

Article

Imparting Strong Antifouling Properties to the Transparent PVB Coating through the Zwitterionic Compound Condensation

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Abstract: Fouling is a ubiquitous and longstanding challenge that causes both economic and environmental problems, especially for underwater detection equipment, as fouling directly limits the normal services and functions of such equipment. Therefore, it is necessary to develop coatings with high transparency and good antifouling performance. Herein, a novel zwitterion compound was synthesized, and an antifouling coating with excellent comprehensive properties was prepared by integrating 3-[[3-(triethoxysilyl)-propyl] amino] propane-1-sulfonic acid (TPAPS) into polyvinyl butyral (PVB) polymer, which possesses excellent mechanical properties and transparency. The physical and chemical, mechanical, and antifouling properties, and the light transmittance of the coating were characterized by the SEM, FT-IR, XPS, UV-VIS. The results show that the coating had good mechanical properties and adhesion to the substrate, and the strong hydration ability of TPAPS endowed the coating with excellent resistance to oil stains and biofouling. More importantly, the structure of the coating was homogenous and its surface roughness was very little, which imparted the coating with high transmittance. This research provides a facile approach for synthesizing high-transparency materials with excellent antifouling and mechanical properties.

Keywords: anti-oil stain; antibiofouling; transparent coating; hydrophilic surface; PVB coating



Citation: Zhang, J.; Bo, S.; Feng, H.; Yu, B.; Yu, Q.; Yang, W.; Pei, X.; Zhou, F. Imparting Strong Antifouling Properties to the Transparent PVB Coating through the Zwitterionic Compound Condensation. *Coatings* **2021**, *11*, 1164. <https://doi.org/10.3390/coatings11101164>

Academic Editor: Joaquim Carneiro

Received: 30 July 2021

Accepted: 14 September 2021

Published: 27 September 2021

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1. Introduction

Marine biofouling is a major problem shared among all maritime sectors employing submerged surfaces [1], and is especially serious for maritime detection equipment, such as sensors, detection windows and optical instruments [2–4]. When detection equipment is immersed in seawater for a long time, oil stain and biological contaminants adhere to its surfaces, leading to substantially lowered operational lifespans, and loss of function if poorly addressed [5,6]. Therefore, there is a growing need for the development of antifouling technology in the exploitation of marine resources in recent decades [7,8].

Due to the toxic effect of organotin on marine ecosystems, the International Maritime Organization (IMO) completely prohibited their extensive use in the marine antifouling coatings in 2008 [9,10]; thus, marine antifouling research has been developed toward to environmentally friendly and nontoxic technologies, and antifouling coatings that are free of biocides have been extensively explored due their many advantages (unique fouling resistance, appropriate mechanical properties and other functional applications) in antifouling fields [11,12]. Among of these coatings, hydrophilic coatings have aroused intensive interesting for the feasibility of their preparation and the wide application for their strong

antifouling properties [13–15]. Hydrophilic coatings' strong antifouling capacity is mainly attributed to their high hydration entropy, which can effectively inhibit hydration exchange between biomass and substrate, and so prevent the adhesion of polysaccharides, proteins and other biomasses without biocides. Therefore, polymers with high hydration, such as hydrophilic polymer brush and hydrogen gel, are widely applied to fabricate antifouling materials [16–18]. Especially, zwitterionic polymers have attracted numerous attentions for their super hydration ability and charge effect [19–21]. A durable antifouling silicone elastomer, modified with zwitterionic silane, was fabricated by the Huang group [22], similarly, Zheng et al. prepared a homogeneous antifouling coating with functional silatrane on glass and silicon wafers [23], achieving surface modification with zwitterionic polymer. Zhou et al. prepared a series of semi-interpenetrating polymer networks to study the contribution of their charges to marine antifouling [24]. However, their poor mechanical properties, loss of light transmittance and difficulty in large-scale preparation seriously limits the application of hydrophilic materials in maritime inspection. To meet the requirements of displays and underwater sensors, these aspects must be greatly improved. Among them, light transmittance is a very critical property for aquatic detection, wherein a value above than 90% is acceptable [25,26]. Modifying suitable polymers is a promising alternative for solving the above problems, due to their unique compositions and properties.

The modification of a universal polymer ideally combines the desired performances of both materials without sacrificing functionality (high transparency, suitability for a biosensor, anticorrosion) gained by the heterogeneous structures of traditional amphiphilic materials [27]. Zhou [28] synthesized a new zwitterionic precursor and designed an antifouling coating by crosslinking it with PDMS, which can generate zwitterion in-situ under ambient environment, addressing the poor miscibility between the hydrophobic and hydrophilic ingredients of zwitterion. Zhang [29] fabricated a foldable, transparent hybrid antifouling coating with superior mechanical properties by blending amine-terminated hyperbranched polysiloxane with epoxy–zirconium particles with a zwitterionic group. These interesting studies indicate that the specific functions of a coating can be achieved by the tailoring thereto of its precursor materials. This almost infinitely modular design concept has led to the industrial application of coatings for transparent plastics, glasses, and metals for preventing mechanical abrasion, permeation, biofouling, corrosion or other adverse effects [30].

Herein, a zwitterionic precursor was designed and synthesized, and was then incorporated into polyvinyl butyral (PVB), through the facile condensation of a siloxane group, to prepare a highly transparent coating with low adhesion to oil stain, and superior fouling resistance, in which the presence of the zwitterionic group endowed the coating with excellent oil repellency and fouling resistance. PVB was adopted due to its wide application in various fields for its excellent mechanical properties and excellent optical clarity [31]. The modified PVB coating has strong adhesion to substrate, strong water resistance and good antifouling performance, and therefore has great potential application for marine detection equipment.

2. Materials and Methods

2.1. Materials and Chemical Reagents

Butvar B-76 polyvinyl butyral (PVB, chemical pure, $M_w = 90,000\text{--}120,000\text{ g}\cdot\text{mol}^{-1}$) and ethylene glycol butyl ether (EGBE, analytically pure) were provided by Meryer Chemical Technology Co., Ltd. (Shanghai, China). The PVB was comprised of vinyl butyral, vinyl alcohol, and vinyl acetate, about 88%, 11–13% and around 1%, respectively (molar ratio). 1,3-propanesultone (analytically pure) was purchased from Energy Chemical Reagent Co., Ltd. (Shanghai, China), and 3-triethoxysilyl-1-propanamine (KH-550, analytically pure) and 3-glycidoxypolytrimethoxysilane (KH560, analytically pure) were obtained from J&K Chemical Ltd. (Shanghai, China). Acetonitrile (CH_3CN , analytically pure) was purchased from Lian-Long Bohua (Tianjin) Pharmaceutical Chemical Co., Ltd. (Tianjin, China). Fluorescein isothiocyanate labeled bovine serum protein (FITC-BSA) was pur-

chased from Beijing Solarbio Science & Technology Co., Ltd. (Beijing, China), and PBS powder (PH = 7.4, chemical pure) was from Shanghai McLean Biochemical Technology Co., Ltd. (Shanghai, China). *Porphyridium* sp., *Navicula* sp., and their respective culture media, Kock and Erdschreiber, were supported by Freshwater Algae Culture Collection at the Institute of Hydrobiology. Unless otherwise specified, the chemicals were used without further purification. The deionized water was prepared in the laboratory.

2.2. Preparation of Hybrid Zwitterionic Precursor

The precursor 3-[[3-(triethoxysilyl)-propyl] amino] propane-1-sulfonic acid (TPAPS) with antifouling activity was synthesized according to the procedure in reference [32]. Briefly, 0.01 mol KH-550 was dissolved using 60 mL anhydrous CH_3CN in a three-neck flask, and stirred under an inert atmosphere for 15 min to remove oxygen. Subsequently, an equivalent molar 1,3-propanesultone was added during 30 min, and the mixture reacted for one hour under room temperature. Then, the system was refluxed for an additional 24 h under 88°C to obtain a milk-white suspension. Notably, the mixture was stirred constantly over the entire reaction. The suspension was subjected to centrifugation, and washed with acetonitrile three times to remove any remaining reactant. Importantly, it was necessary to control the anhydrous environment during the entire preparation process of TPAPS. Finally, the precipitate was dried under vacuum at 40°C for 24 h, and a white powder was obtained. The NMR information of the product was as follows: ^1H NMR (400 MHz, D_2O): $\delta(\text{ppm})$: 4.00–3.81 (m, 2H), 3.65 (q, $J = 7.10$ Hz, 2H), 3.44–3.30 (m, 1H), 3.27–3.14 (m, 3H), 3.12–3.05 (m, 2H), 3.02 (t, $J = 7.30$ Hz, 3H), 2.15 (m, 2H), 1.88–1.54 (m, 3H), 1.33–1.21 (m, 3H), 1.18 (t, $J = 7.10$ Hz, 3H), 0.76–0.62 (m, 2H); ^{13}C NMR (400 MHz, D_2O): $\delta(\text{ppm})$: 57.37, 49.77, 47.83, 46.08, 21.26, 19.44, 16.75, 8.68. The characteristic chemical shifts of TPAPS were assigned in the NMR spectroscopy in Figure 1, and a distinct characteristic peak of $(m+\text{Na})/z$ is shown in the high-resolution mass spectrum (Figure S1).

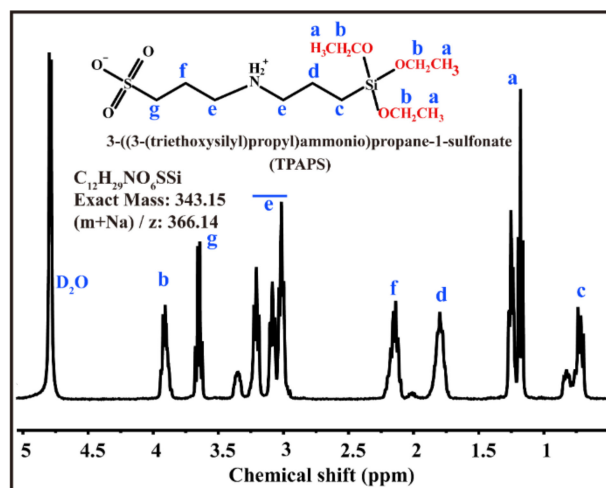
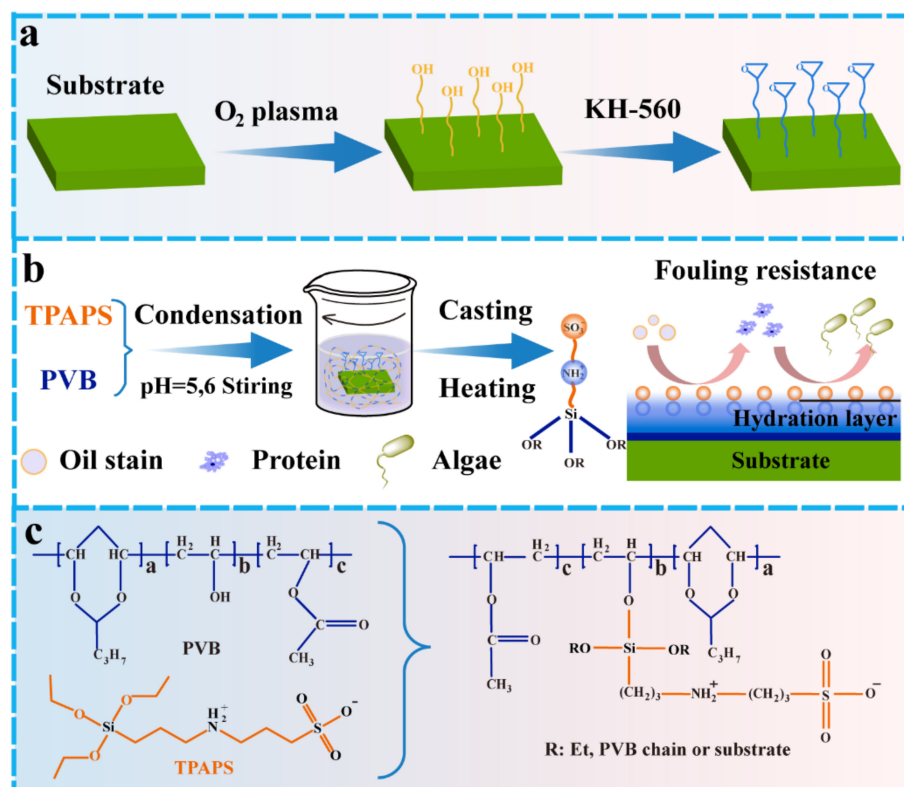


Figure 1. The molecular structure of the designed hybrid precursor (TPAPS) and its corresponding ^1H NMR spectrum; D_2O was used as the solvent for the NMR characterization, and tetramethylsilane was used as an internal standard.

2.3. Preparation of the Zwitterionic Component Embedded in PVB Coating

The PVB-TPAPS coatings were prepared as shown in Scheme 1. First, 0.3 g PVB and 25 g EGBE were mixed in a beaker and magnetically stirred for 30 min to obtain a transparent polymer solution, labeled component A. Afterwards, 0.1 g of zwitterionic precursor was dissolved in 10 g deionized water to obtain component B. Then, components A and B were mixed according to the specific proportion in Table 1, and some acetic acid was added to adjust the pH to 5–6. The mixture system was then stirred for 6 h at room temperature to promote the hydrolysis of TPAPS' triethoxy group to obtain silanol.

Subsequently, the silanol group can condense with various of active groups, such as the hydroxyl group of the PVB chain, the epoxy group and the amino group on the surface of the substrate, as well as itself to form a cross-linking network [33–35]. Before the coating preparation, a layer of KH560 was assembled on the glass substrate to improve the adhesion of the coating to the substrate (Scheme 1a). Finally, the prepared reaction solution was cast and leveled on the glass sheet (0.15 g/cm^2), curing at 40°C for 4 h and 80°C for 6 h, respectively, to fabricate the transparent antifouling coating. For convenience, the coating was named as PVB-X% TPAPS, according to the mass ratio of the zwitterionic precursor to PVB, where X was 10, 20, and 30 in different coatings.



Scheme 1. A schematic illustration of the preparation of transparent coating with fouling resistance. (a) The assembly process of the KH560 molecular layer, (b) the procedure of preparing the PVB-X%TPAPS coatings, (c) the molecular formulas of PVB, TPAPS and the schematic diagram of the condensation reaction between them.

Table 1. The composition formulas of different samples.

Sample	Component A/g	Component B/g
PVB	10	N/A
PVB-10%TPAPS	10	1
PVB-20%TPAPS	10	2
PVB-30%TPAPS	10	3

2.4. Characteristics of the Physicochemical Properties of the Coatings

Using a DSA-100 optical contact angle meter (Kruss Company, Ltd., Hamburg, Germany), the surface wettability of the coating was characterized by the contact angle (CA) of water droplets ($5 \mu\text{L}$) at 25°C in the atmosphere, three CAs from random regions of each sample were tested, and the average the angles was taken as the result. The surface chemical composition was characterized by Fourier transform infrared spectrometer (FTIR, Nicolet iS10, Thermo Scientific, Waltham, MA, USA) and X-ray photoelectron

spectroscopy (XPS, Thermo Scientific, ESCALAB 250Xi), in which the attenuated total reflection mode was applied and the infrared spectra were recorded ranging from 4000 to 400 cm^{-1} with a resolution of 4 cm^{-1} , while a Al K α radiation was used for the XPS characterization. The surface morphologies of the coatings were inspected by scanning electron microscopy (FE-SEM, JSM-6701F) at 10 kV. Surface roughness was measured by a non-contact three-dimensional profilometer (Dataphysics, SPA25, 10 $\times$ lens). Each coating was tested randomly in three different regions. Apparent roughness is expressed as the root-mean-square of height (S_q). For each scanning area, the software automatically provides the corresponding S_q value, and the average of three dependent tests was calculated to express its final roughness. The thermal stability of the coating was analyzed by Differential Thermogravimetry (DTG, NETZSCH-Gerätebau GmbH, Wittelsbacherstraße, Germany STA449F3) in the N_2 atmosphere with the heating rate 10 K/min, and there was no preheating treatment before the test. The transmittance of the coating was measured by UV-VIS spectrophotometer (UV-2600, Shimadzu, Japan). The wavenumber ranged from 200 to 800, and the primitive glass plate was adopted as the control group.

2.5. Characteristics of the Mechanical Properties of the Coatings

As Scheme 1b indicated, the precursor solution was casted in the polytetrafluoroethylene (PTFE) substrate to prepare the PVB-X%TPAPS coating, and the tested samples were prudently peeled off when the PFPE substrate panel was heated for one hour at 60 °C in an oven. The tensile test was conducted by an electrical universal material testing machine with a 500 N-load cell (EZ-Test, SHIMADZU). To ensure the sample was broken at the middle position when stretched, the peeled coating was cut into a standard dumbbell-shaped strip by a steel cutter. The length of the sample was 12.5 mm, the width was 2 mm, the thickness was approximately 0.15–0.2 mm, and the moving speed of the upper clamp was 5 mm/min. Strain was calculated from the tensile displacement divided by the gauge distance, the stress was obtained from load divided by the section area of the sample, and the elastic modulus was calculated from the slope of linear region (0.5–1.5%) of tensile stress versus the strain curve. Samples of each coating were tested in triplicate, using three independent duplicates. Furthermore, a knife-scratch test, based on the ASTM D3359-09 standard, was performed to evaluate the adhesion between the coating and substrate [36]. The coating on the PVC substrate was cut by a knife to form multiple grid shapes, followed by a quick-stripping experiment using 3M tape to observe the peeling state of the coating on the small squares, and then determined the adhesion classification according to the ASTM D3359-09 [37].

2.6. Characteristics of Anti-Oil Adhesion Property of Coating

Testing of the underwater anti-adhesive behavior of the coating was carried out in a square channel filled with water. The coating was fixed on triangle brackets at an inclination of 30 degrees, and for visual observation, the coatings were applied to the glass sheet and white paper was placed as a background. Then, crude oil was dripped evenly onto the coating and the state of the oil drops on the coating surface was recorded by a camera (ISO: 200, exposure time: 1/60 s). In addition, to quantitatively measure the adhesion of oil stain to the coating's surface, n-hexane was also used as a model stain to evaluate the adhesion force on these coatings. When testing, the cantilever containing the oil drops was adjusted to a suitable position, then moved downward by 3 mm at a constant speed, and finally returned upward to its original equilibrium position. The mass change of the oil stain on the cantilever was recorded by the microbalance (DataPhysics Instruments TCAT 11, DataPhysics Instruments GmbH, Raiffeisenstraße, Filderstadt, Germany) during the entire process, and droplets wiped from the coating surface was used to express adhesion to the contact surface.

2.7. The Resistance for Protein Settlement of Coating

The FITC-BSA was adopted for the protein adsorption test. Prior to testing, these coatings were cut into $1 \times 1 \text{ cm}^2$ pieces and immersed in PBS (pH = 7.4) for 4 h to achieve swelling equilibrium. Subsequently, the coatings were dried with filter paper and transferred into small vials to which 5 mL FITC-BSA (0.2 mg/mL) solution was added. The vials were incubated in the dark for 4 h at 37 °C to avoid the fluorescence quenching of FITC-BSA. After adsorption, the samples were rinsed with PBS three times to remove the non-adhered protein. The adsorption behavior of the proteins was inspected by a laser scanning confocal microscope (LSCM, Olympus, FV1200, magnification $10\times$) under the standard conditions (excitation wavelength, exposure intensity, contrast, brightness). The average fluorescence intensity emitted by the adsorbed FITC-BSA was calculated by the software Image J ($2 \times 2.1.4.6 \text{ ud4}$) according to the literature [38]. In short, all images were converted into gray-scale images, and the average gray values of the images were calculated by the software Image J, and the average number of gray values over ten images was regarded as the amount of protein adsorption.

2.8. The Resistance for Marine Algae of Coating

Testing of the coatings' anti-biofouling performance was performed by employing two kinds of marine algae in laboratory conditions. The protocols of this assessment are shown in our previous research [39]. In short, the algal density of the suspension was constant, at $5 \times 10^6/\text{cm}^3$. The samples were cut into blocks (area of $1 \times 1 \text{ cm}^2$) and placed individually in Petri dishes. Subsequently, 6 mL of algae suspension was poured into each dish. After 24 h incubation in an incubator, fluorescence images were acquired by microscope to determine the number of attached algae. Ten fields of view, each at 0.14 mm^2 , were captured for each sample, and the average densities were regarded as the algal quantities adhered to the surfaces.

2.9. The Marine Field Test of Coating

Marine are typical fouling environment due to their diversity of fouling organisms and the biofouling are detrimental to devices in marine, as they cause severe corrosion due to the changes in temperature, salinity and pH of sea water caused by ocean current movement. To comprehensively inspect the antifouling capacity and the mechanical stability of the coatings under realistic circumstances, marine field tests were performed at Daya Bay Marine Biology Research Station, Chinese Academy of Sciences, in April 2021, for 15 days. The temperature of the seawater ranged 25 °C from 28 °C, the salinity was below 35‰, and there was no large fluctuation in temperature or salinity. The samples ($15 \text{ cm} \times 15 \text{ cm} \times 5 \text{ mm}$) were applied to PVC sheets without any pretreatment, and the edges of the samples were sealed with a mixture of paraffin and rosin (mass ratio 1:1). For testing, the samples were immersed in seawater at a depth of approximately 2–3 m. After 15 days, the coated panels were retrieved and their antifouling properties assessed, after washing with seawater.

3. Results and Discussion

3.1. The Physicochemical Properties of the Coatings

Surface wettability is a crucial physicochemical property indicating the interaction between coating and a surface-contact liquid, and, furthermore, determined the contact state between the coating and a fouling substance by changing the swelling performance of its surface in a seawater environment. The wettability of the coating was evaluated using contact angle (CA), as shown in Figure 2a. After being wetted with dropped water for 5 s, the CA was captured. The CA of the PVB coating was 88°, and them of other coatings was 70°, 62° and 38°, with the increase of the zwitterionic compound TPAPS. Additionally, immersion testing of the coatings for different durations was conducted. As Figure S2 shows, the CA of pure PVB was almost unchanged throughout the test. For the PVB-10% TPAPS and PVB-20% TPAPS, swelling equilibrium was reached after immersion in water

for three days, after which CA remained constant. The CA of PVB-30% TPAPS continued to decrease; after three days, many wrinkles were present and contact angle could not be measured. These results indicated that the introduction of zwitterions into the PVB chain effectively improved the wetting ability of the coating and promoted the formation of a stable hydration layer, indicating a strong antifouling ability due to the hydration entropy effect. In addition, the quality of the PVB coating, modified by TPAPS, was studied through its thermal stability, as shown in Figure 2b. The PVB and TPAPS coatings showed only one peak on their DTG curves, at 394 °C and 268 °C, respectively. For the PVB-10% TPAPS coating, there was only one maximum weight-loss rate. For PVB-20% TPAPS and PVB-30% TPAPS, there were two peaks of weight-loss rate, between 268 °C and 394 °C. In addition, the decomposition temperature gradually decreased from 350 °C to 300 °C along with the increase in TPAPS, and the corresponding residual mass of the coatings also slightly increased (Figure S3). These results indicate that TPAPS was successfully integrated into the PVB matrix.

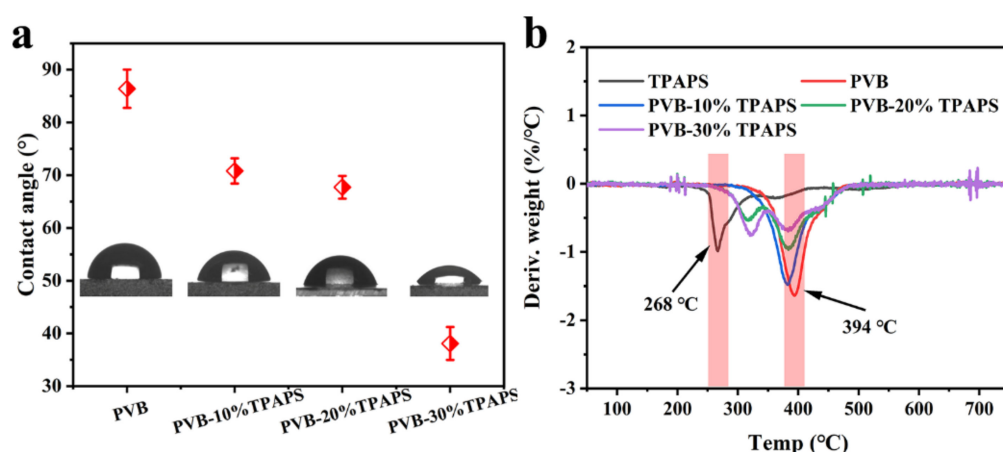


Figure 2. The surface wettability and thermal stability properties of PVB-X% TPAPS. (a) Water-droplet contact angles of the coatings; insets are corresponding images. (b) The derivative thermogravimetric (DTG) curves of the coatings.

As Figure 3a shows, when TPAPS was introduced into the PVB chain, the characteristic stretching vibration peak at 3540 cm^{-1} of its hydroxyl group disappeared and a stretching vibration peak at 3450 cm^{-1} and a bending vibration peak at 1630 cm^{-1} of its amino group could be observed. Meanwhile, with the increase of TPAPS, the characteristic absorption peaks (1170 cm^{-1} , 1040 cm^{-1}) of the $\text{S}=\text{O}$ bond became more apparent. Importantly, the characteristic absorption peak (1700 cm^{-1}) of the carbonyl group had tended to shift to low-wavenumber regions and the absorption intensity was increased, which are attributed to the fact that the addition of the zwitterion promoted association between molecules, resulting in the decrease of the intramolecular force constant and the increase of the molecular vibration dipole moment of the carbonyl group [40]. Furthermore, XPS spectroscopy was also applied to characterize surface element changes (Figure 3b–d). After integrating TPAPS to the PVB network, the characteristic absorption peaks of Si 2p and S 2p affiliated with TPAPS appeared in the full spectrum of the XPS, which can be more clearly observed from their fine spectra in Figure 3c–d.

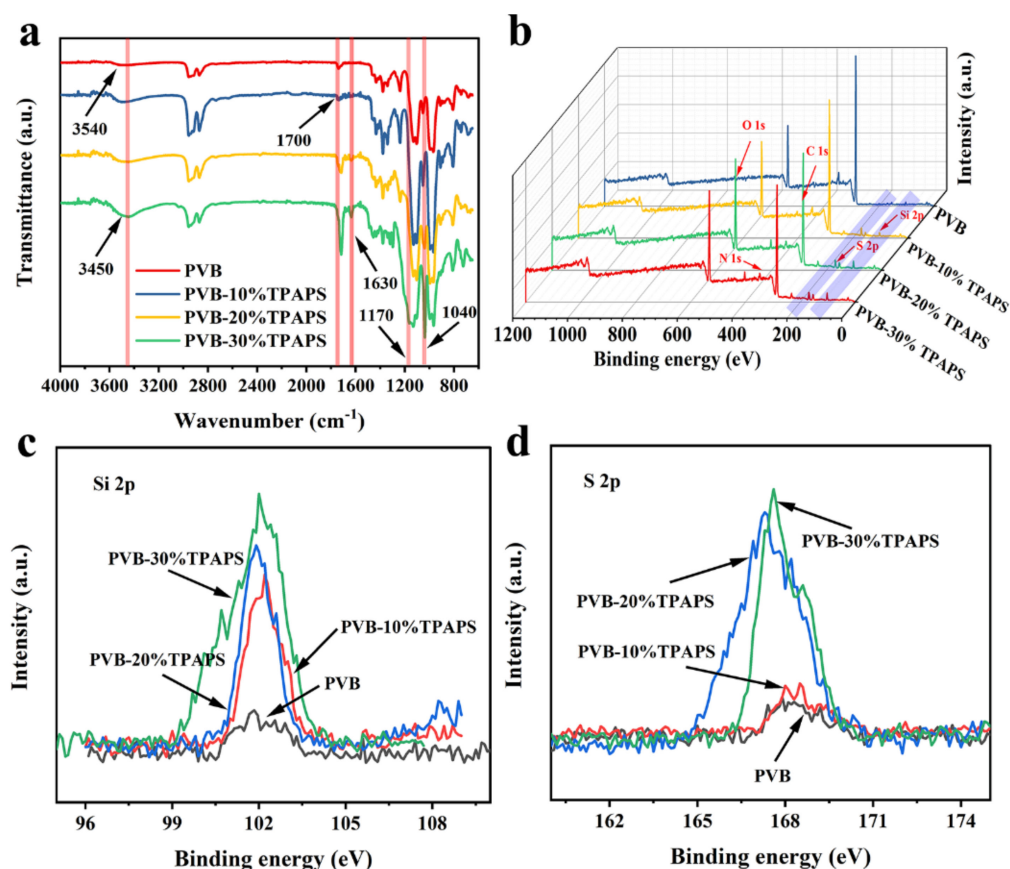


Figure 3. Analysis of the surface chemical composition of PVB-X% TPAPS coatings. (a) The FTIR spectrum, (b) the XPS full spectrum and fine spectrum of characteristic elements Si 2p (c) and S 2p (d), respectively.

Considering the coating properties are not only determined by the chemical composition, but also subject to the microstructure, the surface morphology of the coating was inspected. As shown in Figure 4a,b, all the coating surfaces and section area were smooth without any wrinkles and apparent defect, which indicated that the zwitterionic compound TPAPS were well compatible with the PVB polymer network. Therefore, the compromise of other functional properties of the coatings caused by the unintended local phase separation was effectively avoided, such as of the mechanical properties and optical transmittance [27]. As illustrated in the three-dimensional profile images in Figure 4c, the surface roughness of the coatings gradually increased from 230 nm to 430 nm with the increase of TPAPS. These results were consistent with the discussion of previous surface wettability.

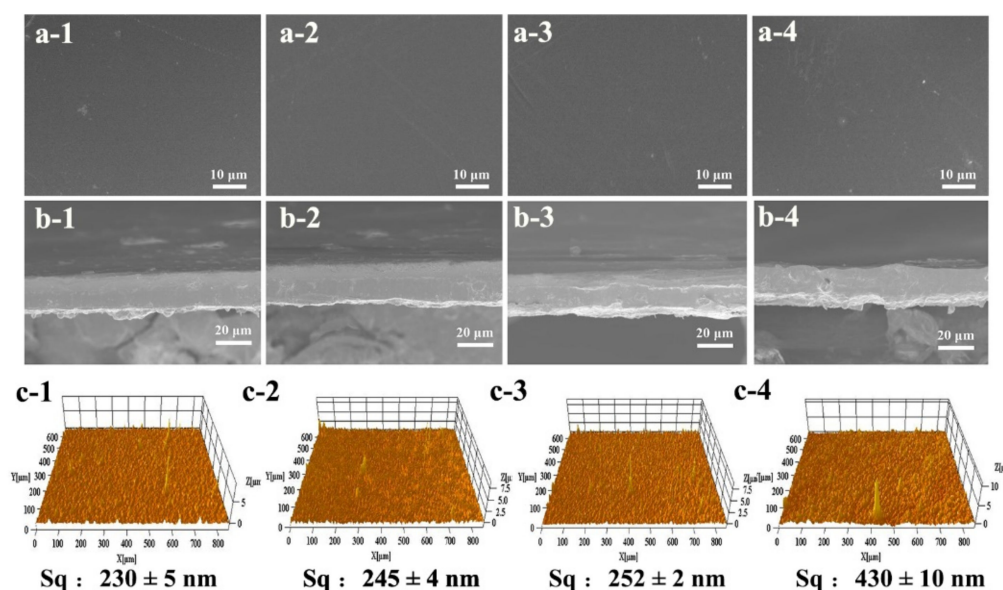


Figure 4. Characterization of surface morphology and roughness of PVB-X% TPAPS coatings. The SEM images of surface (a,b) section morphology, (c) typical three-dimensional contour height images of the coating surfaces for (1) PVB, (2) PVB-10% TPAPS, (3) PVB-20% TPAPS, (4) PVB-30% TPAPS and their corresponding roughness, respectively.

3.2. The Mechanical Properties of Coating

The mechanical properties of the coating were characterized by tensile tests. The results show that the PVB coating possessed the lowest elongation and the strongest breaking strength, and there was no obvious yield process. Interestingly, when the TPAPS content exceeded 20%, obvious yield and necking process emerged in the stress-strain curves. Meanwhile, with the increase of TPAPS, the breaking strength and yield strength of the coating first grew and then shrunk, and the corresponding elastic modulus continuously decreased. However, compared with the counterparts of the PVB coating, the break elongation kept increasing, from 8% for the PVB-10%TPAPS to 22% for the PVB-30%TPAPS sample (Figure 5a,b). These results were caused by the fact that zwitterionic TPAPS bonds to the PVB polymer network in a silicon-oxygen bond, and the PVB polymer networks had sufficient flexibility to develop an almost perfect homogeneous distribution of the internal structure. The previous surface morphology characterization also has provided favorable support for this conclusion. In addition, the interface adhesive ability of the coatings was measured according to the standard ASTM d3359, in which the standard operating method and the grade-level by which to value the extent of the adhesion of the coating were described. For the standard operating method, grade 5B indicates the strongest adhesion to a substrate and 0B means the poorest adhesion [41]. As shown in Figure 5c, for PVB and PVB-10%TPAPS coatings, the intersection of the incision was completely smooth after testing; the small grid did not fall off, and the remaining coated parts even withstood quickly peeling 3 M tape from it. As a result, their corresponding adhesive grades were 5B, based on the ASTM d3359. While for the PVB-20%TPAPS and PVB-30%TPAPS, in whose peel tests only a small amount of coating peeled off, their adhesive grade was 4B (Figure 5d). These test results demonstrate that the coating modified with zwitterionic TPAPS possessed good adhesive capability to their substrates and provide a promising prospect for practical application.

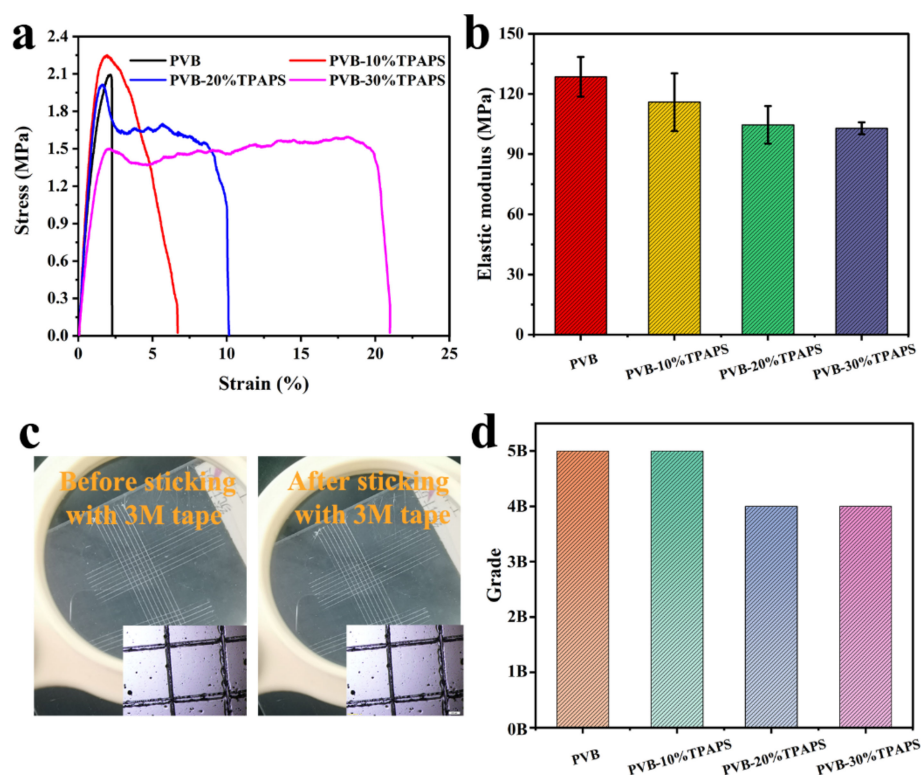


Figure 5. The mechanical properties and adhesion determinations of the coatings by a cross-cut test. (a) The stress–strain curves and (b) their corresponding elastic modulus. (c) Digital photographs of the PVB-10%TPAPS coating before and after peeling with 3M tape, the bottom right of the image is the microscope photo of the grid. (d) Corresponding statistical chart of the adhesion classification of PVB-X% TPAPS coatings.

3.3. The Light Transmission Properties of Coating

The high transparency for underwater detection equipment is necessary, due to its service behavior. Therefore, the transmittance of the coating applied to a glass sheet with high transparency was measured by a UV photometer (Figure 6). Obviously, in the visible light region (400–800 nm), compared with the original or PVB-only coated plates, the transmittances of the PVB-X% TPAPS coatings were slightly reduced, but they all maintained a transmittance above 90%, and were nearly the same as the primitive glass slide (92%) (Figure 6a). To further determine the water resistance and stability of the coating, the change in light transmittance of the coating before and after immersion in water was explored as well. As shown in Figure 6b, the PVB-30%TPAPS coating has apparently swelled and partially turned white after having soaked in water for 7 days, inducing a blurry background. Although for the other coatings (PVB-10%TPAPS and PVB-10%TPAPS), transmittance saw a slight decline, they remained in their initial state, and the characters written to the background behind the coating was still legible; these results indicate that very good light transmittance and water resistance of the coatings was achieved by adjusting their TPAPS content.

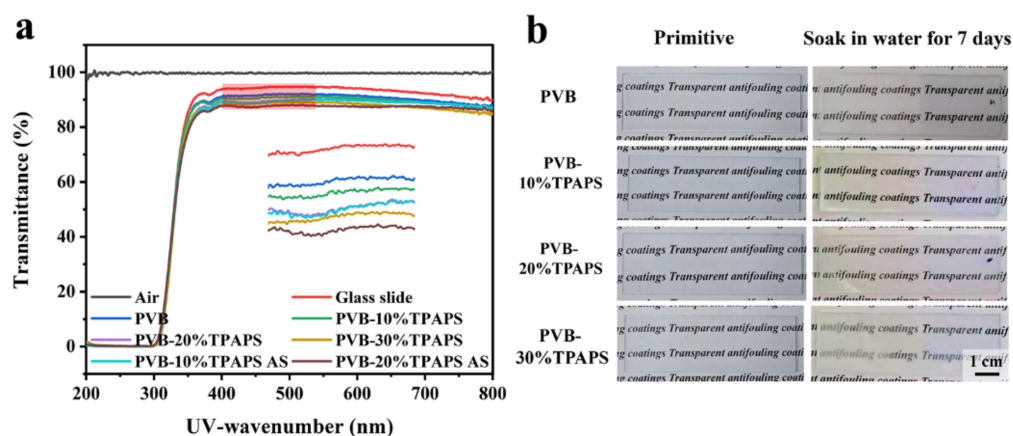


Figure 6. Optical transmittances of the PVB-X% TPAPS coatings. (a) Transmission curve of visible light (400–800 nm) compared with the glass slide and (b) photographs of coating before and after soaked in water for 7 days.

3.4. The Anti-Oil-Adhesion Properties of the Coatings

Due to tanker transportation accidents or oil leakage from offshore platforms, oil contamination has been a serious problem for marine equipment. The two representative oil stains were used to study their adhesion behavior on the surfaces of the coatings. As the demonstration in Figure 7a,b, for the pure-PVB coating, the crude oil flowed in a stream, and there was a large amount of residual crude oil along the flow path. When the coating was removed from the water tanker, serious contamination on the coating's surface was obvious. However, for PVB-20% TPAPS, the crude oil continuously rolled down, and there was almost no crude oil residual on the surface (Figure 7c,d). On the other hands, n-hexane measurements were taken to accurately assess its adhesion to the coating surface, due to its lower surface tension and susceptibility to oil stain (Figure 7e–g). For the PVB coating, when the n-hexane droplets reached its surface, it vibrated violently, hence, in the curve, a large jump emerges. While the oil droplets receded after full exposure, some liquid residue remained on the substrate (inset of Figure 7e), which indicated that the adhesion of the n-hexane droplet to the coating was greater than its cohesive energy, therefore adhesion force of the n-hexane to the PVB coating was invalid. However, for the other coatings, when the n-hexane was completely wiped from the surfaces, no residue remained. Importantly, the observed adhesion force of n-hexane to the coatings decreased with the increase of TPAPS (Figure 7g), which was mainly attributed to the gradually improved hydration ability it provided. These results indicate that TPAPS can effectively decrease oil's adhesion to a PVB coating, therefore, more practical applications of the PVB-X% TPAPS beyond its efficacy in light transmittance coating can be expected.

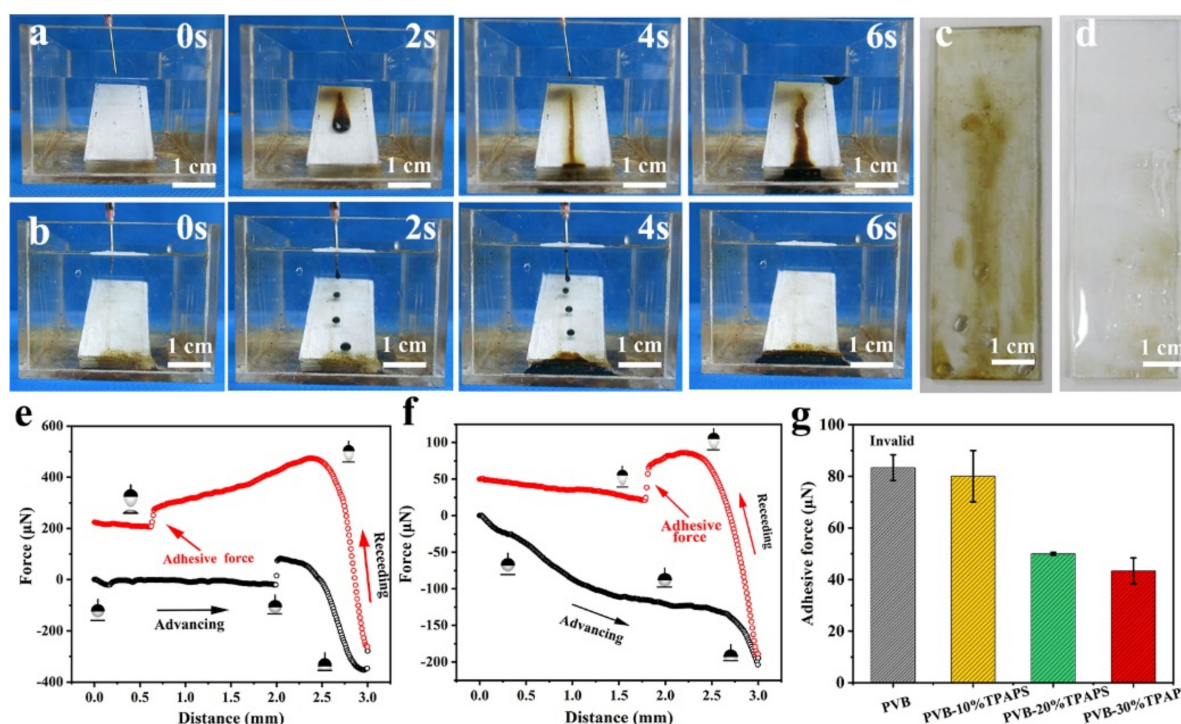


Figure 7. The anti-contamination properties of the PVB-X% TPAPS coatings. Selected snapshots show the crude oil impinging on the coated surfaces for the PVB coating (a) and the PVB-20% TPAPS coating (b) at various times; the optical photographs of the PVB (c) and PVB-20% TPAPS (d) were taken from the water tank when the tests had finished; the typical underwater adhesive curves of the PVB coating (e) and the PVB-20% TPAPS coating; (f) the statistical adhesive forces of n-hexane on the coatings (g), the insets illustrate the oil-drop state at different time periods.

3.5. The Resistance Capacities of the Coatings to Proteins

When the test surfaces were immersed in a marine environment, biofouling generally occurred by the formation of a condition film in seconds or minutes, in which protein adsorption was closely involved. Afterwards, this quick propagation and aggregation of bacteria, algae and other microorganisms caused irreversible macro biofouling, which is the reason that resistance to proteins is of such great significance for antifouling coatings. Here, the extensively used FITC-BSA was chosen as a model protein to investigate the effect of TPAPS content in a PVB coating on its resistance to protein adsorption. As shown in Figure 8, stronger fluorescence implied more protein adsorption at the surfaces. The experimental results show that the anti-protein adsorption ability of the PVB coating was significantly enhanced by introducing TPAPS, as the corresponding fluorescence intensity decreased from 155 to 50. Additionally, increasing the amount of TPAPS in the coating also increasingly augmented its protein adsorption-restraining capacity (Figure 8), which is attributed to the strong hydration ability induced by the high-density molecular water layer on the solid surface. The TPAPS-modified PVB coating showed strong ability in reducing protein adsorption on the surface [42].

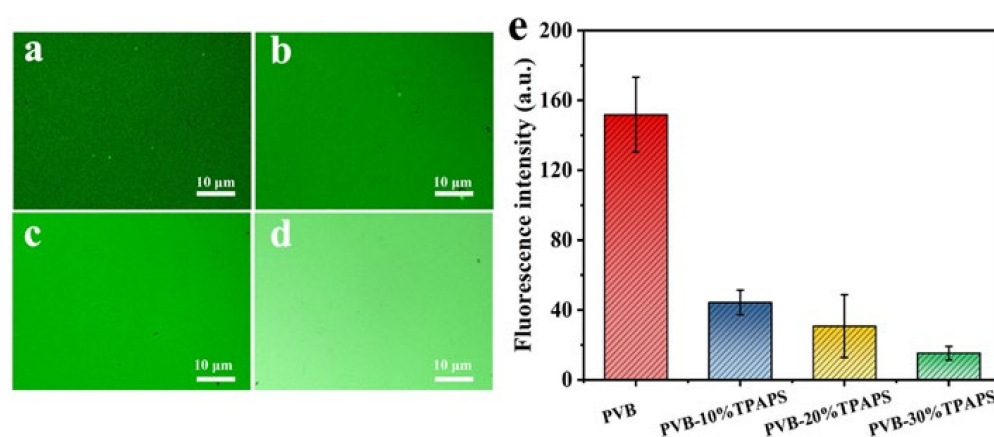


Figure 8. The representative fluorescent images of (a) PVB, (b) PVB-10%TPAPS, (c) PVB-20%TPAPS and (d) PVB-30%TPAPS after the adsorption of FITC-BSA. (e) The statistical fluorescence intensity for PVB-X%TPAPS coatings calculated from corresponding fluorescent images. Error bars represented the standard deviation of six independent duplicates.

3.6. The Antifouling Capacity for Marine Algae of Coating

After the protein adsorption test, anti-algae-adhesion tests were conducted, employing two kinds of typical fouling algae. It was apparent that both algae caused severe fouling of the PVB coating, though the number of adhered algae was notably diminished for the coating containing zwitterionic compound TPAPS (Figure 9a,b). According to the statistical chart, for *Porphyridium* sp., adhesion density diminished from 5140/mm², for PVB-only, to 60/mm² for PVB-30% TPAPS. Importantly, compared with the PVB control sample, the corresponding antifouling ratios were all above 96% for the coatings with TPAPS. Moreover, for the diatom *Navicula* sp., the adhesion density decreased from 1420/mm² for the PVB-only coating to 90/mm² for the PVB-30%TPAPS coating, and the corresponding antifouling ratios were 82%, 93% and 94% for PVB-10%TPAPS, PVB-20%TPAPS and PVB-30%TPAPS coatings, respectively (Figure 9c,d). For both attachment and separation of cells from solid surfaces, the interaction between them is defined by various types of surface forces, including van der Waals, structural, electrostatic [43]. Among of them, steric forces were the important component, here, for defining the proneness of cells to adhesion [44]. Interestingly, although the surface roughness (430 nm) of PVB-30%TPAPS was the greatest, it also showed the strongest resistance to algae, which was attributed to the fact that the roughness was much smaller than the size of the algae cells. These results demonstrate that a proper content of TPAPS can significantly improve the anti-algae-adhesion capacity of a PVB coating.

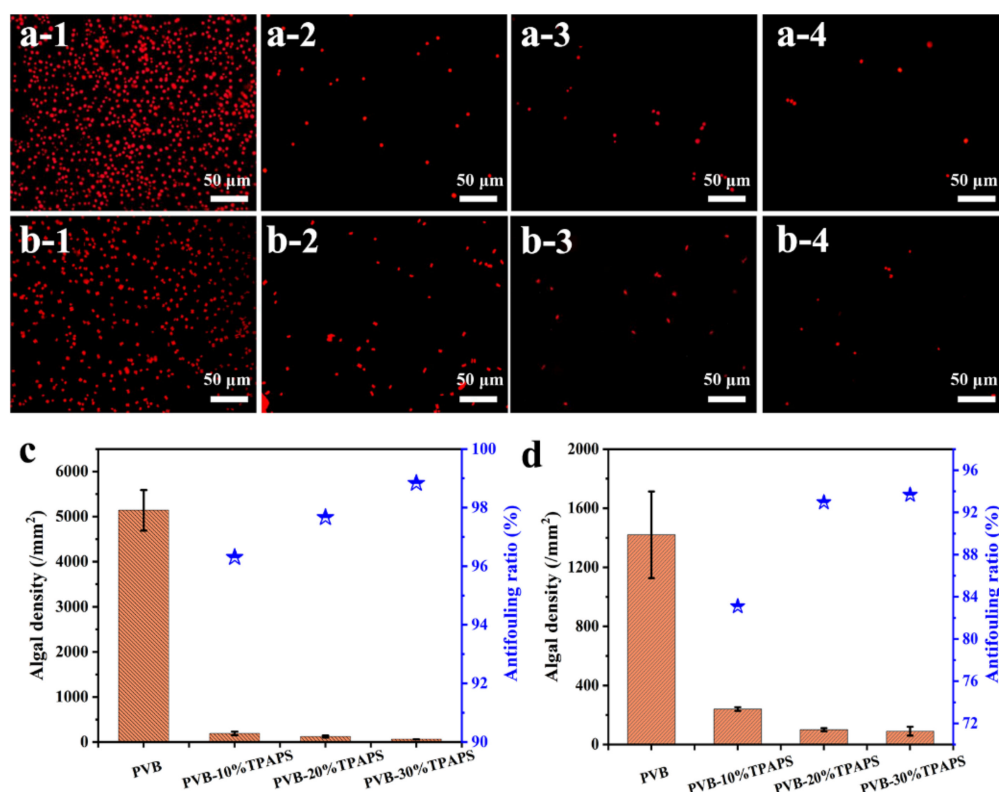


Figure 9. Anti-algae-adhesion performance of PVB-X%TPAPS coatings. The typical fluorescence microscopy images of the adhered *Porphyridium* sp. (a) and *Navicula* sp. (b) for PVB (1), PVB-10%TPAPS (2), PVB-20%TPAPS (3) and PVB-30%TPAPS (4) after 24 h incubation. The statistical charts of adhesive algae densities and their antifouling ratios (the blue stars) for *Porphyridium* sp. (c) and *Navicula* sp. (d), respectively.

3.7. The Marine Field Test of the Coatings

Actual marine field testing is a more visual and effective method for evaluating both the antifouling performance and the stability of the antifouling materials. The typical fouling organism, the barnacle, is commonly used to evaluate the antifouling performance of hanging plates, due to their special adherence properties [45]. The marine field tests of our PVB coatings modified with TPAPS, were conducted using barnacles, and the number of adhered barnacles was measured. As Figure 10a shown, for the PVB coating, numerous barnacle larvae had adhered to the surface after 15 days of immersion; it is reasonable to assume that serious macro biofouling would, in a real-world setting, happen quickly. Whereas TPAPS-modified coatings effectively prohibited the adhesion of barnacles. As our statistics show in Figure 10b, the number of adhered barnacles were 72, 45, 12, 7 for PVB, PVB-10% TPAPS, PVB-20% TPAPS, PVB-30% TPAPS, respectively. Moreover, the background behind the coating was still clear after the sludge was removed, which also indicated that the coating had good mechanical stability and transparency. Consequently, the marine field experiment shows good potential for the application of TPAPS-modified coatings in maritime detection.

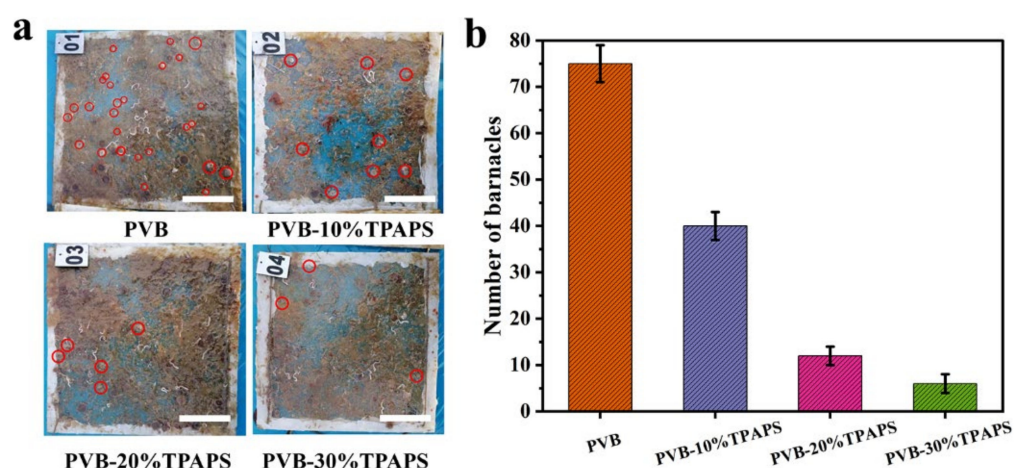


Figure 10. Antifouling test of PVB-X%TPAPS, measuring barnacle settlement under the marine field. (a) Photographs of the actual marine antifouling performance (without cleaning), partially apparent barnacles were marked with red circles in the graphs. (b) A chart showing the number of adhered barnacles. The plate size was 15 cm × 15 cm × 5 mm in this test.

4. Conclusions

In this research, a novel zwitterionic compound (TPAPS) with high hydration ability was synthesized and integrated into PVB-polymer network, engineered at the molecular scale to obtain a highly light-transmitting coating with excellent fouling-resistance properties. Anti-oil adhesion, anti-protein adsorption and marine algae fouling-resistance experiments showed that the as-prepared coating with an appropriate amount of TPAPS (20% mass content) could significantly reduce the contamination of oil stains and marine biofouling on the coated surfaces. Interestingly, the high transparency of visible light was achieved due to the homogenous structure, robust mechanical properties and excellent water resistance displayed by our coatings. More importantly, the superior antifouling ability of the PVB coatings containing TPAPS was indicated in the data, and their excellent comprehensive properties were further supported by the marine field test. Considering the facile preparation, excellent mechanical properties, strong antifouling ability and high transparency of the coating, this research has provided an attractive alternative material for marine detection applications.

Supplementary Materials: The following are available online at <https://www.mdpi.com/article/10.3390/coatings11101164/s1>, Figure S1: The high-resolution mass spectrum of TPAPS. Figure S2: Contact angles of coatings under different immersion time, Figure S3: The thermogravimetric curve of PVB-X% TPAPS coatings.

Author Contributions: J.Z.: Conceptualization, Investigation, Software, Formal analysis, Data curation, Writing—original draft, Visualization. S.B.: Investigation, Methodology, Data curation, Validation. H.F.: Methodology, Validation. B.Y. and Q.Y.: Writing—review and editing, Resources. W.Y. and X.P.: Conceptualization, Methodology, Supervision, Funding acquisition. F.Z.: Project administration, Funding acquisition, Supervision. All authors have read and agreed to the published version of the manuscript.

Funding: This research was funded by NSFC (22072169 and 21773274) and the project of Western Young Scholar “B” of Chinese Academy of Sciences.

Institutional Review Board Statement: Not applicable.

Informed Consent Statement: Not applicable.

Data Availability Statement: Data sharing not applicable.

Acknowledgments: The authors acknowledge the financial support from NSFC (22072169 and 21773274) and Wufang Yang also thanks the project of Western Young Scholar “B” of Chinese Academy of Sciences.

Conflicts of Interest: The authors declare no conflict of interest.

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