shown in Figure 3, compared to the standard spectrum. As can be seen from the figure, the Raman spectra of Specimen 1 only have one broad peak near 1590 cm^{-1} , corresponding to the G peak, which is a typical amorphous DLC film structure [26]. While in Specimens 2 and 3, there is a sharp peak at 1590 cm^{-1} . In Specimens 4 and 5, there are two distinct peaks in the spectra, located at 1340 cm^{-1} and 1590 cm^{-1} , respectively. The results prove that DLC film can be successfully deposited on the polyurethane rubber by the cathodic discharge plasma method.

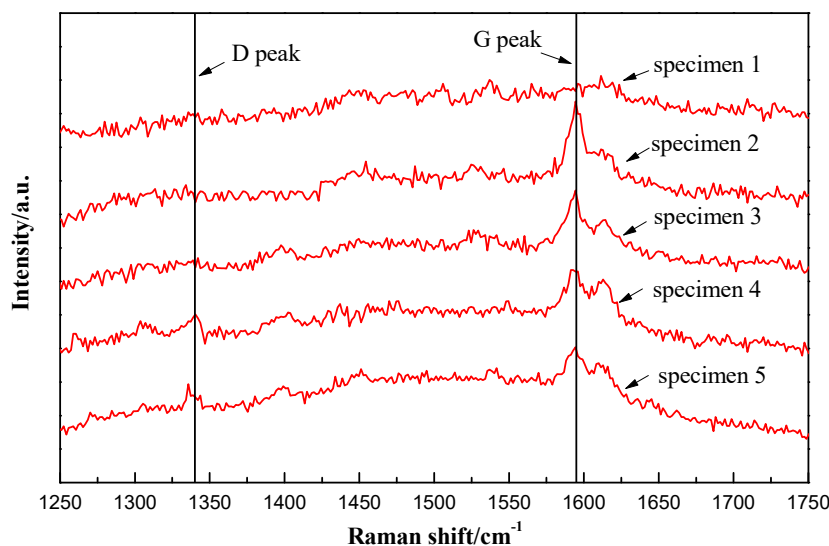


Figure 3. Raman spectrum of different specimens.

3.3. Tribological Characteristics

The tribological behaviour of DLC films deposited on rubber substrates was investigated using an MTT-1M tribometer under dry friction conditions. For comparative purposes, the result of the tribological test conducted on bare rubber substrate is also presented. Figure 4 displays the evolution of the coefficient of friction of the specimen as a function of the friction time. As shown in Figure 4, the bare polyurethane rubber has the maximum coefficient of friction among all the test specimens, which is approximately 0.52. The coefficient of friction for the uncoated substrate decreased to 0.48 after 600 s and then remained stable. Due to the frictional heating, the plasticizer would gradually melt and precipitate to the surface, and lubricate the friction interface. Hence, the coefficient of friction decreases after the initial friction stage. Compared with the rubber substrate, the coefficients of friction for the DLC films varied in a range from 0.3 to 0.4, which is 0.2–0.3 less than that for bare substrate under a dry sliding condition, indicating that deposited DLC film can effectively improve the wear resistance of polyurethane. From Figure 4, the coefficient of friction curve of Specimen 1 fluctuates violently with an increase in time. The coefficient of friction remains stable at the beginning and shows a sudden rise to 1.0 after 500 s. The films deposited on the substrate with ultrasonic treatment by tetrachloroethylene have much more flat curves of the coefficient of friction under the same condition. As shown in Figure 4, the friction curves of Specimens 2 and 3 also show a gradual increase in coefficients of friction after the initial friction stage, which is due to the peeling off of the films. It was found that Specimens 2 and 3 kept a much longer stationary stage compared to Specimen 1, which implies that samples with pre-treatments in tetrachloroethylene have better film adhesion and wear resistance. Comparing the four curves (2–5), it is seen that Specimens 4 and 5 maintain more steady and lower coefficients of friction during the whole experiment time, approximately 0.3. Due to the removal of plasticizer, samples 4 and 5 have less stress induced by precipitation of plasticizer compared to other samples. Previous studies have shown that high stress has a detrimental effect on film adhesion [27]. This can explain why the DLC films prepared on the rubber substrate with ultrasonic treatment in 50 °C tetrachloroethylene have better tribological properties. The scattering of COF after 50 min in Specimen 5 could be caused by furrow-like wear tracks formed at the film surface, which can be confirmed in Figure 5 (slightly higher mass loss than specimen 4) and Figure 6 (wear track morphology).

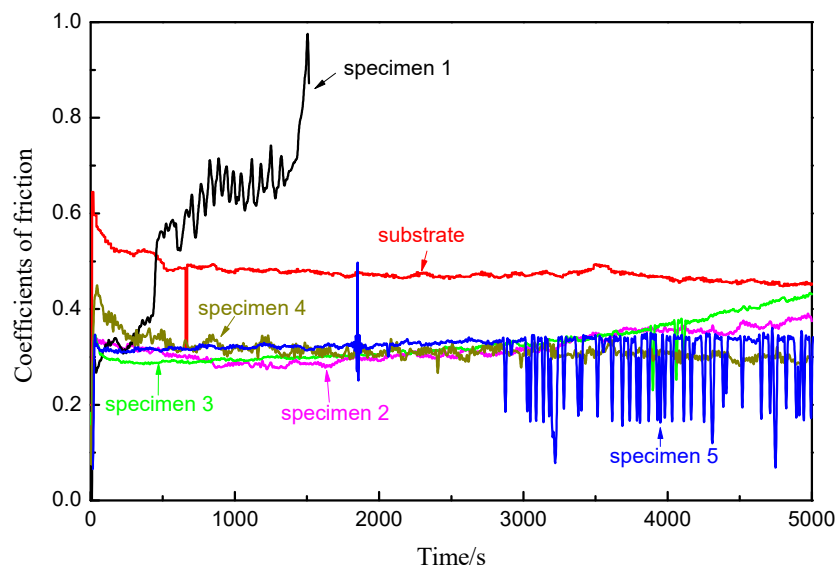


Figure 4. The friction coefficients of different specimens.

Figure 5 compares the mass loss of each coated specimen after the dry friction test. It is observed that Specimen 1 coated on substrate without pre-treatment has the maximum wear loss weight. A reduction in mass loss of more than 30% was observed for the DLC films deposited on PU rubber with pre-treatment compared to the rubber without pre-treatment. Meanwhile, with the increase in temperature and time of ultrasonic treatment in tetrachloroethylene, the wear loss of different deposited specimens first decreases and then increases slightly. Among the five coated specimens, Specimen 4 has the smallest mass loss, which was consistent with the results of the tribological tests.

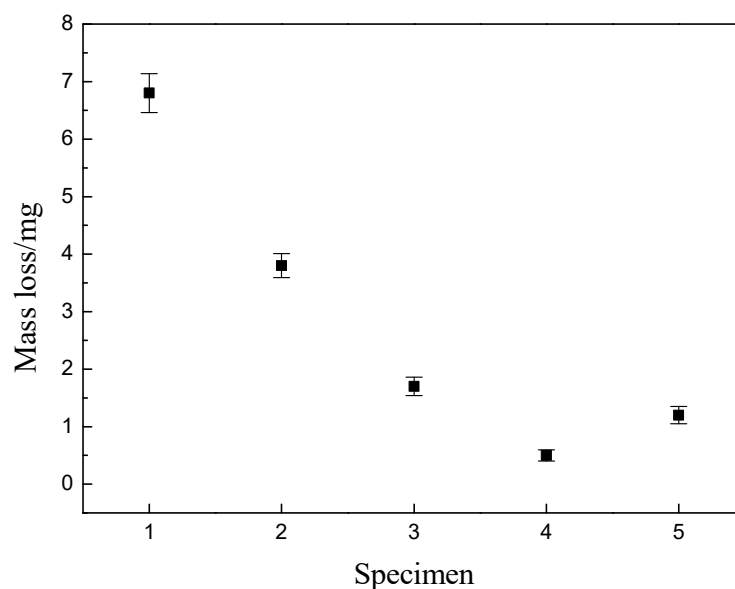


Figure 5. Mass loss of specimens under a dry friction condition.

The surface morphologies of the specimens after tribo-tests can not only be used to investigate the tribological behaviour of materials, but also to analyse the wear mechanism particularly. The typical surface morphologies of the deposited DLC films extracted from the dry friction test are shown in Figure 6. It is shown that with the increasing temperature and time of substrate ultrasonic pre-treatment in tetrachloroethylene, the deposited DLC films maintained higher integrity. For Specimen 1 (Figure 6a), the worn surface of the DLC film is covered by a series of grooves caused by a ploughing action and

micro-cutting of the hard asperities on counterpart chrome steel and the particles derived from the piece of DLC film, which is in accordance with the greatest mass loss.

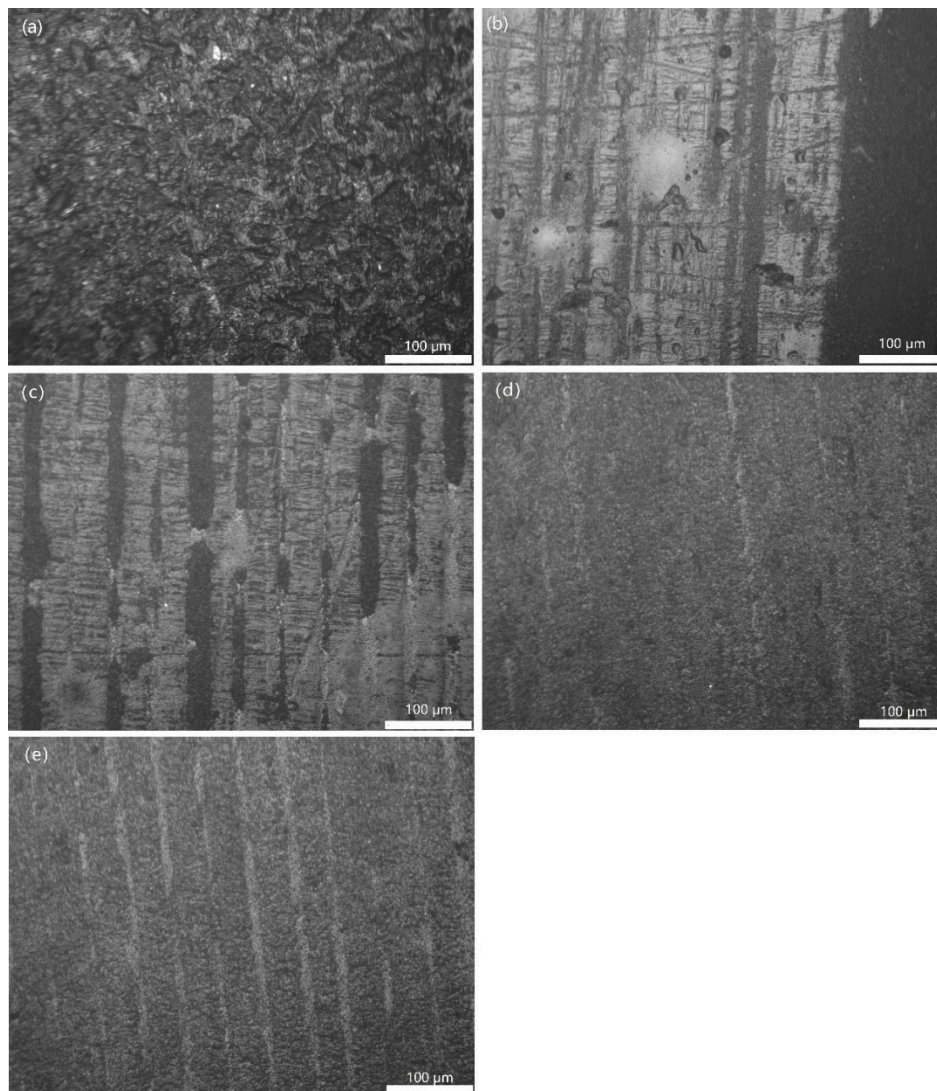


Figure 6. The wear track of the specimens under a dry friction condition. (a) Specimen 1; (b) Specimen 2; (c) Specimen 3; (d) Specimen 4; (e) Specimen 5.

The phenomena confirm that the wear mechanism of Specimen 1 is largely dominated by abrasive wear under a sliding condition. As for films 2–5, the features of the wear tracks appear to exhibit a smooth morphology with a few furrows after the tribo-tests. It can be observed that the specimens with less pre-treatment time and lower pre-treatment temperature are more prone to wear damage. The above damage patterns suggest that ultrasonic pre-treatment with tetrachloroethylene can enhance adhesion between the film and rubber substrate, and DLC films can effectively improve the friction behaviour and wear resistance of polyurethane rubber.

As shown in Figure 7, the wear mechanism of the DLC films has been analysed through the COFs and the wear tracks. For the DLC film deposited on polyurethane rubber without pre-treatment (Figure 7a), the main wear mechanism is distinctly dominated by abrasive wear under dry sliding friction. The micro-cracks initiate from the part of the DLC film having poor adhesion with the substrate. Simultaneously, the friction heating leads to the melting and oozing of the plasticizer, resulting in a pressure concentration at the interface between the DLC film and the rubber substrate. Due to the combined effects of poor film adhesion and the pressure concentration, the cracks in the film rapidly

expand and connect with each other, causing a large piece of fracture and peeling off. The stripped pieces act as a hard abrasive debris, further accelerating the tribological performance deterioration. Figure 7b shows the adhesion mechanism of DLC films coated on polyurethane rubber substrates with ultrasonic treatment in tetrachloroethylene. With a smooth surface, DLC films have a higher bonding force to the substrates, resulting in less sliding friction. Meanwhile, the plasticizer has been dissolved and removed via ultrasonic pre-treatment in tetrachloroethylene, eliminating the stress concentration by precipitation of the plasticizer, and further avoiding peeling off of the DLC film under the action of shear stress. According to the Raman spectra, the main peak for these films is the G peak located around 1590 cm^{-1} , which is close to the graphite vibrational density of states [28]. The graphite-like phase in the DLC films has a self-lubricating effect further improving sample friction performance and film working life.

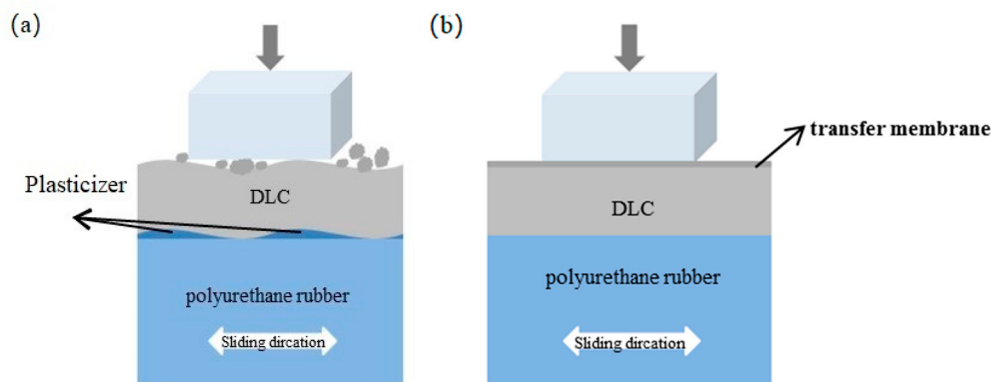


Figure 7. Schematic diagrams of wear mechanisms for DLC films deposited on two different substrates: (a) PU rubber without the pre-treatment, (b) PU rubber with the pre-treatment.

4. Conclusions

In this paper, DLC films were deposited on polyurethane rubber using the pulsed cathode arc method. The effects of temperature and time of ultrasonic pre-treatment in tetrachloroethylene on the morphology and friction properties of DLC films were studied. The following conclusions were drawn:

1. The surface morphologies of PU rubber samples after ultrasound treatments show that the fiber reinforcements precipitate from the substrate after ultrasonic pre-treatments in the tetrachloroethylene. This indicates that plasticizer is washed out after the tetrachloroethylene cleaning process. All deposited films showed cracked networks as a result of thermal mismatch stress between the films and substrates. Raman spectroscopy was performed on the deposited films, proving that the films deposited are typical DLC films.
2. Under a dry friction condition, the COFs of the DLC films are significantly lower than those of the uncoated polyurethane rubber. By comparison, it is clear that with the increase in temperature and time of ultrasonic pre-treatment, the COF and wear loss of the coated specimen decreased dramatically. Among the deposited films, the COF of Specimen 4 is the smallest, approximately 0.3, and also has the smallest mass loss under friction. In order to obtain the DLC film with the best anti-wear ability on polyurethane substrate, the appropriate ultrasonic treatment temperature and time in tetrachloroethylene is $50\text{ }^{\circ}\text{C}$ for 15 min.

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