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The Biological Functionality of Electro-Galvanized Steels Coated with a Hybrid Composite Containing Pyrethroid

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The electronic industries require environmentally-friendly and highly functional materials to enhance the quality of human life. Home appliances require insect repellent steels that work to protect household microwave ovens from incurring damage by insects such as fire ants and cockroaches in tropical regions. Thus, POSCO has developed new types of functional steels, coated with an array of organic-inorganic hybrid composites on the steel surface, to cover panels in microwave ovens and refrigerators. The composite solution uses a fine dispersion of hybrid solution with polymeric resin, inorganic and a pyrethroid additive in aqueous media. The hybrid composite solution coats the steel surface, by using a roll coater and is cured using an induction curing furnace on both the continuous galvanizing line and the electro-galvanizing line. The new steels were evaluated for quality performances, salt spray test for corrosion resistance and biological performance for both insect repellent and antimicrobial activity. The new steels with organic-inorganic composite coating exhibit extraordinarily biological functionalities, for both insect repellent and antimicrobial activities for short and long term tests. The composite-coating solution and experimental results are discussed and suggest that the molecular level dispersion of insecticide on the coating layer is key to biological functional performances.

Keywords: *Functional coating, Insect repellent, Antimicrobial activity, Galvanized steel*

1. Introduction

Recently, household electronic industries require environmentally-friendly and highly functional materials to enhance the quality of human life. Especially, home appliances require insect repellent steels to protect household electronic appliances such as microwave ovens, washing machines, and refrigerators from damage (e.g. wires short, sanitation) of insects such as fire ants and cockroaches in tropical regions. In this development, we tried to prepare aqueous insect repellent composite solution by fine dispersion of a pyrethroid insecticide to the aqueous polymeric resin solution which has high corrosion resistant properties. In principle, by the addition of ingredients to inhibit the release of neurotransmitters of insects on the resin coated film, highly functional products can be designed to prevent sanitary and physical damage to electronic equipment by causing paralysis or the insect to flee. The coated layer contains synthetic pyrethroids, which are less harmful in the human body but are highly effective for insects such as cockroaches, ants, flies, mosquitoes, moths, spiders, etc. [1]. Insecticide shows kill, knock-down, or repellant properties of insects depending on concentration of insecticide on the coated layer. Therefore, it is important to control the content of insecticide to show the performance of the insect repellent steel.

Pyrethrins are a natural organic compounds normally derived from the dried flower heads of chrysanthemums that have potent insecticidal activity and are neurotoxins that attack the nervous systems of all insects [1]. When present in amounts not fatal to insects, they still appear to have a repellent effect [2]. Pyrethins are usually broken apart by sunlight and the atmosphere in several days, and do not significantly affect groundwater quality [3]. The chemical structure of pyrethrins inspired the production of a variety of synthetic insecticides, shown in Fig. 1, called pyrethroids. Pyrethroids interfere with sodium transport channels in insect nerve cells. When the toxin is present in the channels, the nerves cannot repolarize, leaving the membrane permanently depolarized, thereby paralyzing the organism [4].

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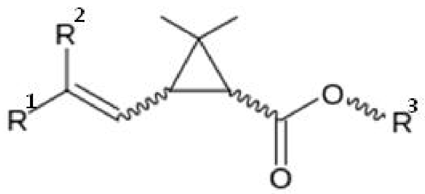
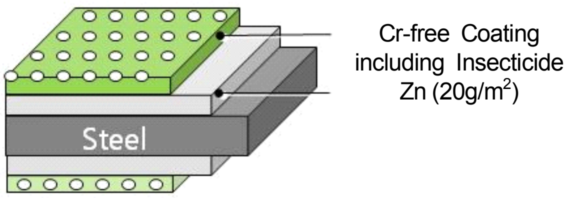


Fig. 1 Chemical structure of synthetic pyrethroids with different alkyl substituents.

<Scheme 1>



In this development, we prepared a well-dispersed hybrid composite Cr-free solution with pyrethroid insecticide and coated the surface of galvanized steel sheets, shown in <Scheme 1>, to provide repellent properties when the insects approach and make contact. The biological tests were performed for both insect repellent activity—with a specially designed shelter for cockroaches—and anti-microbial activities with several species of bacteria and fungi.

2. Experimental Details

2.1 Preparation of composite solution

The composite solution was prepared from mechanical dispersion of an acryl modified polyurethane resin binder (Buhmwoo Chemical Co.), melamine hardener (Cytec Industries Inc.), micronized mesoporous silica (Dow Chemical Co.) and a pyrethroid compound (LG Chemcial Ltd.), respectively. The insecticide solution was prepared by a Soxhlet extraction method because of extremely low solubility in alcohol. Ultra-high concentrated pyrethroid solution was combined with a hollow type of mesoporous silica and then dissolved with a surfactant to obtain a higher stability of insecticide molecule. This solution was combined with an aqueous organic resin solution to produce an aqueous organic-inorganic hybrid composite. Subsequently, several miscellaneous additives were put into the resin solution: anticorrosive agent, wetting and stabilization agent of pigments, wax lubricant, and defoamer. The solid content was measured by the weight portion after drying at 150 °C for 30 min. and viscosity of the composite solution was measured by Brookfield method.

2.2 Production of hybrid composite-coated steel sheets

The hybrid composite solution was prepared from water-borne solution that has 8 ± 1 cP in viscosity and 16 ± 1% of solid content at 25 °C. The production was carried out on both the electro-galvanizing line (EGL) and continuous galvanizing line (CGL) that the processes consisted of pre-treatment, galvanizing, roll coating, induction curing, and cooling, in that order. The composite solution was coated by a two-roll reverse operation on the strip surface. The curing temperature was set at 160 ± 5 °C by induction oven which consisted of three oven segments connected by bellows. The coated layer was dried in an induction oven and then cooled to room temperature *via* air cooling and water quenching. The weight of the coated layer was measured by both a portable IR wavelength measurement instrument and wet weight method.

2.3 Performance evaluation

Quality performances for corrosion, insect repellent activity, and antimicrobial activity were carried out. The corrosion resistance was evaluated by salt spray test (JIS Z2371) with edge sealing by scotch tape. The insect repellent test was carried out in the Korea Research Institute of Bioscience and Biotechnology and measured by a specially designed apparatus with shelters for cockroaches made of both the test and control steels [5]. The apparatus criteria are as follows: Apparatus dimensions: 300 x 300 x 20 mm, temperature: 25 ± 1 °C, sample steel size: 80 x 80 mm, shelter size: 80 x 80 x 10 mm, shelter entrance: 20 x 10 mm, and 50 *Blatella germananica* cockroaches. The activity was measured at hourly intervals for 24 hours and calculated by [(number of controlled sample - number of tested sample)/ number of controlled sample] x 100]. Additionally, we measured insect repellent activities with microwave ovens with applied steel panels. To conduct this application, we designed a special apparatus for insect repellent efficiency (Fig. 2). The microwave oven set was composed of a combination of cover panel, rear cover, and bottom plate coated with hybrid composite-coated steels instead of conventional steel sheets (Fig. 3). The detailed evaluation conditions are as follows: Microwave oven set: 480 x 290 x 260 mm, transparent chamber size: 1260 x 490 x 360 mm, and 100 *Blatella germananica* cockroaches). The efficiency data were obtained from video recording each hour for 24 hours and activity was calculated.

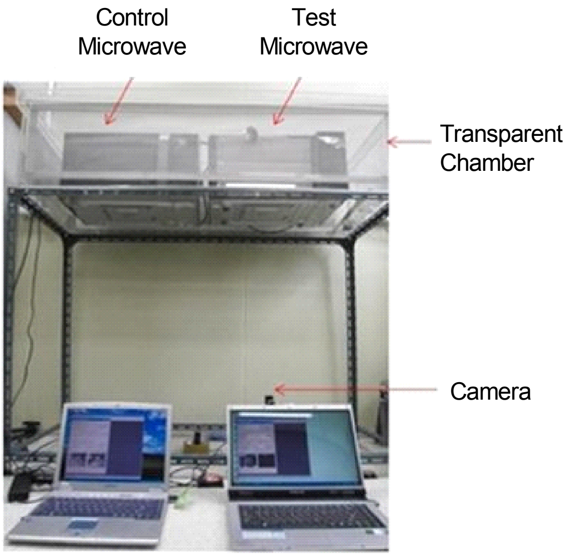


Fig. 2 View of specially designed evaluation apparatus including microwave oven and video recording.

The microbial test was carried out by Korea Conformity Laboratories and conducted with three kinds of bacteria (*Escherichia coli., Pseudomonas aeruginosa, Staphylococcus aureus)* and five kinds of fungi (*Aspergillus niger, Penicillium pinophilum, Chaetomium globosum, Gliocladium virens, Aureobasidium pullulans*). In the bacteria tests, evaluation was carried out by the standards of KCL-FIR-1003:2011. For the fungal tests, fungi was cultivated for 4 weeks and evaluated according to the standards of ASTM G21: 2009. For both bacterial and fungal trials, the hybrid composite-coated steel was compared with conventional anti-fingerprint steel

3. Results and Discussion

3.1 Preparation of composite-coated steel sheets

We have prepared a new type of hybrid composite solution which includes insecticide. In the preparation process of the coating solution, there are important requirements to making the Cr-free coating solution to apply in the galvanizing line. To get an environmentally-friendly coating solution of both low cost and high efficiency, it is necessary to create highly concentrated solution of insoluble insecticide and stabilize the insecticide in that solution. The concept of the Cr-free composite-coating layer was designed to incorporate a conventional Cr-free coating solution with insecticide to afford an insect repellent property. However, most insecticides are fairly insoluble in water or in alcohol solvent. To overcome the solubility of insecticides, we invented extraction equipment which provided a drastic increment by about 10^5 fold increase of solubility in a 2-propanol solvent. The extract solution was combined with aqueous mesoporous silica to yield insecticide embedded composite solution. Next, it was mixed with aqueous Cr-free resin solution that had an acryl modified polyurethane binder resin, melamine hardener and micronized silica for anticorrosive pigment, wax as a slip agent, and miscellaneous additives to improve rheological properties.

New composite-coated steel sheets were produced in both the electro-galvanizing and continuous galvanizing lines from roll coating operation. Both lines consist of a cleaning section, galvanizing section, roll coating section, induction oven, and cooling section, in that order. The cleaning section-that washes out dust, scale, and press oil on the strip-consists of three separate sections that are alkaline degreasing, acid cleaning, and electro-degreasing. The electro-galvanizing process consists of horizontal cells which are commonly adopted for high-speed production. With high-speed production, roll coating technology is more important for obtaining excellent surface appearance and accurate coating thickness. Generally reverse (*reverse-forward-reverse* or *reverse-forward-forward* mode) coating using three rolls is more favourable for fine coating quality. Another technology to attain high-speed production is induction curing using resistant heat induced by an inductive current. The surface heating of steel is easier to get high curing temperatures for the resin layer compared to the conventional thermal method. During rich

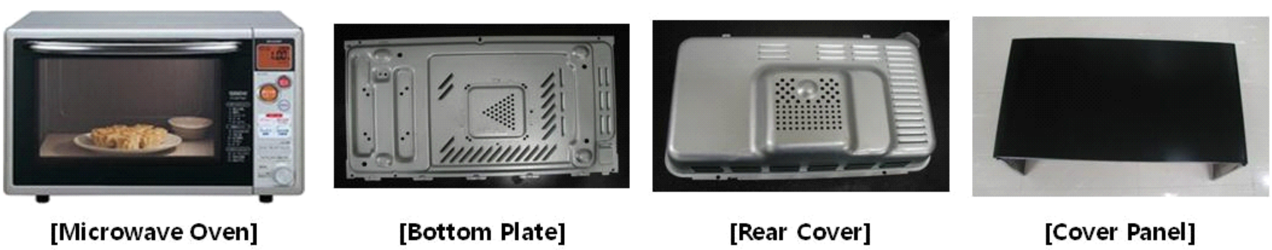


Fig. 3 Steel panels for household microwave ovens consist of a bottom plate, rear cover and cover panel.

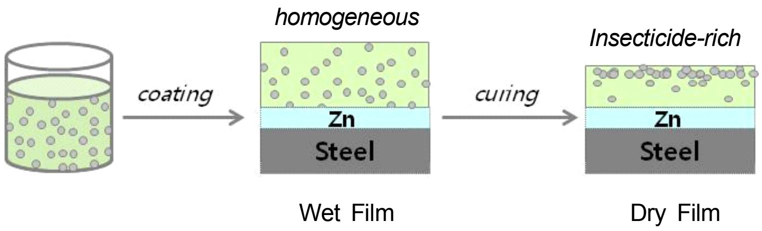


Fig. 4 Preparation of functional composite-coated steels with an insecticide-rich layer on the steel surface.

layer shown in Fig. 4, which provides for superior coating quality. The cooling section consists of both air blowing for slow cooling and water quenching for rapid cooling of the strip surface. Finally, hot air is necessary to dry residual water on the wet surface from the cooling section.

Salt spray test for new composite-coated steel with coating weights of 1000 ± 200 mg/m^2 exhibit no white rust corrosion during evaluation; 96 hours in flat panel and 48 hours in Ericksen drawn part as like common anti-figerprint steels, shown in Fig. 5. The composite coated products show excellent corrosion resistance even though incorporation of pyrethroid molecule in organic-inorganic hybird network. This can be provide a geruntee for more than 10 years use as a panel in home appliances.

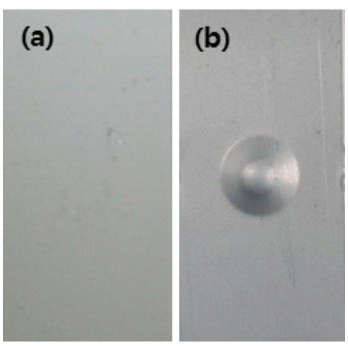


Fig. 5 Corrosion resistance evaluation for composite coated steels by salt spray test; (a) after 96 hours in flat panel, (b) after 48 hours in Ericksen drawn part.

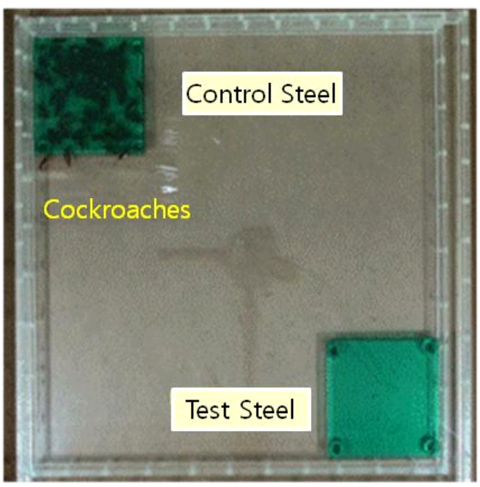


Fig. 6 View of the cockroaches staying on the surface of controlled steel instead of tested steel of functional composite-coated steel after 12 hours elapsed time.

3.2 Insect repellent evaluation

In this development, we have examined functional properties such as insect repellent activity and anti-microbial tests. Firstly, insect repellent activity was measured by a specially designed apparatus, shown in Fig. 6, which was comprised of a shelter for housing insects and cockroaches.

Usually cockroaches like to occupy or inhabit narrow spaces. Even though cockroaches were initially staying in random shelters, after some period of time, the cockroaches moved to the control steel. Insect repellent efficiency was calculated by the aforementioned expression in the experimental details section. The activities were measured for both short- and long-term efficiency for the composite-coated steel sheets. In the evaluation, conventional steel, which did not contain an insecticide, showed no efficiency, as indicated by the graph in Fig. 7. However, tested steel showed improved efficiency, over 95%, after 10 hours of time. And, efficiencies were drastically increased according to duration of cockroaches in the environment. During long term exposure of the steels, the pyrothroid activity was proven by accelerated insect repellent measurement test using the aged steel sheets for 4 months at 60 °C and 90% relative humidity. Both tests exhibited more than 95% insect repellent activities, which may allow for a 10 year guarantee of insect repellent activity for about 10 years of customer use of the steels, shown in Fig. 7.

We have tested activities for a microwave oven with household appliance composite-coated steel sheets applied. The microwave oven adopts three steel panels which are the bottom plate, rear plate, and cover panel. We have

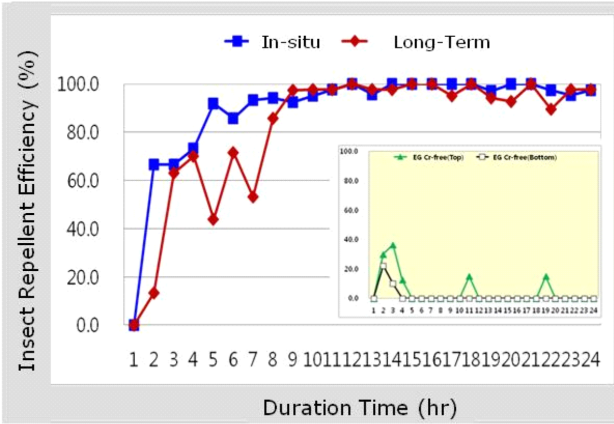


Fig. 7 Insect repellent efficiencies of functional composite-coated steel that measured both in-situ and long term durability of 10 years. Superimposed graph represents control steel.

measured insect repellent activities, shown in Table 1, and compared with an anti-fingerprint steel sheet panelled microwave as reference for the combination of composite-coated steel sheets. The test criteria were: i) bottom part only, ii) cover part only, iii) bottom and rear parts, iv) bottom and cover parts, and v) bottom, rear and cover parts. The microwave set consisting of conventional steel showed no insect repellent activity. However, increasing the number of parts with the new composite-coated steel showed improved efficiency, which is consistent with the adapted area of the test steel, shown in Table 1 and Fig. 8. In these tests, the activities were in the order: i) bottom part only < ii) cover part only < iii) bottom and rear parts < iv) bottom and cover parts < v) bottom, rear and cover parts. That order coincides with the increasing area covered by composite-coated steel sheets. As the result, case v) of three adapted parts exhibited the best efficiency within the shortest time. However, all cases reached 100% efficiency after 48 hours of duration except case ii. Therefore, to provide better quality of insect repellency in microwave oven applications, customers may prefer to adopt the new composite-coated steels.

Table 1 Results of insect repellent efficiencies of microwave oven substituted with parts of composite-coated steel obtained from Fig. 7

Steel	Duration of Test	Application Parts				
		i	ii	iii	iv	v
Anti-fingerprint Steel	24 hr	-	-	-	-	0%
Composite Coated Steel	12 hr	0%	58%	0%	100%	100%
	24 hr	50%	64%	100%	100%	100%
	48 hr	100%	93%	100%	100%	100%

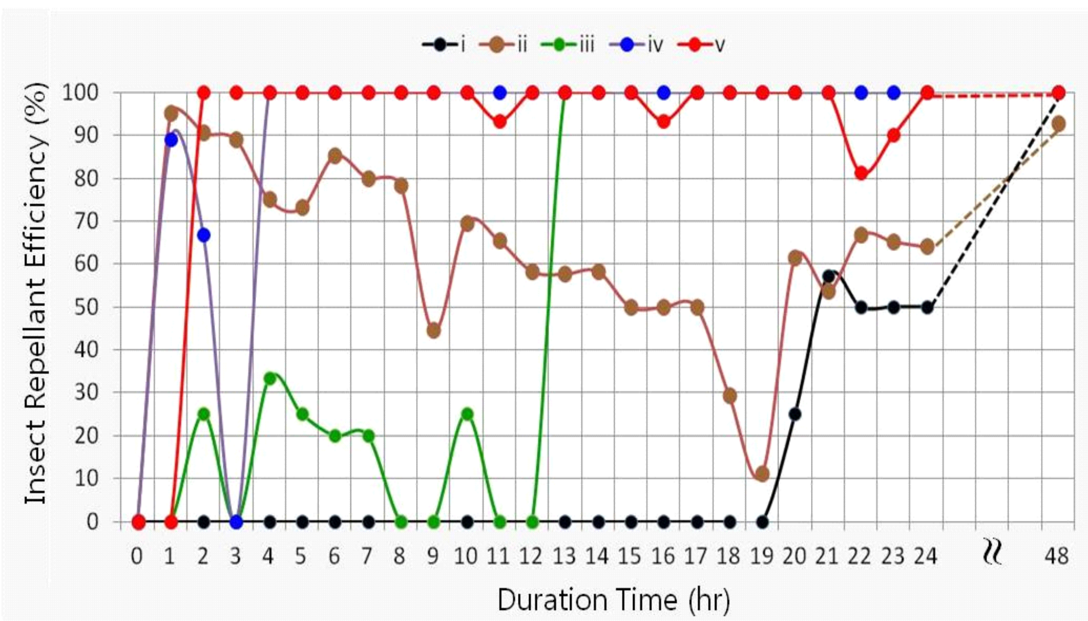


Fig. 8 Results of insect repellent efficiencies of microwave oven set substituted with parts of composite-coated steel.

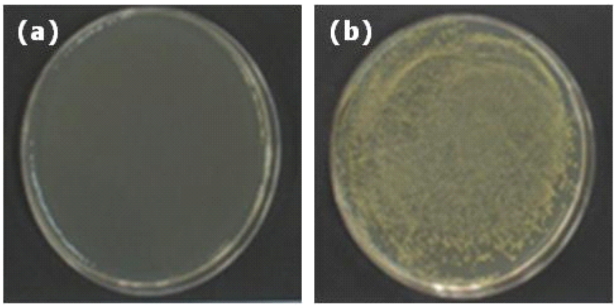


Fig. 9 View of anti-fungal efficiencies of both (a) composite-coated steel and (b) control anti-fingerprint steel after 24 hours of incubation.

3.3 Microbial evaluation

We have tested and compared antibiotic and antifungal activities for composite steel sheets with anti-fingerprint steel sheets as a reference. Incubation tests were conduct for three common viruses, which were composed of *Escherichia coli., Pseudomonas aeruginosa, and Staphylococcus aureus*. The composite-coated steel showed 99.9% antibiotic efficiency from perfect no growth observances in bacteria concentration for all bacteria during 24 hours; however anti-fingerprint steel as a reference increased 1.5 fold in bacterial concentration, shown in Fig. 9 and Table 2. And, incubation tests for five common fungi, which were comprised of *Aspergillus niger, Penicillium pinophilum, Chaetomium globosum, Gliocladium virens, and Aureobasidium pullulans,* were conducted. The composite-coated steel exhibited 99.9% anti-fungal efficiencies for all fungi during 4 weeks of incubation due to no cultivation of any species of fungus, shown in Table 3. From these results, the new composite-coated steels are clearly having an antibiotic functionality; moreover; excellent dual functionalities of both antibiotic and antifungal activities are due to fine dispersion of pyrethroid insecticide molecules in the coating solution.

4. Summary

A new composite-coated steel sheet has been developed that protects against damage from insects to, and also inhibits growth of common bacteria and fungi on household microwave ovens. The composite-coating solution was prepared by fine dispersion of both aqueous polymer resin solution and mesoporous silica solution of highly-concentrated pyrethroid insecticide, and then treated on the steel surface in the in-line electrolytic and continuous galvanizing lines to provide composite-coated steel sheets. The newly developed steels exhibit excellent corrosion resistance as well as biological functionalities that have both excellent insect repellent and antimicrobial activities. In

Table 2 Results of antibiotic efficiency of composite-coated steel for three common virus compared with anti-fingerprint steel as a control

Test	Starting concentration (CFU/mL)	Concentration after 24 hours (CFU/mL)	Antibiotic efficiency (%)
Escherichia coli.			
Anti-fingerprint Steel	3.3×10^5	5.0×10^5	0
Composite Coated Steel	3.3×10^5	< 10	99.9
Pseudomonas aeruginosa			
Anti-fingerprint Steel	3.6×10^5	5.2×10^5	0
Composite Coated Steel	3.6×10^5	< 10	99.9
Staphylococcus aureus			
Anti-fingerprint Steel	2.9×10^5	4.5×10^5	0
Composite Coated Steel	2.9×10^5	< 10	99.9

Table 2 Results of antibiotic efficiency of composite-coated steel for five common fungi

Test	Antibiotic Efficiency after Incubation Duration (%)			
	1st week	2nd week	3rd week	4th week
Eschelichia niger	0	0	0	0
Penicillium pinophylum	0	0	0	0
Chaetomium globosum	0	0	0	0
Gliocladium virens	0	0	0	0
Aureobasidium pullulans	0	0	0	0

the microwave oven test with substituted composite steels instead of commercial steels, higher insect repellant efficiency corresponding to the number of adapted panels was observed. In the antimicrobial test, composite-coated steels exhibited excellent efficiencies for all of the tested fungi and bacteria. The new composite-coated steel has newly proven dual functionalities of both insect repellent and anti-fungus activity that operate by different mechanisms. Experimental results suggest that molecular level dispersion of pyrethroid insecticide on the coating layer plays a key role in the dual biological performances. The new product is under mass production for supplying a variety of household electronic appliances such as refrigerators and washing machines.

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