

RESEARCH ARTICLE

Investigating the Impact of Interference on the Structure and Characteristics of Self-Stratifying Coatings

Zihan Lin¹ | Xingyu Wang² | Huan Zhou² | Weili Li^{1,3}  | Fan Yang⁴ | Ruofei Liu¹ | Fangming Wang¹ | Zhengbai Zhao¹ | Hui Yan⁵ | Lixin Xu³

¹School of Material Science and Engineering, Jiangsu University of Science and Technology, Zhenjiang, China | ²China Ship Development and Design Center, Wuhan, China | ³Pinghu Institute of Advanced Materials, Zhejiang University of Technology, Pinghu, China | ⁴Jiangsu Renna New Material Co. Ltd, Zhenjiang, China | ⁵Department of Chemistry, The University of Louisiana at Lafayette, Lafayette, Louisiana, USA

Correspondence: Weili Li (liweili@just.edu.cn) | Hui Yan (huiyan@louisiana.edu) | Lixin Xu (gcsxli@163.com)

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ABSTRACT

Self-stratifying coatings, with their convenient painting process and superior coating properties, are considered to be an important direction for replacing traditional coatings. However, due to the relatively complex composition of a coating and its curing process, it is necessary to find a suitable method to track and investigate the film-forming mechanism of coatings. In this paper, we have modified PHMS (polyhydromethylsiloxane) to equip it with the same functional groups as epoxy resin and then physically blended it with epoxy resin to prepare a composite coating with self-stratifying characteristics. To study the preparation, curing, and aging properties of the coating in real time, the AIEgens were introduced into the coating materials, which are capable of emitting fluorescent light (under excitation), depending on whether the molecular rotors of AIEgens are constrained or free to move. Research has proven that the modified PHMS (G-PHMS) can effectively interact with epoxy resin to form a composite coating with a self-stratifying structure. The effective mutual compounding between the two endows the coating with good hydrophobicity and self-cleaning properties, good thermal stability, excellent mechanical properties, and corrosion resistance. With the simple process of coating and its superior performance, it has promising applications in industry.

1 | Introduction

In 1976, Funke et al. first introduced the concept of self-stratifying coatings and integrated it into the realm of powder coatings, thereby delineating a significant research direction to address the issue of poor adhesion between different coating layers [1]. The specific principle of fabricating self-stratifying coatings involves selecting two or more polymer resins with distinct polarities and solubility parameters. These are then compounded through physical or chemical means to create a composite resin with self-stratifying properties. During the preparation process of the coating, phase-driving forces such as solvent evaporation and differences in surface energy are responsible for ultimately

yielding a self-stratifying coating with multifunctional performance and structural diversity [2, 3].

The self-stratifying coatings not only significantly mitigate the phenomenon of interfacial adhesion failure, but also preserve the advantages of a multilayer system [4, 5]. Specifically, they offer the following benefits: (1) the formation of a multi-coat system in one application, conserving coating materials and reducing coating costs; (2) the amalgamation of the benefits of layered coatings to enhance interlayer adhesion; (3) the selective permeation of porous substrates to improve the coating's adhesion; (4) the enhancement of the coating's surface gloss, water resistance, wear resistance, impact resistance, chemical resistance, light

resistance, and weather resistance. Such advanced coatings are currently at the forefront of various uses in a wide range of new products for extensive applications such as automotive, civil, structural, and marine-based substrates. Chunfeng Ma et al. reported the fabrication of a bioinspired self-stratifying coating, which is composed of polyurethane with dopamine and silane pendant groups and bi-silanol-terminated poly(dimethylsiloxane) with fluorocarbon and poly(ethylene glycol) segments as a reactive amphiphilic polymer (RAP). Their coating can be applied in marine antifouling, biomedical instruments [6–9], and other fields [10]. Zhong Chen et al. prepared transparent and eco-friendly anti-icing coatings based on a bioepoxy resin, hydrophobic additives, and silanes [11].

The self-stratifying coatings, characterized by their unique structure and components, exhibit significant advantages in corrosion resistance, mechanical performance, and environmental stability. Regarding corrosion resistance, these coatings balance flexibility and rigidity, thereby reducing permeability and enhancing adhesion. They also incorporate dynamic reversible chemical bonds to achieve self-healing capabilities, providing long-lasting anticorrosion effects. Mechanically, self-stratifying coatings improve the impact strength and toughness of the coating by optimizing its structure and introducing flexible chains and dynamic chemical bonds, without compromising its fundamental properties. In terms of environmental stability, these coatings enhance surface characteristics such as gloss and wear resistance and increase resistance to chemicals, light, and weathering. By forming gradient coatings, they improve inter-layer adhesion and extend the service life. Additionally, the incorporation of weather-resistant topcoat components enhances the coating's resistance to ultraviolet (UV) aging, making it suitable for outdoor applications.

The mechanism for self-stratifying coatings has been explicitly described in various literature. M. Jimenez et al. reported a design of a three-component self-stratifying system, based on epoxy and silicone resins, and an amine curing agent. They found that the Hansen approach is insufficient to predict the compatibility of the epoxy/silicone/amine system, whereas, the model based on surface tension and interfacial energy gives consistent results. In addition, solvent and cross-linkage induced by a curing agent are thought to have an influence on the stratification level of coatings [12, 13]. J. L. Keddie et al. studied the stratification of bimodal mixtures of waterborne polyurethane particles and larger acrylic particles, using ultralow angle microtoming to prepare cross-sections of coating samples and analyze their compositions quantitatively with Raman mapping [14]. Peng Hu et al. have developed a self-stratifying coating with outstanding adhesive strength and hardness [15]. Diksha Sharma et al. have developed a self-stratifying coating with antifouling properties and strong adhesion to substrates [16].

Besides, the dynamics of the self-stratifying process of the coating during the drying process of a coating are also important. Previously, our group introduced aggregation-induced emission (AIE) luminogens (AIEgens) to the synthesis of a self-stratifying coating, studied its mechanism and reactions between the individual components of the coating resin, its film-forming properties, and its response to the environment in real time. The chemistry of AIEgen relies on the freedom of movement of

their core chemical structures (the rotors) [17, 18]. Indeed, the means of controlling the AIEgen emission by tuning the molecular structure trigger many unique fundamental functions of AIE luminogens [19–22]. It is the intramolecular rotations of rotor-based AIE molecules that control the AIE fluorescence behaviors when they are placed in different environments. Thus, AIE molecules have been used to study various chemical and physical processes in materials in real time, as these processes directly affect the AIE rotors' environment [23–28].

In this work, PHMS has been chemically modified to incorporate the same epoxy groups as epoxy resins, to optimize its effective dispersion in the blended organic solvents. Then, a series of self-stratifying coatings based on the GMA-modified PHMS (G-PHMS) and epoxy resin were prepared. In addition, a trace amount of AIEgen was also knitted onto the G-PHMS, which was used as the trace marker to enable real-time observation of the preparation, curing, and accelerated aging of the self-stratifying coatings. Furthermore, the correlation between the composition, structure, and performance of the coating is also discussed.

2 | Experimental

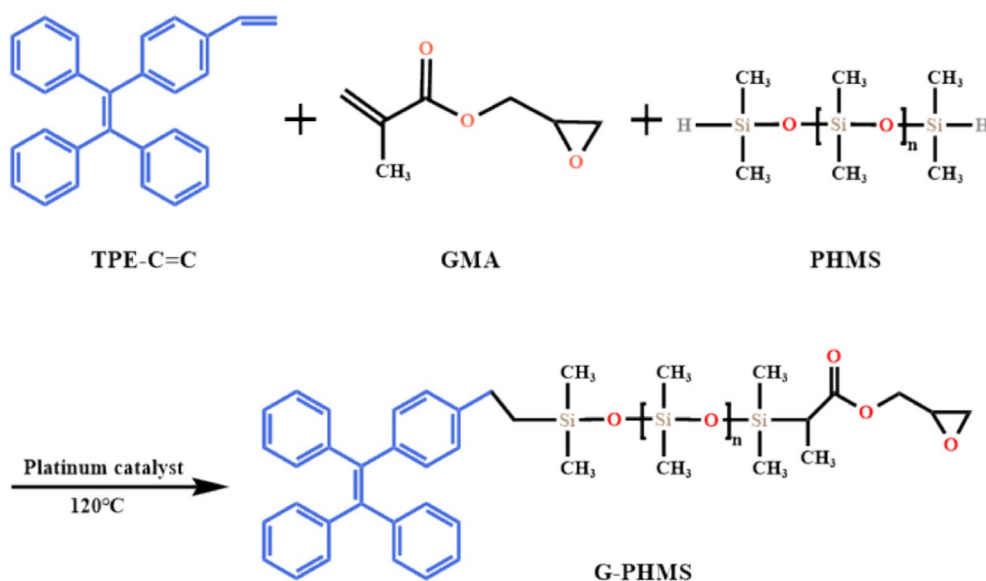
2.1 | Materials

Polymethylhydrosiloxane (PHMS, hydrogen content: 0.1) was purchased from Shanghai Xibao New Material Co. Ltd.; platinum catalyst (KJC-PT3000) was supplied by Shenzhen Kejunqi Technology Co. Ltd.; epoxy resin (epoxy value = 0.51 mol/100 g) was obtained from Nantong Xingchen Synthetic Material Co. Ltd.; glycidyl methacrylate (GMA, AR), xylene (A.R.) and butyl acetate (A.R.) were provided by Chinasun Specialty Products Co. Ltd.; methyl tetrahydrophthalic anhydride (MTHPA) was purchased from Guangdong Wengjiang Chemical Reagent Co. Ltd. AIEgen (vinyl-TPE) was purchased from Sigma-Aldrich. All chemicals were used directly as received without further process.

2.2 | Preparation of the Fluorescent Self-Stratifying Coating

The self-stratifying coatings were prepared by blending the GMA-modified PHMS (G-PHMS) and epoxy resin in the mixed solvents. To track the treatment processes of blended resins in real time, a trace amount of AIEgen (vinyl-TPE) was attached to the G-PHMS during synthesis. Detailed routes are described below.

G-PHMS was synthesized by blending GMA with PHMS in equimolar proportion. Subsequently, a trace amount of vinyl-TPE, constituting relative 0.1% of the total mass of the reactants, and a platinum-based catalyst, also at 0.1 wt%, were introduced into the blending to form a pre-reaction mixture. This mixture was then subjected to mechanical stirring at 150°C for 1 h to ensure a thorough mixing and accomplishment of the reaction. The pathway for synthesis is delineated in Scheme 1, and the FTIR spectra of raw materials and products are presented in Figure S1. Then, the synthesized G-PHMS was blended with epoxy resin,



SCHEME 1 | Synthetic route of G-PHMS. [Color figure can be viewed at [wileyonlinelibrary.com](https://onlinelibrary.wiley.com/doi/10.1002/app.56846)]

characterized by an epoxy value of 0.51 mol/100g. The blending process involved stirring at a temperature of 60°C for a period of 2–3 h, aimed at achieving a homogeneous mixture. Before the completion of the reaction, a small volume of blended solvents of xylene and butyl acetate (1:2 by weight ratio) was introduced, and the concentration of the blended polymers was controlled at 60 wt% because the mixed solvents can modulate the viscosity of the system to a more manageable level at room temperature; Secondly, the blended two resins can homodisperse into the blended solvents according to the principle of similarity compatibility. To evaluate the effect of the composition of the two polymers on the self-stratifying behavior of the cured coating, the quantity of G-PHMS was varied when incorporated into the epoxy resin, specifically at weight fractions of 10, 20, 30, 40, and 50 wt% to the total mass of the mixture. For simplicity, the blended resins, with their respective G-PHMS content, are hereby designated as EP/G-PHMS-X, where “X” denotes the percentage by weight of G-PHMS in the blending resins.

2.3 | Coating Procedure

Three sets of thin steel panels were prepared for various tests for water contact angle (WCA), mechanical properties, and potentiodynamic polarization curves. Each set underwent a standardized pretreatment procedure, starting with polishing the steel panels using metallographic sandpaper to achieve a uniform surface finish. Subsequently, the panels were thoroughly washed with isopropyl alcohol to eliminate any residual dust or debris from the polishing process. In addition, the substrates for the photoluminescence (PL) test, which consisted of quartz glasses, were also cleaned using isopropyl alcohol and dried by wiping with a lint-free paper towel to ensure a clean surface. During coating, the corresponding content of MTHPA was used as a curing agent and was uniformly mixed into the series EP/G-PHMS-X resins. The blends were then applied to steel substrates and quartz glasses using the automatic coating machine (model BGD 218). After coating, the panels were subjected to a curing process at 150°C for 1 h. The thickness of the dried coating was

meticulously controlled and maintained at approximately 60 μm to ensure uniformity and repeatability in the subsequent tests.

2.4 | Characterizations

FTIR spectroscopy was performed on a Nicolet iS10 Fourier transform infrared spectrometer (Thermo Electron Corporation, USA). Spectra of the samples were recorded in the range of 4000–500 cm^{−1} with a resolution of 4 cm^{−1}. The photoluminescent (PL) properties of materials were characterized using the FS5 FL spectrometer (Edinburgh Instruments, UK). DSC analysis was carried out by the Diamond DSC 8000 differential scanning calorimeter apparatus, and the heating and cooling cycles were conducted between −50°C and 120°C at a rate of 10°C min^{−1} under a 50 mL min^{−1} flow of nitrogen. The thermal stability of the coatings was analyzed by a Diamond TG-DTA thermogravimetric analyzer Perkin Elmer Instruments. Contact angle measurements were conducted with a Theta Lite Contact Angle Meter from Biolin Scientific in Germany using distilled water ($\gamma = 72.8 \text{ mN m}^{-1}$; $\gamma_d = 21.8 \text{ mN m}^{-1}$; $\gamma_p = 51 \text{ mN m}^{-1}$). SEM-EDX analyses were performed on a Hitachi S4700 (Tokyo, Japan) with a field emission gun at 13.0 kV and 25 μA. To facilitate cross-section analyses, coatings were cut in liquid nitrogen. The mechanical properties of the coating were evaluated through a series of standardized tests. Hardness was ascertained by using the Trolley pencil hardness tester BGD 506/1 according to the GB/T 6739-2006 method. Flexibility was assessed with a QTX-type paint film elasticity tester, manufactured by Tianjin Jinghai Kexin Test Machine Factory, in accordance with GB/T1731-2020. Impact resistance was determined utilizing the BGD302 tubular film impactor, adhering to the guidelines of GB/T 20624.2-2006. Tensile adhesion was quantified with a BGD500 coating digital display testing machine, following the protocol of GB/T 5210-2006. Product of Biuged Precision Instrument (Guangzhou) Co. Ltd. All testing equipment was provided by Biuged Instruments Co. Ltd. The anticorrosion properties of coatings were tested by using the American Gamry electrochemical workstation. A 3.5% NaCl solution is used as the corrosion medium. For Tafel polarization curve tests, the polarization curve scan rate was 2.5 mV/s, and

the dynamic potential scan range was 1~1.5V (relative to open circuit potential). The exposed area of the coating was 9.6cm². Sample coatings are cut into specific dimensions, weighed (m_0), and immersed in deionized water for 70h. The surface moisture was wiped off and weighed (m_1) every 10h. Each sample was measured three times, and the average value was taken.

3 | Results and Discussion

3.1 | Real-Time Tracking of the Processes of the Fluorescent Self-Stratifying Coating

Since AIEgens act as fluorescent markers, self-stratifying coatings at various stages of synthesis, such as preparation, drying, curing, and aging, can readily be tracked via their PL spectra based on the intramolecular rotation (RIR) mechanism [29, 30].

At first, the condensation of PHMS and GMA was studied. The joining of chemical bonds and the gradual enchainment of polymer chains can restrain the intramolecular rotation of the

knitted AIEgen (vinyl-TPE), hence tuning its emission properties. Figure 1a depicts the PL spectra during the reaction of GMA and PHMS. The gradual increase in emission intensity at around 490nm with time indicates that AIEgen reacts with PHMS gradually by addition reaction. Interestingly, the intensity of the peak at around 410nm increases first and then disappears after 30min. During the reaction, the active H atom released from PHMS can react with vinyl-TPE. Due to the $p-\pi$ conjugation, the electron cloud distribution of vinyl-TPE molecules changes accordingly, which can interfere with the PL spectrum of AIEgen. At the end of the reaction, the peaks at 410nm disappear, indicating the disappearance of active free hydrogen atoms and PHMS, and the polycondensation reaction is complete. According to the FTIR spectra (Figure S1), GMA and PHMS have been effectively linked via chemical bonds. The modified PHMS, due to the knitted epoxy groups, can improve its compatibility with epoxy resins; on the other hand, it can also react with epoxy curing agents to increase the cross-linking density of the cured coatings.

Taken EP/G-PHMS-40 as an example, using MTHPA as the curing agent, the drying and curing process of the self-stratifying

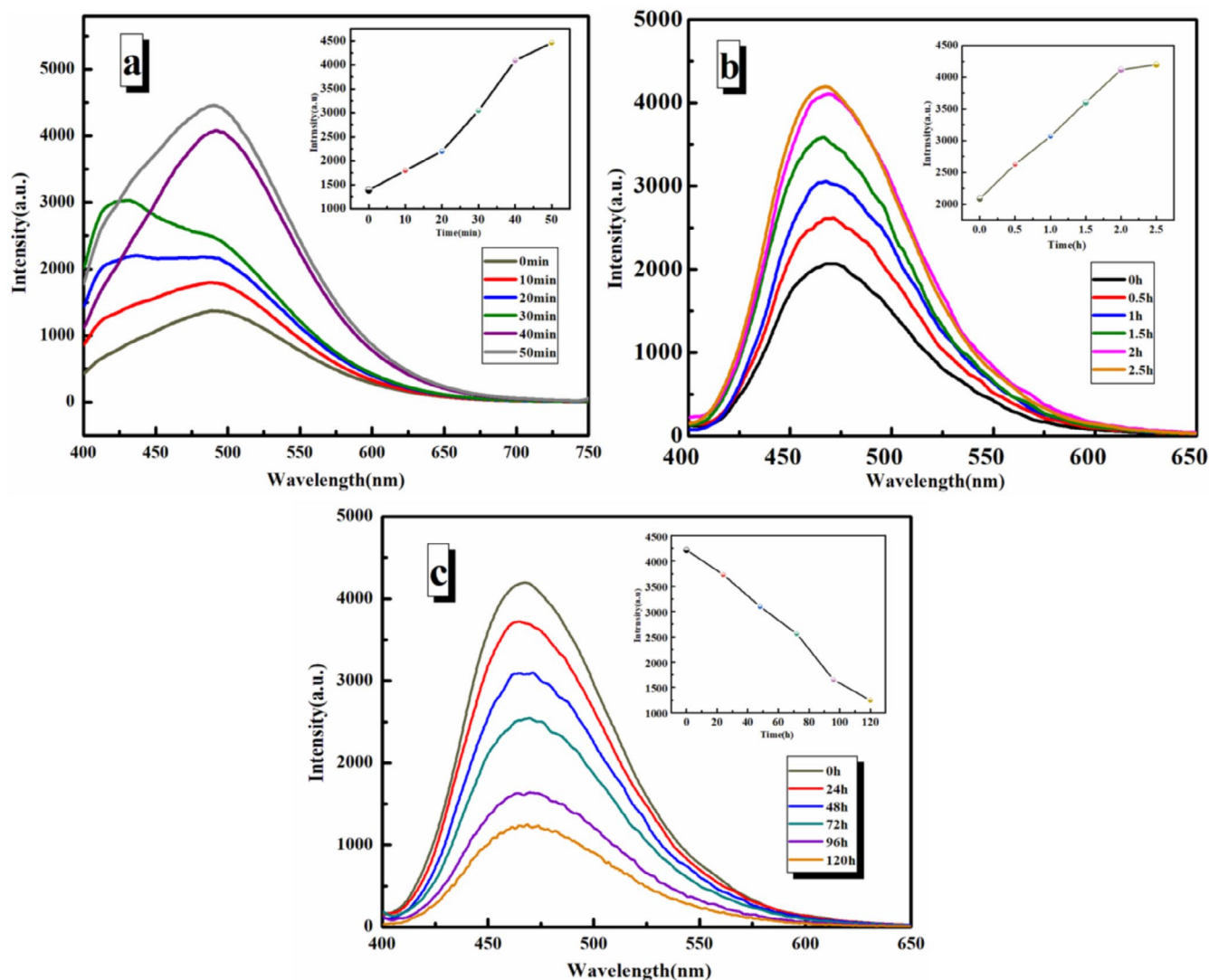


FIGURE 1 | PL spectra of (a) GMA and PHMS during a reaction; (b) the curing process; and (c) the aging process of the self-stratifying coating (EP/G-PHMS-40). [Color figure can be viewed at [wileyonlinelibrary.com](https://onlinelibrary.wiley.com)]

coatings was studied via fluorescent labeling. The continuous evaporation of solvent and the gradually cross-linked structure tend to limit the free movement of AIEgens, leading to an increase in PL intensity of the coating. At the end of the curing process, the PL intensity tends to be stable (Figure 2b).

At last, the cured EP/G-PHMS-40 coating was placed in a Xenon lightbox, and the weatherability of the coating was also tested using PL intensity. The coating was taken out and tested every 24 h. According to Figure 2c, the PL intensity centered at 475 nm decreases linearly with the tested time. When the coating is placed in a Xenon lightbox, it undergoes a violent photooxidation with the combined action of UV light, moisture, and temperature, which causes the polymer to decompose. After AIEgen is chemically knitted on the polymer network, and when the chemical bond of the polymer chain is broken, the restriction on the internal rotation of the AIEgen can be partially weakened, resulting in a decrease in PL intensity according to the RIR mechanism.

Therefore, AIEgen (vinyl-TPE as the example) can be used to track the different statuses of the coating in real time, providing a new strategy for monitoring the processing and performance of the coating.

3.2 | Morphologies and Properties of EP/G-PHMS-X Coatings

To determine whether the EP/G-PHMS-X coatings exhibit self-stratifying properties, pure epoxy and EP/G-PHMS-40-based coatings were selected as representative samples, and the coatings' cross-sectional and surface morphologies were scrutinized by using scanning electron microscopy (SEM). Figure 2a illustrates

the cross-sectional morphology of EP/G-PHMS-40 coating, a relatively smooth surface indicates a typical brittle fracture associated with thermosetting resin. In contrast, the cross-section of EP/G-PHMS-40 coating exhibits a clear self-stratifying behavior. The bottom layer of the coating's cross-section closely resembles the feature of a pure epoxy coating, while the top layer features a rough texture with numerous cracks, which indicate a ductile fracture. The PHMS component, with its long bond lengths and large bond angles, possesses a flexible helical structure that allows for easy expansion and contraction under external forces. The disparity in polarity between various polymer resin structures leads to the formation of this unique self-stratifying layering within the coating. Furthermore, energy dispersive spectroscopy (EDS) measurements reveal a distinct elemental distribution between the two layers, with a notably higher silicon content in the top layer. The density of the PHMS resin component, which ranges from 0.995 to 1.015 g cm⁻³, is lower than that of the epoxy resin (1.2 g cm⁻³). This density difference facilitates the PHMS component's tendency to rise to the surface during the curing process, contributing to the self-stratifying structure of the coating. From Figure 3c,d, despite the self-stratifying cross-sectional formation of EP/G-PHMS-40, the coating's surface remains flat and smooth, akin to a pure epoxy-based coating, which ensures its superior mechanical and anticorrosion properties.

3.3 | Understanding the Influence on the Thermodynamic Properties of the Cured Self-Stratifying Coatings

In this part, the thermodynamic characteristics of the cured self-stratifying coatings were investigated via differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA)

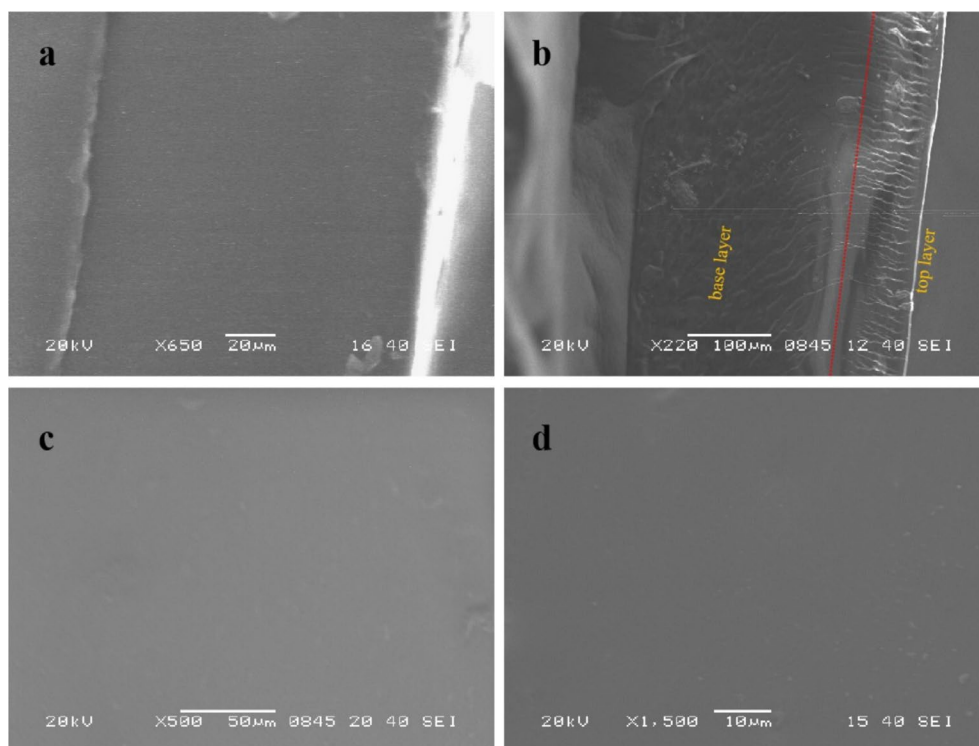


FIGURE 2 | SEM images of the cured epoxy and EP/G-PHMS-40 coatings, the morphology of their cross-section (a and b) and their surface (c and d). [Color figure can be viewed at [wileyonlinelibrary.com](https://onlinelibrary.wiley.com/doi/10.1002/app.56846)]

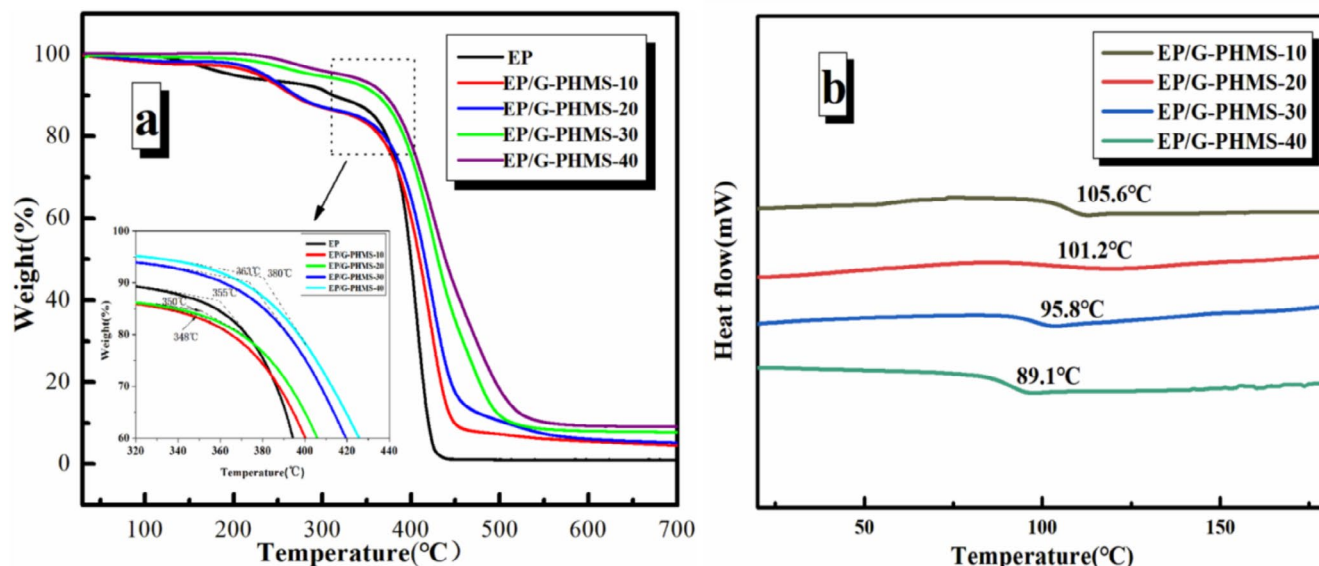


FIGURE 3 | (a) TGA results of the epoxy and the series EP/G-PHMS-*X* coatings; (b) DSC spectra of the series EP/G-PHMS-*X* coatings. [Color figure can be viewed at [wileyonlinelibrary.com](https://onlinelibrary.wiley.com/doi/10.1002/app.56846)]

measurements. The results obtained from these measurements are shown in Figure 3a,b.

Upon temperatures higher than 100°C, there is a slight reduction in weights of all samples, which is attributed to the decomposition of residual organic matter during the preparation process. Once the temperature surpasses 355°C, a significant loss-on-heat platform is observed for the epoxy-based coating. The point of inflection for weight loss in the self-stratifying coatings occurs later, and this trend becomes more pronounced with the increased content of G-PHMS. The maximized thermal decomposition temperature of the self-stratifying coating is 380°C for EP/G-PHMS-40, 24°C higher than that of the pure epoxy resin-based coating. The elevation in thermal decomposition temperature is due to the high covalent bond energy of Si—O in PHMS at 450 kJ/mol, which is higher than that of C—C (332 kJ/mol) and C—O (326 kJ/mol) bonds. The dissociation of Si—O chemical bonds needs a greater amount of thermal energy. Furthermore, the G-PHMS is completely mixed with the epoxy resin, and it crosslinks and solidifies in conjunction with the epoxy resin during the curing and film-forming process, forming interpenetrating polymer networks with a higher degree of cross-linking. Consequently, the thermal stability of the organosilicon-modified epoxy resin is substantially enhanced compared to that of the pure epoxy resin. In addition, it should be pointed out that the residual of the test samples aligns with the quantity of G-PHMS added after the test temperature exceeds 451°C. It is demonstrated that after being subjected to combustion, the PHMS forms silicate, the mass of which no longer decreases.

Figure 3b presents the DSC curves for different samples. It is obvious that the glass transition temperature (T_g) value of the self-stratifying coating progressively diminishes with a gradual increase in the proportion of G-PHMS. For EP/G-PHMS-10, the T_g value is observed to be as high as 105.6°C. Conversely, upon elevating the G-PHMS concentration to 40%, the T_g value

is noted to decrease to 89.1°C. This reduction in T_g value is attributed to the incorporation of G-PHMS, which introduces low-polarity and flexible silicone chains into the coatings. These chains serve to reduce the intermolecular forces among the composite polymer chains, consequently lowering the T_g of the hardened composite coating. Moreover, the introduction of G-PHMS affects the cross-linking density of the epoxy-based resin, resulting in a more relaxed network structure. This modification addresses a key limitation of traditional epoxy resin coatings by enhancing their flexibility and lowering resistance. The adjusted cross-linking provides a balance between the rigidity typically associated with epoxy resins for potential applications.

3.4 | Understanding the Role of Mechanical Properties of the Cured Self-Stratifying Coatings

The augmentation of a coating's protective capabilities and the subsequent prolongation of the substrate's service life are predicated based on the enhancement of the coating's mechanical performance metrics. Key indicators of the mechanical performance of the coatings include hardness, flexibility, adhesion, and impact resistance. A complete understanding of these properties, coupled with strategic optimization, is important to guarantee the superior quality and efficacy of the coating in potential application. By tailoring these properties, coatings can be engineered to provide a robust barrier against environmental degradation, mechanical abrasion, and other forms of wear and tear, thereby guarding the integrity of the underlying material and preserving its functional longevity.

Mechanical properties of the self-stratifying coatings are presented in Table S1. With a longer bond length (1.64 Å) and a larger bond angle (approximately 142.5°) of the silico-oxygen bond, the copolymerized G-PHMS may endow the coating with more flexible properties. In terms of pencil hardness of the self-stratifying coatings, it decreases with the increased content of

G-PHMS, which is attributed to the fact that the incorporation of G-PHMS leads to a reduction in the glass transition temperature (T_g) of cured coatings. Furthermore, the adhesiveness behavior of cured coatings is somewhat diminished with the increased content of G-PHMS due to its low polarity. However, the cured coatings remain adequate to meet the requirements of practical applications as the blended epoxy resin maintains good adhesion with the metal substrate. In addition, it is noteworthy that the cured coatings consistently exhibit superior flexibility and impact resistance compared to pure epoxy-based coatings, thereby ameliorating the significant brittleness that is characteristic of epoxy resins upon curing. At a molecular level, the enhanced flexibility of the cured coatings can be ascribed to the free rotation of the Si—O—Si bonds within the siloxane backbone and the low intermolecular interactions between the methyl groups. Consequently, the organosilicon-modified coatings demonstrate excellent elasticity in expansion and contraction under impact or tensile stress.

3.5 | Analyzing the Factors Affecting the Surface Properties of the Self-Stratifying Coating

To elucidate the correlation between the structure and surface performance of a self-stratifying coating, the effect of G-PHMS content on surface tension was investigated by measuring WCA and testing for water absorption. To mitigate the impact of surface roughness, the thickness of coatings was kept at $110 \pm 4 \mu\text{m}$, prepared under identical conditions. The WCA values and water absorption rate for various coatings are depicted in Figure 4a,b, respectively. As the content of G-PHMS is increased from 0% to 40%, the WCA of the different self-stratifying coatings rises from 85° to 121° . Concurrently, the water absorption ratio after a 60-h immersion decreases from 2.51% to 0.77%. Furthermore, diiodomethane was utilized as a test liquid, and the surface free energy (SFE) of the different self-stratifying coatings was calculated through the Wu (WU) model using SFE. Results are depicted in

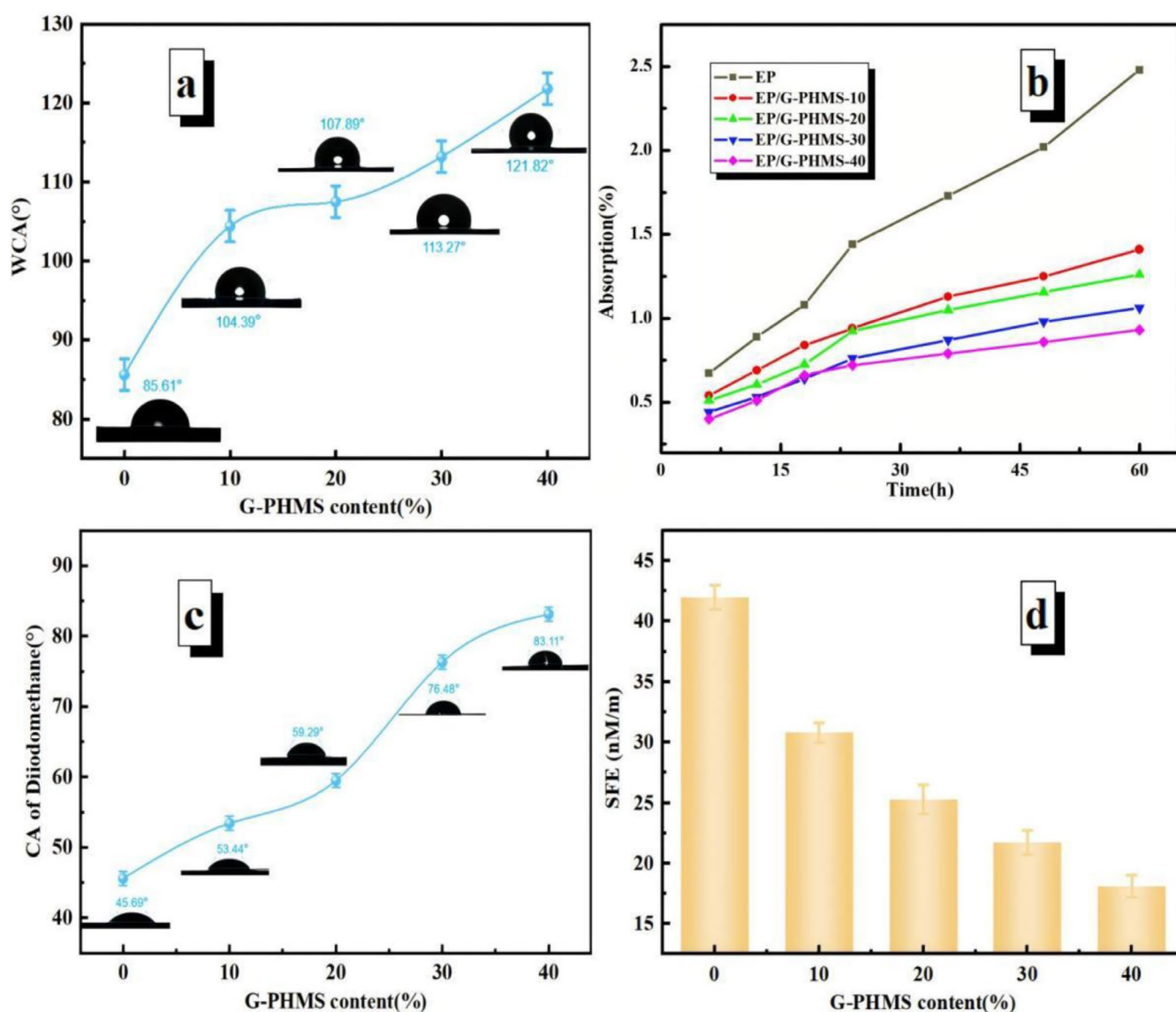


FIGURE 4 | The surface properties of the EP/G-PHMS-X coatings varied with the content of G-PHMS: (a) water contact angle; (b) water absorption of the EP/G-PHMS-X coatings; (c) contact angle of diiodomethane; (d) the SFE value of the EP/G-PHMS-X coatings. [Color figure can be viewed at [wileyonlinelibrary.com](https://onlinelibrary.wiley.com)]

Figure 4c,d. It is observed that the wettability of the coating toward diiodomethane gradually decreases with the increased content of G-PHMS. Meanwhile, the SFE of the coatings drops from 42.1 ± 1 to 18.5 ± 1 mN m⁻¹. The findings indicate that the incorporated G-PHMS can effectively enhance the hydrophobic properties of the coating surface and suppress the swelling of water, which further elucidates the reason behind the variation in the WCA of the coating. As is observed from SEM, it shows that the hydrophobic G-PHMS resin component, due to its relatively lower density, tends to float on the surface of the coating during the curing process. Due to the low polarity of the PHMS component, it shows the characteristic of low surface tension to the self-stratifying coatings. The coating designed in this paper exhibits a maximum contact angle of merely 120°, endowing it with hydrophobic characteristics. Although it does not meet the criteria for an ideal superhydrophobic self-cleaning coating, when water passes over the coating surface, the inherent incompatibility between water and the coating enables the water flow to potentially dislodge some loosely adhered dust particles, thus exerting a certain cleaning effect. For example, in outdoor scenarios with a light dust accumulation, occasional rainfall washing over the surface of such a coating can remove a portion of the dust, thereby realizing a relatively feeble self-cleaning performance.

3.6 | Potential Application of the Self-Stratifying Coatings

UV radiation, situated in the high-energy spectrum of sunlight, is an invisible form of light with wavelengths ranging from 220 to 400 nm. It possesses substantial energy that is capable of disrupting the chemical bonds within organic polymers. Additionally, UV radiation can induce photooxidation reactions, leading to the scission or cross-linking of polymer chains, which in turn affects the performance of the material. It is well known that the resistance of epoxy resins to photodegradation is relatively low, while the organic silicon resin can alleviate the problem. So, firstly, the impact of two components, for example, epoxy resin versus G-PHMS, on the UV aging property of the self-stratifying coatings was investigated by examining the variation patterns of the gloss performance of coating [31].

Data from the UV aging experiments indicate that the glossiness of coatings diminishes to varying degrees as UV irradiation proceeds. This phenomenon is attributed to the degradation of polymer chains over extended periods of UV aging test as discussed above. Epoxy resins, which contain aromatic ring groups with an energy of 250–320 kJ/mol, are particularly susceptible to damage under UV light. In contrast, the Si–O covalent bonds in G-PHMS possess a bond energy of 450 kJ/mol. The energy of 300 nm UV light is 399 kJ/mol, which significantly exceeds the energy required to break various chemical bonds within the polymer chains. Consequently, UV radiation is capable of disrupting the chemical bonds that constitute the polymeric structure. As shown in Figure 5, the glossiness of the coating gradually decreases with the extension of ultraviolet light irradiation time. However, due to the copolymerization of silicone resin, the weather resistance of the coating can be effectively improved, resulting in a relatively small decrease in the glossiness of the paint film.

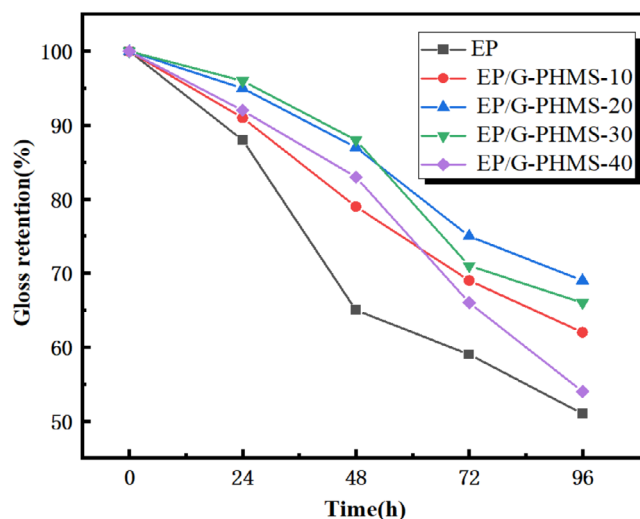


FIGURE 5 | Changes in the glossiness of the self-stratifying coatings with the prolongation of the UV aging test. [Color figure can be viewed at [wileyonlinelibrary.com](https://onlinelibrary.wiley.com/doi/10.1002/app.56846)]

The anticorrosion performance is a crucial factor for the protective coatings of metals. Tinned steel plates coated with different self-stratifying coatings were immersed in a 3.5 wt% NaCl solution and analyzed using the Tafel polarization curves test to study the corrosion process of the coatings. The Tafel polarization curves can evaluate the corrosion resistance of the coatings by measuring the change in the self-corrosion current density with potential. According to Faraday's law, the corrosion current density of the coating is directly proportional to the corrosion rate (CR). Besides, the corrosion potential (E_{corr}) and the Tafel slope also reflect the extent of corrosion, a more positive E_{corr} and a steeper slope indicating a better corrosion resistance. By comparing the Tafel polarization curves, a coating with superior anticorrosion properties can be selected [32, 33]. Figure 6 shows the Tafel polarization curves of different self-stratifying coatings after being immersed in a 3.5 wt% NaCl solution for 60 days. The CR can be calculated using the Tafel polarization data (Table 1) and Equation (1).

$$\text{CR} = I_{\text{corr}} / (n \cdot F \cdot \rho) \quad (1)$$

In conjunction with Table 1, it can be observed that as the content of G-PHMS increases from 0% to 40%, the self-corrosion current density of the coatings gradually decreases from 1.102×10^{-6} to 5.232×10^{-8} A cm⁻², and the CR also decreases from 1.23×10^{-2} to 4.57×10^{-3} mm year⁻¹. As discussed above, more content of G-PHMS in the system leads to a better hydrophobic property of the self-stratifying coatings. The cross-linked coating, in combination with the low-polarity symmetrical Si–O–Si chain segments, reduces the coating's water absorption properties, hinders the penetration of corrosive media, and thus effectively inhibits the occurrence of corrosion on the metal substrate. However, the adhesion property of the cured coatings can be ruined with G-PHMS. This can impact the wet adhesion properties of the coatings, which in turn compromise the corrosion resistance of the coating. The results further confirm that G-PHMS can effectively slow down the CR of the coating, and

the optimal amount of G-PHMS added is in the range between 10 and 30 wt%.

Next, the EIS test was adopted to investigate the corrosion resistance performance of the coating. The equivalent circuit diagrams fitted by the EIS results in the early and late stages of

coating corrosion are presented in Figure 7, R_s and R_c , respectively, represent the solution resistance and micro-control resistance on the coating surface, R_{ct} indicates the charge transfer resistance, CPE_c represents the coating capacitance, CPE_{dl} represents the constant phase angle element during the metal corrosion process, and W represents the Warburg impedance [32]. Commonly, the corrosion process is divided into two principal stages. In the initial stage (Figure 7a), the corrosive medium gradually penetrates the coating through inherent micropores as channels, but has not reached the metal surface at this point. In the second stage, the corrosive medium gradually penetrates the metal surface (Figure 7b), followed by the accumulation of corrosion activities at the interface between the metal and the coating. The latter stage is crucial for determining the anticorrosion performance of the composite coating. To explain the above observations, we noticed that the penetration of the corrosive medium increases with the increase in immersion time, which is regarded as twice the time constant for all coatings. The high-frequency time constant is determined by R_s and CPE_c , while the low-frequency time constant is determined by R_{ct} and CPE_{dl} . The emergence of R_{ct} and CPE_{dl} marks the second stage of corrosion. In the second corrosion stage, initially, the Nyquist plots of pure epoxy and composite coatings can be fitted using the model in Figure 7a. However, with the increase in test time, the Nyquist plots of the coatings are more appropriately fitted using the model in Figure 7b. This indicates that as the corrosive substances accumulate, the epoxy layer on the steel surface gradually loosens, thereby facilitating the penetration of the corrosive

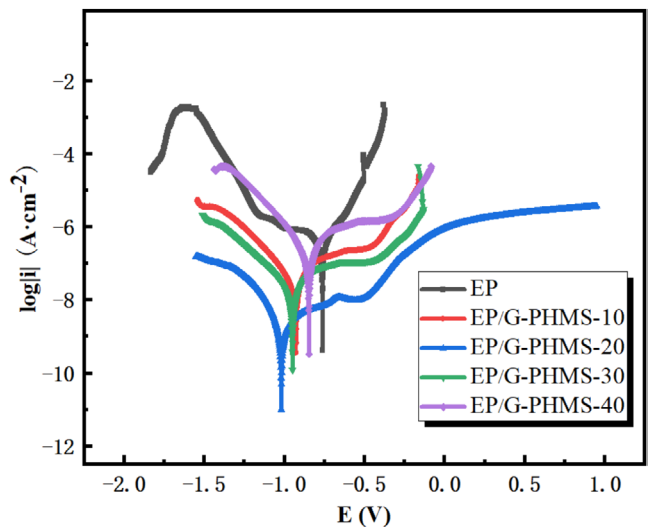


FIGURE 6 | Polarization curves of EP-based self-stratifying coatings after being immersed in 3.5 wt% NaCl solution for 60 days. [Color figure can be viewed at [wileyonlinelibrary.com](https://onlinelibrary.wiley.com)]

TABLE 1 | The Tafel extrapolation results obtained.

Sample	E_{corr} (V)	I_{corr} (A/cm ²)	CR (mm/year)
EP	-0.74232	1.102×10^{-6}	1.23×10^{-2}
EP/G-PHMS-10	-0.91466	7.386×10^{-7}	3.32×10^{-3}
EP/G-PHMS-20	-0.98234	5.232×10^{-8}	4.57×10^{-3}
EP/G-PHMS-30	-1.09302	7.891×10^{-7}	1.21×10^{-3}
EP/G-PHMS-40	-0.86432	4.402×10^{-6}	2.54×10^{-2}

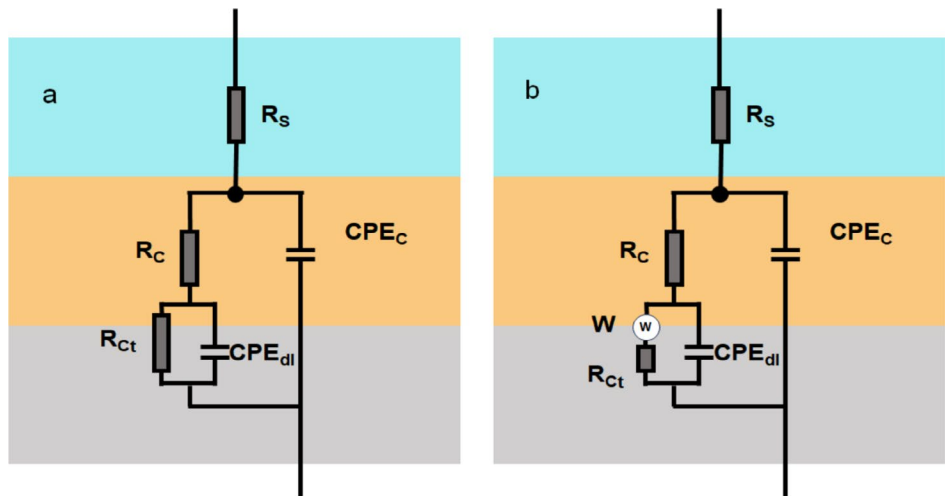


FIGURE 7 | Equivalent circuit diagram of EIS result fitting of (a) early corrosion and (b) late corrosion. [Color figure can be viewed at [wileyonlinelibrary.com](https://onlinelibrary.wiley.com)]

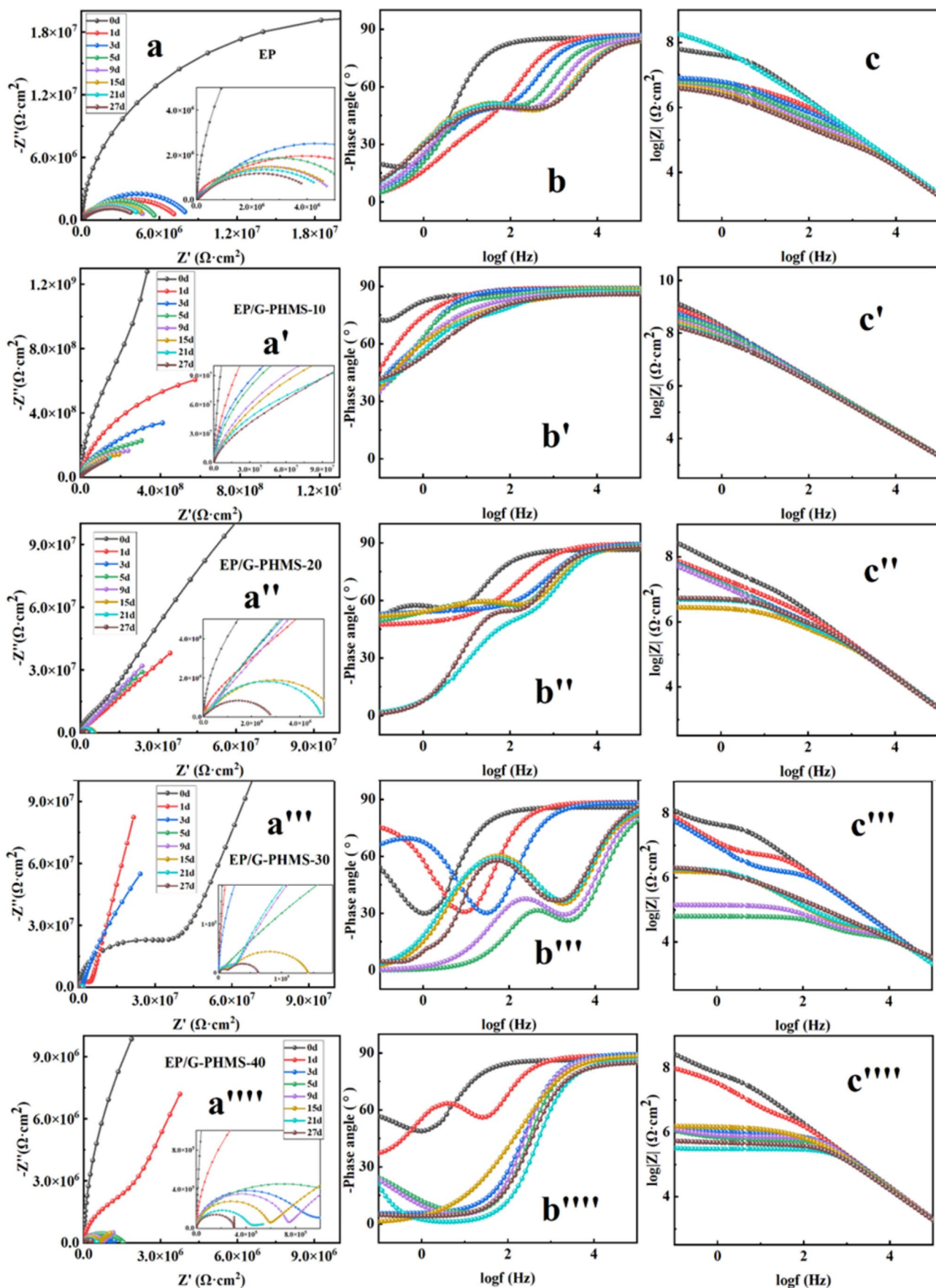


FIGURE 8 | (a) Nyquist plots, (b) Phase angle plots, and (c) Bode plots of acrylic coatings with different D-PHMS contents immersed in 3.5% NaCl solution for 27 days. [Color figure can be viewed at [wileyonlinelibrary.com](https://onlinelibrary.wiley.com)]

medium and forming the Warburg impedance element. The results suggest that the diffusion of the corrosive medium at the interface between the metal and the coating leads to a sharp decline in the coating's corrosion resistance. In the EP/G-PDMS-X coating, the organosilicon hydrophobic coating on the surface can delay the penetration of the corrosive medium. Therefore, the composite coating only exhibits the Warburg impedance element after a longer immersion time. Its equivalent circuit remains consistent with the model in Figure 8a, indicating excellent corrosion resistance performance.

Figure 8 shows the Nyquist plots, phase angle plots, and Bode plots of the different coatings immersed in a 3.5 wt% sodium chloride solution for 27 days. Figure 8a shows the Nyquist plots of various coatings with changes in immersion time. The impedance radius arcs of all coatings show a continuous decrease with the extension of immersion time, indicating that the corrosion resistance of the coatings decreases over time, which is a common phenomenon in many coating substrates [34]. For the pure EP coating, the impedance radius arc significantly reduces after 1 day of immersion in a 3.5 wt% sodium chloride solution, indicating a decrease in charge transfer resistance, suggesting that the coating has been corroded and consumed, and even the corrosive medium has penetrated the coating and corroded the metal surface. Meanwhile, the soluble metal ions from the corrosion products have transferred from the metal surface to the electrolyte solution. When G-PDMS is introduced and compounded with epoxy resin in the system, the corrosion resistance of the coating first significantly enhances and then decreases. For the EP/G-PDMS-10 coating, the impedance radius arc in the Nyquist plot is relatively large throughout the entire test process, indicating that these coatings effectively inhibit the penetration of the corrosive medium on the metal surface during the test. However, there is also a limit to the relative content of G-PDMS. For the samples EP/G-PDMS (20, 30, 40) coatings, a significant reduction in the impedance radius arc also occurs in the later stage of the test. A higher content of G-PHMS in the system leads to a better hydrophobic property of the self-stratifying coatings. The cross-linked coating, in combination with the low-polarity symmetrical Si—O—Si chain segments, reduces the coating's water absorption properties, hinders the penetration of corrosive media, and thus effectively inhibits the occurrence of corrosion on the metal substrate. However, the adhesion property of the cured coatings can be ruined with G-PHMS. This can impact the wet adhesion properties of the coatings, which in turn compromise the corrosion resistance of the coating.

Figure 8b shows the phase angle plots of the coatings with changes in immersion time. The width of the platform close to “ -90° ” can be used as an indicator of the coating's corrosion resistance, and a wider platform indicates superior corrosion resistance [35]. In the early stage of immersion, all coatings have relatively wide phase angle platforms, indicating that they provide good protection for the metal. However, in the middle and later stages of immersion, only the EP/G-PDMS-10 coating still maintains a relatively wide platform, indicating that it still has relatively good anticorrosion performance after 27 days of immersion. Figure 8c shows the Bode plots corresponding to all sample coatings, reflecting a similar pattern to the impedance spectra [36, 37]. It is notable that at a frequency of 0.01 Hz, the impedance of the EP/G-PDMS-10 coating is one to two orders of magnitude higher than that of the other coatings. Additionally,

the impedance value of the EP/G-PDMS-10 coating remains stable within 27 days and always remains at around $10^8 \Omega \text{ cm}^2$. For the other coatings, their impedance values undergo a continuous and significant decrease, with the impedance in the low-frequency region dropping from 10^8 to $10^6 \Omega \text{ cm}^2$ (even to $10^5 \Omega \text{ cm}^2$ for EP/G-PDMS-30), indicating relatively poor long-term anticorrosion ability.

In conclusion, the appropriate compounding of G-PDMS successfully improves the corrosion resistance of the coating. Among them, the long-term corrosion resistance of the EP/G-PDMS-10 coating surpasses that of the other coatings, indicating that the optimal modification amount of G-PDMS is approximately 10%.

4 | Conclusion

In summary, a composite coating has been prepared by the effective modification of PHMS and blending with epoxy resin, forming a self-stratified morphology. What is particularly notable is the utilization of the AIE effect by grafting AIEgen onto the polymer chain segments. The film-forming mechanism of the self-stratifying coating has been investigated with AIEgen, whose chemical environment can switch the PL emission of the overall material. Consequently, because the high sensitivity of AIEgen's fluorescence changes with its chemical environment, the synthesis process, including the synthesis of the resin, curing of the coating, and aging of the cured coating, can be tracked in real time through fluorescent labeling. The analysis of the coating morphology and performance reveals that the effective dispersion of the two resins can endow the coating with a self-stratified morphology. The G-PHMS component with low polarity tends to float on the surface of the coating, conferring its unique surface interfacial properties. The addition of G-PHMS, without compromising the basic mechanical properties of the coating, effectively reduces the surface tension of the composite coating, enhancing its resistance to heat and corrosion. Due to the exceptional weather resistance, temperature tolerance, water and stain repellency, corrosion resistance, and low surface energy, the designed coatings in this paper can be widely applied in areas such as exterior building walls, industrial anticorrosion, transportation vehicles, electronic insulation, and nonstick coatings for cookware, and so on.

Author Contributions

Zihan Lin: data curation (lead). **Xingyu Wang:** investigation (equal). **Huan Zhou:** conceptualization (supporting). **Weili Li:** supervision (lead), writing – original draft (lead). **Fan Yang:** methodology (lead). **Ruofei Liu:** data curation (supporting). **Fangming Wang:** software (lead). **Zhengbai Zhao:** validation (lead). **Hui Yan:** writing – review and editing (equal). **Lixin Xu:** supervision (lead).

Conflicts of Interest

The authors declare no conflicts of interest.

Data Availability Statement

The data generated and analyzed during this study are available in the Journal of Applied Polymer Science repository under the <https://doi.org/10.1002/app.56846>.

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Supporting Information

Additional supporting information can be found online in the Supporting Information section.