



Fabrication of Stable Superhydrophobic Coatings with Bicomponent Polyurethane/Polytetrafluoroethylene Composites

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A superhydrophobic coating was fabricated with bicomponent polyurethane/polytetrafluoroethylene (BPUR/PTFE) composites. Bicomponent polyurethane was obtained by cross-linking reaction between polyisocyanate and hydroxylic fluoroacrylate resin, which was synthesized *via* free radical polymerization. Superhydrophobic surface with water contact angle of 158° and sliding angle of 2° was obtained from bicomponent polyurethane and polytetrafluoroethylene at their weight ratio of 2/3 by a simple procedure. An irregular rough structure with dispersed grooves and protuberances observed by scanning electron microscope was considered to be responsible for the surface superhydrophobicity. The coating adhered strongly to the substrate and was stable to corrosive medium. The technique is facile, economical and can be expected for large-scale application in anticorrosion and related areas.

Key Words: Superhydrophobic coating, BPUR/PTFE composites, Stability, Phase separation, Self-cleaning.

INTRODUCTION

Inspired by naturally water-repellent plant leaves and insects, such as lotus and water strider, superhydrophobic surfaces with water contact angle more than 150° have recently drawn much attention in both fundamental research and practical applications due to their self-cleaning, antiicing and anticontamination properties¹⁻³. Up to now, various methods have been reported for the preparation of artificial superhydrophobic surfaces, including electrochemical reaction and deposition^{4,5}, chemical vapour deposition⁶, etching method^{7,8}, electrospinning and lithography^{9,10} or sol-gel technique¹¹ and so on. These approaches adopted could be generally categorized as either creating a rough microstructure on a hydrophobic substrate surface or modifying the rough surface with low surface energy materials such as fluorinated or silicon compounds. However, these methods generally present some shortcomings such as step-complex, expensive and, especially, low surface coverage. Though some researchers¹² have reported that the superhydrophobic surfaces can be prepared by a simple and cost-effective spray process, the preparation process involved the use of aggressive solvent such as dimethyl formamide, which can dissolve the bottom coating, or the so-called lifting phenomenon. Additionally, from practical view point, superhydrophobic surfaces with sufficient adhesive force and long-term stability in corrosive solutions are another two significant issues for them to be used in practice¹³.

Two component polyurethane coatings are widely used in automobile industry, naval vessel and building field due to their high performance of adhesion stress, chemical resistance and so on. It is expected that the application range will be broadened after endowing polyurethane coatings with superhydrophobicity. Polytetrafluoroethylene (PTFE) is a commercially available fluoropolymer with excellent chemical properties and well-known low surface energy (18 mN/m)^{14,15}. Herein, PTFE attracted much attention in fabricating superhydrophobic surface. Yang *et al.*¹⁶ reported a superhydrophobic coating based on furfural acetone resin and PTFE composites after curing at 300°C . The combination of double-scaled structure and surface enrichment of fluorine element made the coating surface superhydrophobicity¹⁶. However, to our knowledge, there is little literature about preparing superhydrophobic coatings based on bicomponent polyurethane (BPUR) and polytetrafluoroethylene (PTFE) composites. In this study, the superhydrophobic surfaces of BPUR/PTFE composite coatings were prepared using conventional spray and curing processes on tin plates. Hydroxylic fluoroacrylate resin was synthesized firstly and then cross-linked with polyisocyanate to obtain BPUR. Surface roughness was created by embedding hydrophobically PTFE particles in BPUR matrix. The composite coatings presented superhydrophobicity and showed irregular rough structure with dispersed grooves and protuberances after curing at 120°C . It should be noted that the superhydrophobic coatings present high

cohesional strength with the substrates and are stable under corrosive conditions. It is expected that this technique will be important for potential applications in future.

EXPERIMENTAL

Methyl methacrylate (MMA) and butyl acrylate (BA), purchased from LingFeng Chemical Regent Co. Ltd. (China), were washed by 10 wt % aqueous solution of sodium hydroxide to remove inhibitor and then by distilled water thoroughly, until pH value of the washings became neutral. The washing-treated monomers were dried over anhydrous magnesium sulfate for 48 h followed by distillation under reduced pressure and then the distillates were stored in fridge. β -Hydroxyethyl methacrylate (HEMA), purchased from JingChun Regent Co. Ltd. (China) and dodecafluoroheptyl methacrylate (DFHMA, $C_{11}H_{18}O_2F_{12}$) purchased from XueJia Fluorine-Silicon Chemical Co. Ltd. (China) were used as received. Polytetrafluoroethylene (PTFE) powders were kindly supplied by XinYing Industrial Development Co. Ltd. (China). Hexamethylene diisocyanate trimer curing agent, with trademark of Desmodur N3600, was provided by Bayer Corp. (Germany). All the other reagents used were analytical grade.

Synthesis of hydroxylic fluoroacrylate resin (HFAR):

Hydroxylic fluoroacrylate resin was synthesized by free radical solution polymerization using benzoyl peroxide (BPO) as initiator in solvent under the protection of nitrogen gas. The synthesis process was employed as follows: In a 250 mL four-necked round-bottomed flask equipped with mechanical stirrer, reflux condenser, dropping funnel and inlet for nitrogen gas, 12 g MMA, 24 g butyl acrylate, 6 g HEMA, 8 g DFHMA and 100 mL butyl acetate were mixed and heated. After the solution was heated to 85 °C, a solution of 0.8 g BPO in 15 mL ethyl acetate was added dropwise into the flask. The reaction mixture was stirred isothermally at this temperature for 3 h. Afterward, another amount of 0.2 g BPO in 5 mL ethyl acetate was added into the flask followed by reaction at 85 °C for another 3 h. Upon cooling at room temperature, the resulting product was precipitated in *n*-hexane, filtered, collected and then dried under vacuum at 25 °C for 24 h. The final monomer conversion (C) was 99.2 %, which was calculated by gravimetric analysis as follows:

$$C = \frac{(W_p - W_i)}{W_m} \quad (1)$$

where W_m is the weight of total monomers, W_p is the weight of polymer synthesized and W_i is weight of initiator put into the flask. The theoretical hydroxyl content of hydroxylic fluoroacrylate resin was 1.5 %. FT-IR characterization was performed on FT-IR spectrometer (Nicolet 5700) with the results (λ , cm^{-1}) as follows: 3446 (-OH), 2800-3000 (C-H), 1728 (ester C=O), 1242 (C-F), 965 ($-C_4H_9$)¹⁷.

Preparation of composite coatings: A series of composite coatings were prepared from BPUR and PTFE by the same procedure. The fabrication process can be described as follows: to obtain BPUR solution, a certain amount of hydroxylic fluoroacrylate resin was dissolved in the mixed solvents (butyl acetate, ethyl acetate and acetone with a volume ratio of 3:3:1) and then N3600 was added with a molar ratio of NCO/OH =

1.1 followed by intensive stirring. Polytetrafluoroethylene was added into the as-prepared solution with a certain percentage by mechanical stirring and ultrasonic treatment for 0.5 h. The overall NCO/OH molar ratio was maintained at about 1.1 to ensure full reaction of OH groups.

Tin plates with a thickness of 0.28 mm were polished with metallographic abrasive papers repeatedly and then rinsed with alcohol thoroughly. The coatings on the tin plates were prepared by spraying the coating precursors with 0.2 MPa nitrogen gas and then cured at the temperature of 120 °C for 2 h. By the same procedure, the pure BPUR coating without PTFE (denoted as sample E) was also prepared as a comparison. The thickness of all cured coatings was about 50-100 μm .

Surface characterization of prepared coatings: The static water contact angles (WCA) were measured based on sessile drop method using a contact angle meter (JC2000C1 of ZhongChen Digital Technical Apparatus Co. Ltd., China). In a typical process, a deionized water droplet (*ca.* 5 μL) was dropped carefully onto the surface at ambient temperature and the images were captured using the accessory digital camera. All the water contact angle values reported herein were obtained as averages of five measurements performed on different points of the sample surface so as to improve the accuracy. The water sliding angle (WSA) was defined as the tilted angle at which a water droplet of a certain amount begins to roll off gradually inclined surface. Morphology characterization of the samples surface was conducted by using scanning electron microscopy (SEM, Hitachi S-3000N).

RESULTS AND DISCUSSION

We made a series of composite coatings based on BPUR and PTFE at different weight ratios and the wettability of the as-prepared coatings was determined by water contact angle and water sliding angle with the results shown in Table-1. It can be seen that water contact angle increased and WSA decreased with the increase of PTFE content in coatings. Sample E presented a smooth and transparent surface. The coating adhered strongly to the substrates and had a water contact angle (WCA) of 91°, indicating a hydrophobic surface. To our knowledge, water contact angle on fluoroacrylate was higher than that on ordinary polyacrylate¹⁸. This phenomenon might be attributed to the low surface energy of the coating surface derived from the migration of fluorine-containing units to surface layer during the curing process¹⁹. It was found that water contact angle increased sharply from 102° to 144° and then to 158° as the weight ratio of BPUR to PTFE changed from 2:1 to 1:1 and to 2:3. In the case of sample B, water drops could roll off easily from the surface at a tiny titling angle and even roll back and forth freely on the horizontal surface under a slight moving, which made it difficult to measure the water contact angles. When the weight ratio of BPUR to PTFE was 1:3, maximum WCA value of 161° was achieved. However, the amplitude was small relative to sample A. It should be noted that there is a tradeoff between surface roughness and mechanical properties. It is obvious that PTFE particles are helpful to construct rough structure, but high concentration of PTFE particles in coatings would weaken the adhesion force between coatings and substrates due to a

TABLE-1
SURFACE HYDROPHOBICITY PROPERTY
OF VARIOUS SAMPLES

Sample	Weight ratio of BPUR to PTFE	Concentration of PTFE (wt %)	WCA (°)	WSA (°)
A	1:3	75.0	161	1
B	2:3	60.0	158	2
C	1:1	50.0	144	51
D	2:1	33.3	102	67
E	1:0	0	91	79

possibly reason that the particles restrained the curing and cross-linking process, leading to poor scratch resistance. Therefore, weight ratio of 2:3 is the optimum proportion; the coating is of superhydrophobicity with a WCA of 158° and WSA of 2°. Fig. 1 shows the profiles of water droplets placed on the BPUR/PTFE composite coatings with different weight ratios. It was found that the shapes of water drop nearly spherical on the surfaces of samples A and B.

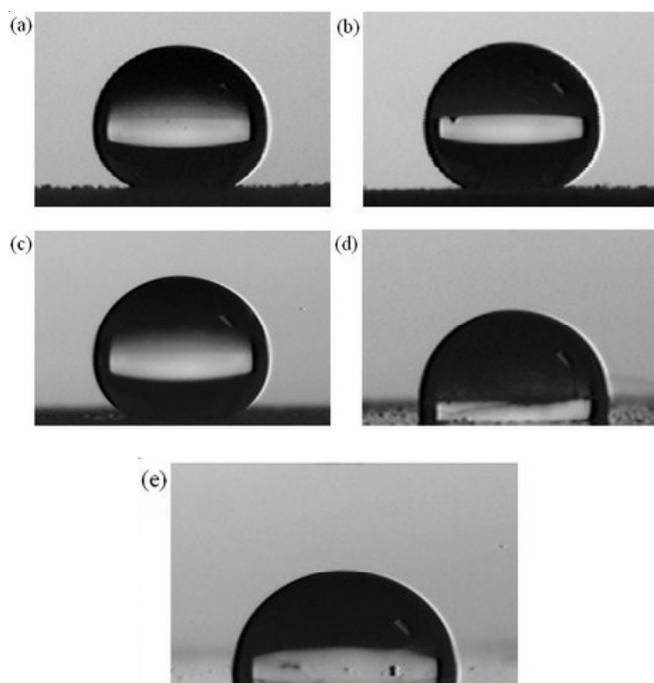


Fig. 1. Images of water drop on the surfaces of samples A (a), B (b), C (c), D (d) and E (e)

In order to get an insight of the surface morphology, the microstructures of the as-prepared coating surfaces were observed by SEM. Fig. 2 shows the SEM images of the surfaces prepared at different contents of PTFE particles. From the surface morphology of Fig. 2d, we can see the surface embedded with scattered PTFE particles, while areas surrounding them are flat. Compared to Fig. 2d, apparent fluctuation liking undulating hills with the size ranging from approximately 1–4 μm can be observed in Fig. 2c. The tremendous change in surfaces microstructure is the reason for the sharply increase of WCAs from 102° to 144°. Higher surface roughness of sample B was obtained as shown in Fig. 2b, from which we can see micro-bumps with nano-sized protuberances on the top of them. Additionally, the surface exhibits valleys and grooves on the order of 0.5–3.0 μm . The formation of irregular rough surface was ascribed to random-packed PTFE particles at high weight

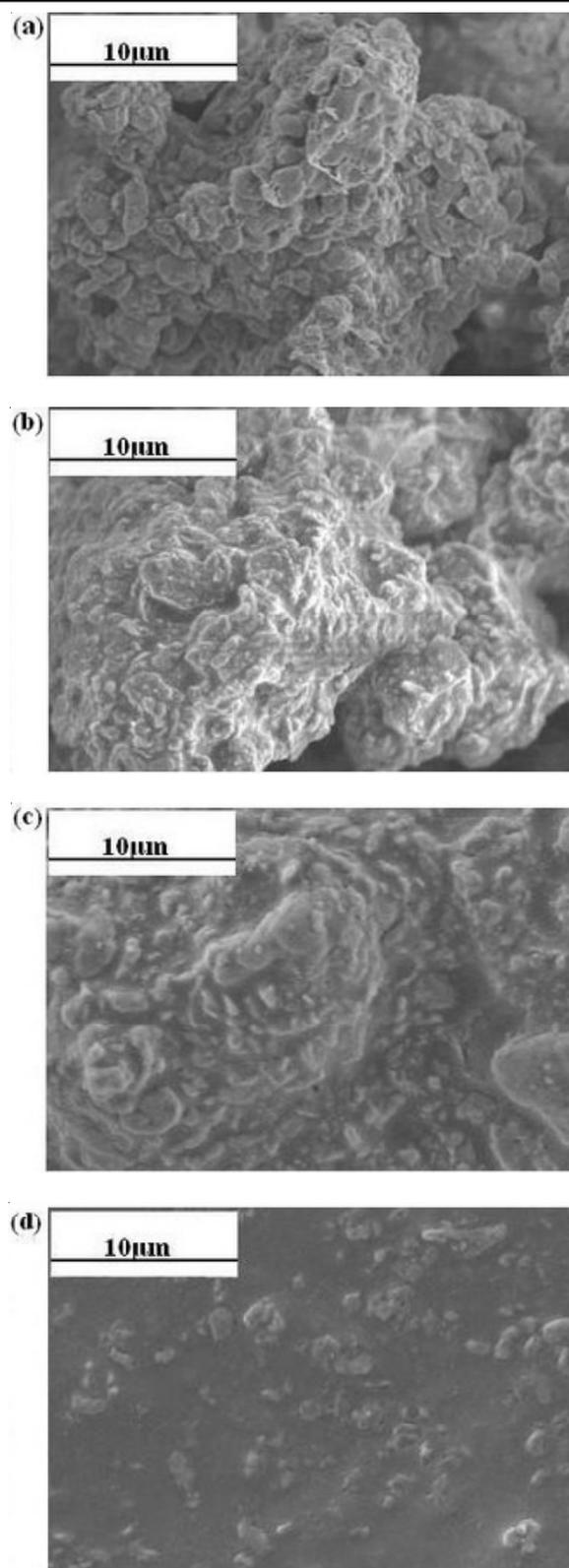


Fig. 2. SEM images of the surfaces of samples A (a), B (b), C (c) and D (d)

ratio and shrinkage of polymer chains as well as volatilization of solvent during the curing process. Upon spraying the homogeneous solution on the substrates, solvent in upper layer evaporated faster than it in bottom-layer, leading to the increase of polymer concentration and then polymer separate out on surface layer. With the solvent evaporated continuously, the remaining solvent cannot maintain all components at a

homogeneous state resulting in phase separation and the formation of rough structure. Air captured among this rough structure plays a role in air-cushion as the water droplet lies on it. This is the reason that the droplet can roll off easily from the surface and the WSA is ultralow²⁰. As the weight ratio of PTFE to BPUR was increased to 3:1, the surface morphology (Fig. 2a) was similar to that of sample B (Fig. 2b) but with a higher clarity in protuberance boundary. Similarity in microstructure of samples A and B results in almost equivalent WCAs of them. These results indicate that the weight ratio of BPUR to PTFE within a certain range dramatically influence the structures of composite coatings and related hydrophobicity.

As many literatures have reported, surface roughness plays an important role in surface superhydrophobicity. Generally, the Wenzel model and Cassie-Baxter model were proposed to explain the water contact behaviour on a rough surface²¹. The former assumed that the liquid penetrated grooves of the rough structure surface and the apparent contact angle with this model, θ_w , was given by $\cos \theta_w = r \cos \theta_i$. Here r is the surface roughness factor, defined as the ratio of the real surface area over the projected one. θ_i is the intrinsic contact angle for a flat surface of the same materials. In this model, we know that hydrophobic surface will be more hydrophobic as the surface roughness improved. However, rough structure can also increase the area of liquid-solid interface between the surface and the water droplet, leading to a high contact angle hysteresis. The latter assumed that the droplet partially wetted the rough surface due to the air trapped in the spaces of microstructures. The apparent contact angle according to this model, θ_c , was given by $\cos \theta_c = f_1 \cos \theta_i - f_2$. Here f_1 and f_2 are the fractions of liquid-solid interface and liquid-gas interface, respectively ($f_1 + f_2 = 1$). It can be deduced from this equation that the increasing in f_2 would increase θ_c . Meanwhile, since f_2 is greater than f_1 , the water droplet is unstable when it lies on such surface. For the composite coating prepared with the PTFE concentration of 50 wt %, although the WCA reaches 144°, the WSA is also as high as 51°. When a water droplet is placed on the surface, water penetrates into the microstructure and then a large area of surface is occupied by the liquid. Thus, the stick force between them is strong with the observed high WSA. For the composite coating prepared with the PTFE concentration of 60 wt %, the surface is rougher and a large amount of air is trapped in it. As a result, the WCA reaches 158°, while WSA sharply decreases down to 2°, indicating that the as-obtained coating may have important application in self-cleaning fields. The dramatic change in WSA demonstrated that a transition from Wenzel model to Cassie-Baxter model occurred as the concentration of PTFE increased in the composite coating system.

Recently, the stability of superhydrophobic surfaces subjected to solutions with a wide pH range has drawn more interest for their industrial applications. However, they only evaluated the corrosive resistance by measuring WCAs on the surface with different pH water droplets²². Here, we immersed sample B in hydrochloric acid, pure water and sodium hydroxide aqueous solutions for a period of time to investigate the stability of the coating in a wide range of pH values. The results are shown in Fig. 3. It is observed apparently that the WCAs almost keep at a constant value about 157° within the

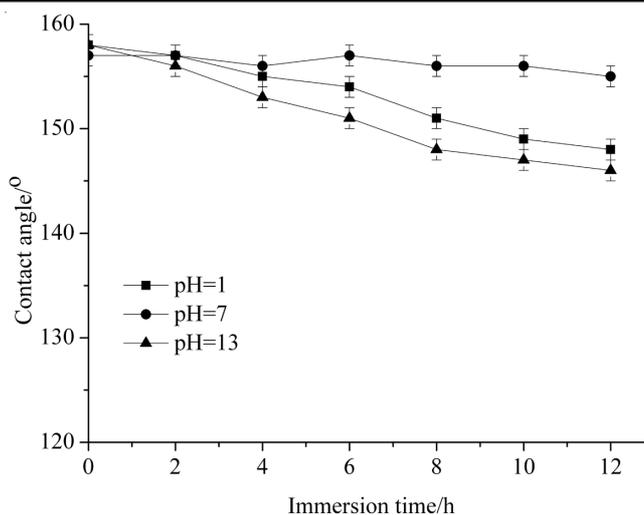


Fig. 3. Effect of immersion time on the water contact angle of sample B at different pH values

experimental error in pure water for 12 h, indicating a high stability of the coating soaking in pure water. The WCAs decrease gradually *versus* immersion time as the coatings soaking in solution of pH 1 and 13. The WCAs of acid solution and basic solution changed from 158° to 148° and 157° to 146° within 12 h, respectively. Though there is a tiny increase of WSA for acid solution and 10° increase for basic solution, the coatings retain superhydrophobicity as original state after drying at 60 °C for 15 min. The salt-resistance of sample B was tested by immersing the coating in sodium chloride solutions at the concentration of 1, 5 and 10 wt %. The result is displayed in Fig. 4, from which it is observed that there is no obvious change of WCAs in the sodium chloride solutions of 1 and 5 wt %, but a little decrease about 8° in that of 10 wt % for 12 h, indicating that the immersion time has little influence on the WCAs for the coatings soaking in sodium chloride solutions at low concentrations. The superhydrophobicity was restored after a simple heat-treatment process. Two reasons were considered to be responsible for the coatings corrosion-resistance. Fluorinated polyurethane and PTFE are the materials that intrinsically possess excellent chemical and environmental durability. Additionally, in Cassie-Baxter state, the air trapped in the surface can prevent the direct contact between corrosive solutions and surface. Both these two factors retard the deterioration process of the coating, leading to the observed high contact angle value and related superhydrophobic property. These results are of great significance of anticorrosion for the use of metal as engineering materials in corrosive environment.

Furthermore, adhesion is an important issue we need to be concerned with in view of practical applications. Superhydrophobic coatings cannot find valuable use without sufficient adhesion force. Adhesion of all prepared coatings was tested by a cross-cut test according to the standard of ISO 2409:2007. It was found that the coating showed a high rating of 0 for sample E and a relatively low rating of 3 for sample A. Adhesion decreased as the proportion of PTFE increased in the coating system. Compared to the adhesive force between BPUR and substrate, the adhesion between PTFE and substrate is smaller. As the amount of PTFE increased, contact area between BPUR and substrate decreased, leading to the decrease

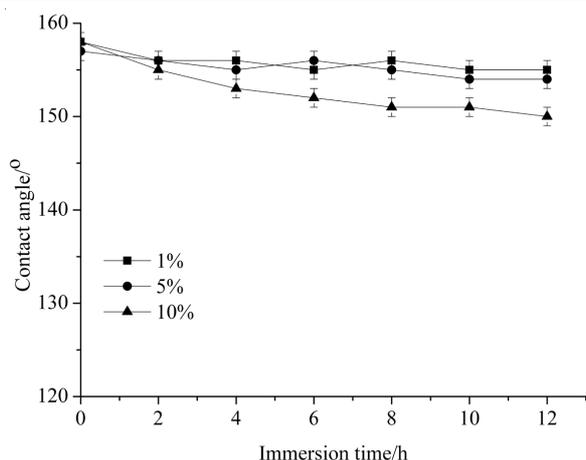


Fig. 4. Effect of immersion time on the water contact angle of sample B in different concentrations of sodium chloride solutions

of adhesion. However, in practice, a whole coating system is usually comprised of bottom coating, intermediate coating and top coating instead of each single one. So we sprayed the precursor of sample B as a top coating on epoxy-coated tin plate. It was found that the adhesion of the coating improved with a rating of 1.

Self-cleaning test of sample B was performed using sprinkled carbon black powders as pollutant. The spherical water drops rolled easily from the upper side to the lower side as the tin plate tilted at an angle of 15°. Carbon black powders were removed entirely as the water drops rolling through them, leaving a quite clean surface as shown in Fig. 5. Remarkably, the composite coatings prepared half a year before exhibited no deterioration in self-cleaning performance as they placed in ambient or high humidity environment.

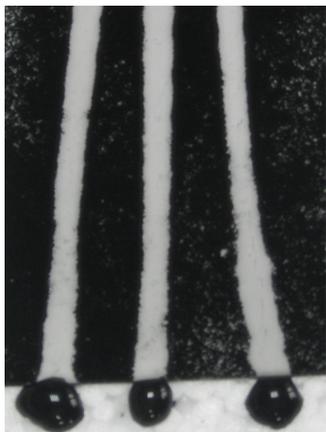


Fig. 5. Self-cleaning test of sample B

Conclusion

Superhydrophobic surface with water contact angle of 158° and sliding angle of 2° has been successfully fabricated from bicomponent polyurethane and PTFE at their weight ratio of 2/3. An irregular rough structure with grooves and protuberances was considered to be responsible for the superhydrophobicity. The composite coatings adhered strongly to the substrates and were stable not only in pure water, but also in acid, basic and salt solutions. Since the preparation technique is simple and economical, we expect that it make it possible for large-scaled application of anticorrosion and self-cleaning in practical industry.

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