

Preparation and Corrosion Resistance of Thermally Cured EP-PVC Composite Powder Coatings

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ABSTRACT Marine metal structures such as ships and submarines are exposed to highly corrosive environments, requiring coatings that provide durable protection while maintaining environmental safety. This study investigates thermally cured EP-PVC composite powder coatings prepared via electrostatic spraying, comparing layer-by-layer and co-curing processes. The EP-PVC primer layer and PVC topcoat were analyzed using FT-IR, Raman spectroscopy, and TEM to understand microstructural evolution. Mechanical tests, including hardness, gloss, adhesion, and impact resistance, along with salt spray and potentiodynamic polarization tests, demonstrated that layer-by-layer cured coatings exhibit superior adhesion, hardness, and corrosion resistance, with corrosion rates as low as 0.0018 mm/a and overall protection reaching 67%. The enhanced barrier properties and interfacial bonding of the composite coatings effectively inhibit corrosive media penetration. These coatings are particularly suitable for electromagnetic engineering applications, such as protective surfaces for antenna arrays, RF transmission structures, and high-frequency marine electronics, where durable corrosion resistance is critical for long-term signal integrity and system reliability.

INDEX TERMS EP-PVC composite coatings, corrosion protection, layer-by-layer curing, electromagnetic engineering

I. INTRODUCTION

THE marine environment is highly complex and contains numerous corrosive factors. For example, the high concentration of chloride ions in seawater makes it generally more corrosive than inland environments. Chloride salts can cause localized corrosion through their surface passivation film [1]. Corrosion protection of marine vessels such as ships and submarines is a major research focus, where the integration of advanced textile-reinforced composites and functional fiber membranes provides a superior barrier against harsh saline environments. These textile-enhanced surface technologies are of great importance for extending service life, reducing economic losses, and contributing to global environmental sustainability.

Heavy-duty anti-corrosion coatings have been a major research focus in marine corrosion protection over the past decades. However, most conventional heavy-duty marine anti-corrosion coatings can only achieve effective and long-lasting protective effects, which seriously damage the marine environment [2,3]. With the increasing global emphasis on marine environmental protection and stricter environmental regulations, traditional heavy-duty marine anti-corrosion coatings are bound to be phased out. Therefore, the development of environmentally friendly marine anti-

corrosion coating materials is currently a research focus internationally. Powder coatings are one such type of coating that meets these requirements. They offer advantages such as environmental friendliness, dense coating structure, and strong adhesion, making them one of the development directions for marine anti-corrosion coatings [4,5]. In general, a highly corrosion-resistant coating must meet two conditions:

- (1) the coating should possess excellent barrier properties to effectively block the ingress of corrosive media;
- (2) The coating must be tightly bonded to the covering material to prevent the penetration, accumulation, diffusion, and peeling of the corrosive material [6,7].

In traditional coatings such as polyacrylates, the incorporation of fillers like graphene [8] and carbon nanotubes [9], or the introduction of polymers such as polyaniline [10], can improve corrosion resistance to a certain extent. However, fillers such as graphene and carbon nanotubes are prone to particle aggregation, leading to larger defects and higher production costs, which limits their large-scale applications.

PVC powder coating is a representative thermoplastic powder coating. Among them, the polarity of the carbon chlorine (C-Cl) double bond is relatively high, which is beneficial for improving the intermolecular forces of the polymer chains; However, due to its large molecular size

and strong steric hindrance, it can effectively prevent the infiltration of corrosive media. PVC coating has excellent chemical corrosion resistance and has been widely used in the coating industry. It also has excellent weather resistance, flame retardancy, insulation, impact resistance, salt spray resistance, and is inexpensive. However, the weak adhesion between PVC coating and substrate greatly limits its corrosion resistance. Improving the comprehensive performance of PVC powder coating by surface modification is currently a research focus in the field of anti-corrosion both domestically and internationally. Epoxy resin (EP) contains polar groups such as epoxy, hydroxyl, and ether bonds, which react with them to form insoluble stereocrosslinked polymers with excellent mechanical and insulating properties. As a result, epoxy resins are widely used as primers in anti-corrosion coatings [11,12]. Bandeira *et al.* [13] investigated the protective performance of polyaniline/PVC composite coatings (with thicknesses ranging from 5 to 30 μm) on AA3-T5 aluminum in NaCl solution. The experimental results demonstrated that the composite coatings exhibited good corrosion resistance.

Thermal spraying, as an efficient protective measure, has been widely used on ships, especially thermal spraying. For example, thermally sprayed aluminum-based coatings exhibit long-term corrosion resistance in corrosive environments [14-16]. A two-layer composite coating system was investigated, consisting of an EP-PVC primer (where the epoxy is cross-linked with a dicyandiamide curing agent) and a pure PVC topcoat. This architecture is designed to leverage the superior adhesion of the cured epoxy network and the barrier properties of PVC. The mechanical properties of the coating were studied, and corrosion experiments such as salt spray and electrolysis were conducted on the coating. In addition, this article also discusses its antibacterial mechanism.

II. EXPERIMENTAL

A. MATERIALS

Table 1 lists the main raw materials used in the manufacture of anti-corrosion coatings. Specifically, dicyandiamide (DCD) was employed as the latent curing agent for the epoxy component within the EP-PVC primer to ensure a stable and dense cross-linked structure upon thermal treatment. The substrate used for the coatings was Q235 carbon steel plates, which were prepared according to standard procedures prior to application.

B. PREPARATION OF POWDER COATINGS

The preparation of the coatings was carried out per five steps.

Step 1: According to the formula requirements, various additives are added to the high-speed mixer to achieve the initial dispersion state of PVC resin.

Step 2: Melting extrusion is accomplished using a twin-screw extruder. For melt mixing, the working temperature

TABLE 1. Main materials used for anti-corrosion coatings

Material	Purity
Polyvinyl chloride	Analytical grade
Epoxy resin	Analytical grade
Dicyandiamide	Analytical grade
Diocetyl phthalate	Analytical grade
Titanium dioxide	Analytical grade
Oxidized polyethylene wax	Analytical grade
Light calcium carbonate	Analytical grade
Leveling agent	Analytical grade
Titanate	Analytical grade

*Note: Q235 carbon steel plates (composition: $C \leq 0.22\%$, $Mn \leq 1.4\%$, $Si \leq 0.35\%$, $S \leq 0.050\%$, $P \leq 0.045\%$) were used as the substrate for all electrochemical and mechanical tests.

is set at 120 °C and the screw speed is set at 20 revolutions per minute.

Step 3: A low-temperature liquid nitrogen cooling and crushing device was employed. After melt extrusion, the materials were pelletized, cryogenically ground, and then sieved through a 180-mesh screen to obtain powder coatings.

Step 4: Implement electrostatic spray. In the electrostatic generating device, the sprayed powder particles carry a negative charge, while the tin plated sheet carries a positive charge, thereby adsorbing the powder onto the substrate.

Step 5: Heat the sprayed paint in a 180 °C furnace for 10 minutes, melt it, flatten it, and obtain a continuous coating film.

The main characteristics of the dual membrane composite system are co-curing and layer-by-layer curing. To clarify the thermal history of each method:

(1) Co-curing system: The EP-PVC primer is first electrostatically sprayed onto the substrate, followed immediately by the application of the PVC topcoat. The entire composite system is then subjected to a single secondary curing cycle at 180 °C for 10 minutes, allowing the layers to fuse simultaneously.

(2) Layer-by-layer curing: The EP-PVC primer is sprayed and separately heated at 180 °C for 10 minutes to ensure full curing and film formation of the bottom layer. Subsequently, the PVC topcoat is sprayed onto this solidified primer layer and subjected to a second heating cycle at 180 °C for 10 minutes for final trimming and leveling. The so-called co curing system is to first spray polyethylene epoxy based bottom coating, then spray PVC based surface layer, and then perform secondary curing.

The so-called layer-by-layer curing refers to first treating the PVC-EP primer, then spraying it onto the already formed primer layer, and then heating and trimming it.

C. CHARACTERIZATION OF PROPERTIES

1) Mechanical Property Tests

(1) Hardness According to ISO 15184-1998, it was tested using the pencil scratch method. The coating is prepared by electrostatic spray method, dried at room temperature for 7 days, and then the hardness of the sample is measured by pencil hardness tester. Use a pencil of the same hardness to conduct three scratch tests to see if the sample is damaged.

The hardness of the coating refers to the hardest pencil, as long as there are no scratches of 3 millimeters left on the surface of the coating.

(2) Gloss Use a 60 degree photometer to measure the gloss of the film, and calculate the average brightness of the three parts of each film.

(3) Adhesion According to ISO2409:1992, the adhesion test uses the cross scratch method to determine the bonding strength between the coating and the substrate. The specific procedure was as follows: the cured coated sample was fixed, and a cross-hatch pattern was cut perpendicular to the coating surface using a grid cutter. Transparent adhesive tape was then uniformly applied over the cut area and subsequently removed. The degree of coating detachment was observed and evaluated according to the standard criteria to determine the adhesion level.

(4) Impact Resistance The impact resistance of the coating shall be tested in accordance with ISO6272-2-2002. Put the prepared paint sample on the anvil of the test equipment, lift the hammer to a certain height, and then let it fall freely to impact the sample. The impact resistance of coatings is expressed in centimeters as the maximum height, which is a critical value that coatings can only maintain as a whole.

2) Structure and Morphology

The composition of the thin film was characterized using Fourier transform infrared and laser confocal Raman microscopy, and the microstructure of the thin film was characterized using transmission electron microscopy.

3) Salt Spray Test

The Q-FOG periodic corrosion test box was used to conduct salt spray tests on coated steel samples. Cut the coated sample with an X-shaped incision and place it in a 3.5% by weight NaCl mist (pH-6.5~7.2) for 360 hours. The experimental temperature is 35 °C. After the experiment is completed, the sample will be evaluated according to ISO4628-2016.

4) Electrochemical Measurements

Electrochemical tests were performed using a CS 310H electrochemical workstation. Evaluation of corrosion resistance of coatings using potentiodynamic polarization curves. Prior to testing, the exposed test area of the Q235 carbon steel substrate was controlled to 1 cm², and all non-test areas on both the front and back sides of the steel substrate were sealed. The use of a consistent Q235 steel substrate ensures the reproducibility of the potentiodynamic polarization results.

The sealing material consisted of a mixture of rosin and paraffin wax at a mass ratio of 1:1. The mixture was heated to 100 °C until fully melted, and the steel samples were immersed to coat the non-test areas. After cooling and solidification, the sealed samples were mounted in the electrochemical cell. A 3.5 wt% NaCl solution was used as the electrolyte.

TABLE 2. Effect of curing methods on the mechanical properties of coatings

Mechanical property	Co-curing	Layer-by-layer curing
Hardness	> 6H + 1750 g	6H + 1750 g
Gloss	32.02	41.25
Adhesion /(grade)	3	1
Impact resistance/ (cm)	Front and back impact 45	Front and back impact 50

III. EXPERIMENTAL RESULTS

A. MECHANICAL PROPERTY RESULTS

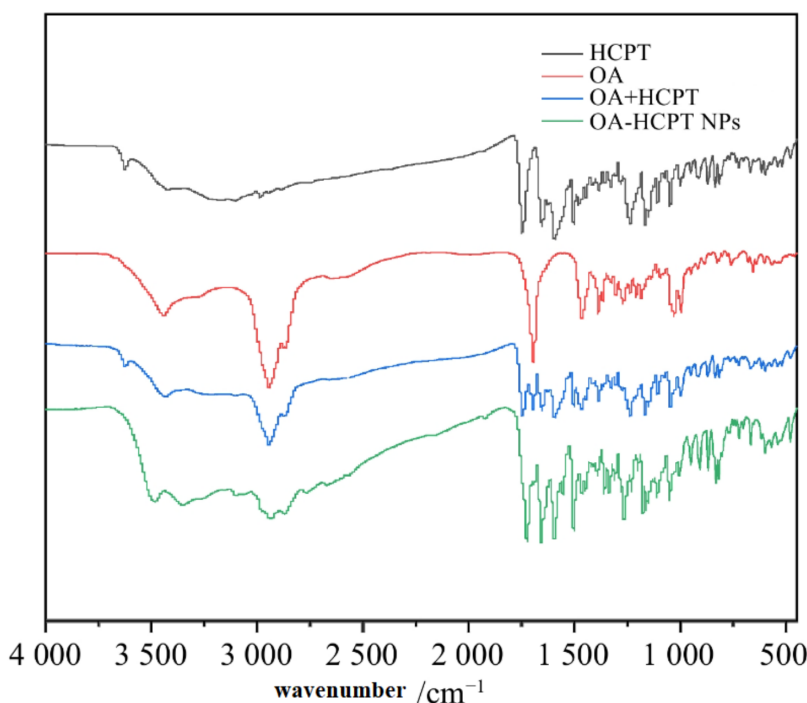
The mechanical property data listed in Table 2 shows that the adhesion, gloss and hardness of the coating after multi-layer composite treatment are significantly higher than those of the conventional method, because it produces an electric field in the electric spray. During the contact process between the powder and the test subject, the generated charges will gradually dissipate and generate a secondary electric field, thereby promoting the settling of the powder. However, as the thickness of the powder increases, its surface electric field weakens, making it difficult for the sprayed powder to form a good bond with the substrate, thereby affecting its mechanical properties.

B. FOURIER TRANSFORM INFRARED (FT-IR) ANALYSIS

The infrared spectrum of the coating was analyzed using infrared spectroscopy. The absorption peak is located at 3431 cm⁻¹, and 1100 cm⁻¹ and 1633 cm⁻¹ are respectively caused by the stretching vibration of O-H, C-O-C, and C-N bonds. An absorption peak related to the vibration of the benzene ring framework was observed at 1607 cm⁻¹ and 1581 cm⁻¹; The spectral peak at 800-600 cm⁻¹ is consistent with the stretching of C-Cl chemical bonds. The study found that the above characteristic peaks are consistent with PVC-EP (DCD). According to the IR spectrum of the curing system, the characteristic epoxy peak is located at 961 cm⁻¹. In addition, the characteristic absorption peak of cyanamide nitrile group at 2205 cm⁻¹ showed a significant decrease compared to the characteristic peak at 2162 cm⁻¹, but the decrease was not significant. This change is mainly due to the alteration of the cyanide group during curing, reflecting the curing reaction between epoxy and curing agent [17]. Epoxy resin epoxy ring opening, epoxy epoxy epoxy epoxidation to generate secondary or tertiary amines.

C. RAMAN SPECTROSCOPY ANALYSIS

From Figure 2, it can be seen that the Raman peak at 641 to 696 cm⁻¹ is formed due to the stretching and contraction of the C-Cl chemical bond, while the peak at 1430 cm⁻¹ is consistent with the flexural vibration of the carbon hydrogen bond. For pure epoxy resin, the Raman spectrum is mainly associated with vibrations of oxygen-containing groups or molecular bonds. Distinct characteristic peaks are observed at 1612 and 1722 cm⁻¹, along with several weak characteristic peaks in the range of 800–1500 cm⁻¹ [18]. A powder coating was made by compounding PVC with epoxy resin and other additives, resulting in a slight shift in

**FIGURE 1.** Fourier transform infrared spectrum

the characteristic peak position. In addition, there are some other characteristic peaks on the EP-PVC powder coating. This change is due to the addition of some additives in PVC/EP, such as leveling agents, heat stabilizers, etc. These additives will react with PVC/EP resin, thereby affecting its bonding with the matrix.

D. TRANSMISSION ELECTRON MICROSCOPY (TEM) ANALYSIS

The surface morphology and microstructure of the coating were analyzed using TEM. Figure 3A shows that the powder coating particles produced are uniformly dispersed. Figure 3B shows the encapsulation of fillers, antioxidants, plasticizers, and other additives in the resin matrix. This is because during twin-screw extrusion, the powder coating melts due to the shear heat of the molten material and the increase in spiral temperature, which can effectively wrap the additive. The present invention provides a new preparation method that can thoroughly stir each component in the resin and evenly distribute it in the resin to achieve the purpose of adjusting and improving the performance of the coating.

E. SALT SPRAY TEST RESULTS

Both curing methods were evaluated for their resistance to neutral salt spray exposure over a period of 30 days. From Figure 4, it can be seen that during the erosion process, the coating has varying degrees of rust and blistering. Under the condition of co solid state, obvious rust spots and rust spots appeared on the surface of the coating, and they extended more severely from the scratch to the surrounding area. Blistering phenomena were also present. SEM photos of

the scratch area showed that the coating was loose and loose in the neutral salt spray environment, and there were more corrosion products accumulated in the scratch area. In contrast, the coating cured by layer by layer method has higher scratch structure, and no further erosion expansion is found along the scratch. This behavior is mainly attributed to the more uniform component distribution and lower porosity of the layer-by-layer cured coatings, which effectively inhibit the penetration of corrosive media and slow down the corrosion process.

F. POTENTIODYNAMIC POLARIZATION RESULTS

The corrosion resistance of multi-layer composite systems was studied using dynamic potential polarization method. Table 3 summarizes the relevant electrochemical indicators, including corrosion potential, current density, Tafel slope, and cathode Tafel slope.

From Table 3, it can be seen that the coating produced by layer by layer curing has the highest polarization resistance ($R_p = 54627 \Omega \cdot \text{cm}^2$). The corrosion rate of layer-by-layer curing is 0.0018, the corrosion rate of co solidification is 0.0031, and the corrosion rate of steel bars is 0.0055 millimeters per year. By combining layering and co curing methods, the protective effect can reach 67% and 51%, respectively. The potentiodynamic polarization test shows that this composite film has good corrosion resistance and can significantly reduce its surface roughness and porosity.

IV. CORROSION PROTECTION MECHANISM

This coating has good properties such as chemical corrosion resistance, alkali resistance, and high temperature resistance.

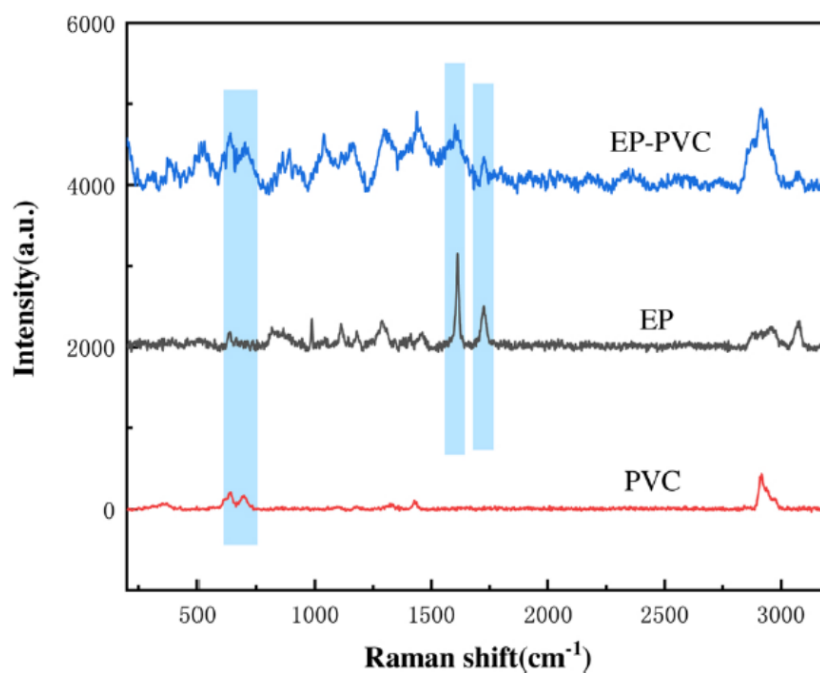


FIGURE 2. Raman spectra of PVC, EP, and EP-PVC powder coatings

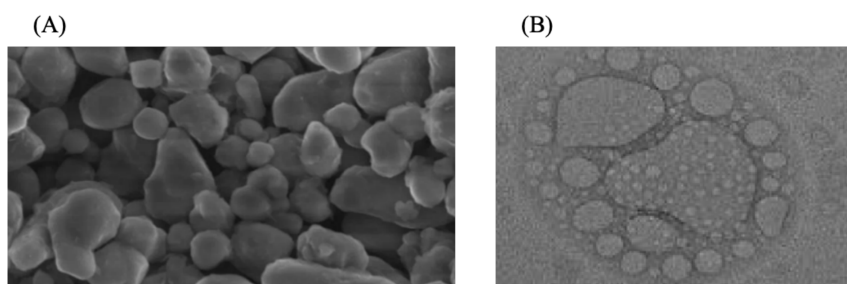


FIGURE 3. TEM images of powder coating

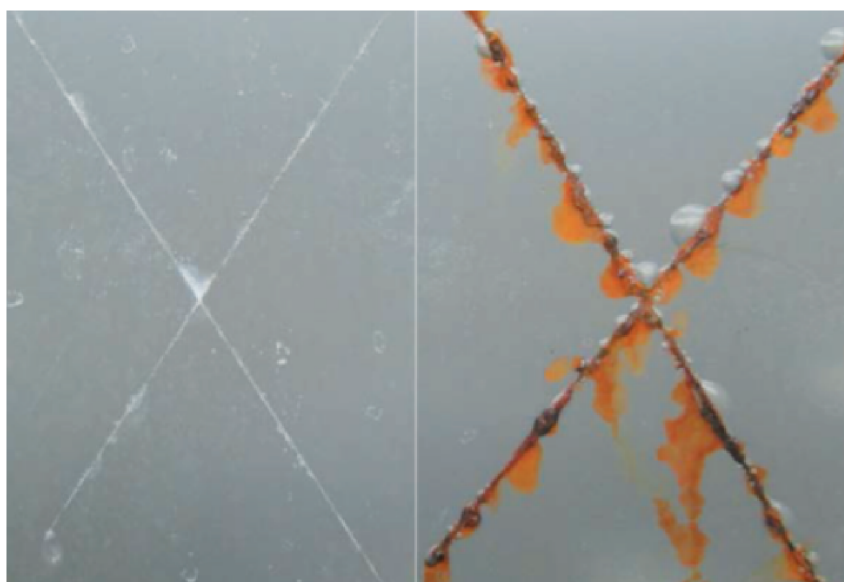


FIGURE 4. Photographs and microscope pictures after salt spray test at the scratch of the coating film

TABLE 3. Electrochemical corrosion measurements under different curing modes

Curing mode	E_{cor} (mV)	i_{cor} ($\mu\text{A}/\text{cm}^2$)	β_a (mV/dec)	β_c (mV/dec)	R_p (Ω/cm^2)	C_R (mm/a)	P_E (%)
Bare steel	−689.8	4.7654	102.1	33.2	2287	0.0055	–
Layer-by-layer curing	−597.0	1.5622	303.4	555.8	54627	0.0018	67
Co-curing	−437.9	2.3586	238.9	269.6	31719	0.0031	51

At the same time, the benzene rings and carbon hydrogen chains in epoxy resin molecules are arranged in a staggered manner, giving it excellent physical and mechanical properties. These substances not only contain abundant hydroxyl groups, ether bonds, and active epoxy groups, but can also form strong chemical bonds with metals through hydrogen bonding [19]. Research has found that using epoxy coating to wrap PVC can improve the bonding strength between the coating and steel.

PVC molecules contain highly polar C–Cl bonds, which increase the intermolecular attraction and cohesive energy between PVC molecular chains. Moreover, the large atomic size of chlorine atoms results in a pronounced steric hindrance effect, providing effective barrier properties against corrosive media. In the EP-PVC primer layer, the epoxy resin undergoes a polycondensation reaction with the dicyandiamide (DCD) curing agent, as evidenced by the evolution of cyanamide nitrile groups in the FT-IR analysis. The results indicate that there is a semi interpenetrating structure between this network structure and polyvinyl chloride resin. This dense organization slows down the infiltration of corrosive media, reduces the erosion of the metal matrix, and thus improves the corrosion resistance [20].

V. CONCLUSION

In double-layer powder coating systems applied to Q235 carbon steel substrates, the superior interlaminar adhesion and mechanical strength achieved through layer-by-layer curing outperform co-curing methods, which often suffer from reduced powder deposition efficiency. This specialized curing sequence ensures that the coating fully encapsulates the textile fibers, resulting in a more durable and resilient composite surface. Regarding the corrosion protection mechanism, comparison between pure epoxy coatings and pure PVC coatings indicates that the PVC topcoat enhances physical barrier performance and inhibits electrolyte diffusion. Meanwhile, epoxy resin modification in the primer improves adhesion between PVC and the metal substrate, thereby preventing interfacial delamination.

AUTHOR CONTRIBUTIONS

Conceptualization – Fei Liu and Tao Cui; methodology – Fei Liu and Tao Cui; investigation – Fei Liu and Tao Cui; writing-original draft preparation – Fei Liu and Tao Cui. All authors have read and agreed to the published version of the manuscript.

CONFLICTS OF INTEREST

The authors declare no conflict of interest.

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