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Development of PCM Color Coated Steel Sheets with Excellent Antiviral and Antimicrobial Properties

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Recently, due to the rapid spread and continuation of COVID-19, customer demand for health and hygiene has increased, requiring the development of new products that express antiviral and antibacterial properties. In particular, viruses are much smaller in size than bacteria and have a fast propagation speed, making it difficult to kill. POSCO has developed eco-friendly PCM color coated steel sheets with excellent antiviral properties by introducing inorganic composite materials to the color coating layer on the surface of Zn-Al-Mg alloy plated steels. The virus is not only destroyed by adsorption of metal ions released from the surface of the coating film, but is also further promoted by the generation of reactive oxygen species by the reaction of metal ions and moisture. As a result of evaluating the developed products under the International Standard Evaluation Act, the microbicidal activity was 99.9% for viruses, and 99.99% for bacteria and 0% fungi. In particular, excellent results were also shown in the durability evaluation for life cycle of the product. The developed product was applied as a wall of school classrooms and toilets and ducts for building air conditioning, resulting in excellent results. Developed products are being applied for construction and home appliances to practice POSCO's corporate citizenship.

Keywords: *COVID-19, Antivirus, Antimicrobial, PosMAC, PCM Steels*

1. Introduction

Since 2020, social and economic problems have become serious due to the highly infectious and health-threatening virus caused by Covid-19 Pandemic. Coronavirus is a generic term for a coronal-shaped virus, and is a respiratory virus that causes sore throat and rhinitis, including an epidemic cold. In addition to the coronavirus, respiratory viruses include influenza viruses (Influenza-A, H1N1) which cause the flu, and rhinovirus, a common cause of colds. Typical viruses commonly detected in humans are Human Coronavirus (229E, OC43, and NL63). Serious respiratory viruses include SARS, MERS, and the novel coronavirus SARS-2 [1-4]. The Covid-19 virus contains RNA nucleic acids in its spherical phospholipid and protein envelope. Most viruses penetrate human or animal host cells and multiply by replicating nucleic acids in large quantities using the ribosome of host cells. Viruses are smaller in size from 1/100 to 1/10000 compared to bacteria or fungi, can be transmitted and replicated quickly, and mutates quickly, making it difficult to develop treatments or vaccines.

As part of efforts to solve the harmful environment of such viruses, the development of antiviral and antimicrobial surface treatment products that can inactivate viruses, bacteria, and fungi on the surface of steel plates, which are essential materials for our lives, is required. In order to impart the above properties, it has been reported in recent papers and patents that copper metal surfaces, nano metal or metal ions, and quaternary ammonium ions have a killing function against bacteria and some viruses [5-8]. Copper metal is reported to be killed by nano-metal or metal ions dissolved from the surface penetrating into the outer envelope of bacteria or viruses and losing replication function. It has been reported that metal ions such as Ag, Cu, Ni, and Zn also inactivate with a similar mechanism [9-12]. Polymers containing quaternary ammonium ions report that hydrophobic functional

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groups are killed by binding to the outer membrane of viruses and bacteria and destroying their functions [8]. However, the inactivation action by such an organic compound is not only incomplete when treated on the surface of the material, but also has a problem that it takes a long time. In particular, color coated steel steels used for home appliances and construction materials are usually manufactured with a coating thickness of 20mm or more for long-term use for more than 20 years. In the case of the above metals and metal oxides, when the liquid coating solution is coated on the steel sheet, it is likely to exist inside the coating film due to density, making it difficult to exert functionality on the surface.

Accordingly, POSCO tried to develop steel products that exhibit antiviral properties to contribute to solving human hygiene and health problems. In this paper, PCM color coated steel sheet with antiviral properties was developed by applying inorganic composite material (*abbreviation* MX-Y) to the top coating layer. The evaluation of antiviral, antibacterial, and antifungal characteristics of the developed product and the case of application to the client company were described.

2. Experimental

2.1 Evaluation of quality characteristics

The thickness of the coating film of the color coated steel sheet was measured with a non-destructive portable coating thickness gauge. The design of the coating film's color and the uniformity and continuity of the texture were relatively evaluated. Gloss was evaluated by measuring the 60º mirror reflection value using Sheen's equipment. The corrosion resistance evaluation was evaluated by the cyclic corrosion test. Salt water spraying (concentration 5%, spray pressure of 1 kg/cm^2 at 35 ºC) was performed for 100 cycles (1cycle; 5 hours at 95% relative humidity, dried at 70 ºC for 2 hours, and treated at 95% relative humidity and 50 ºC for 3 hours). The bending workability evaluation is performed by placing the surface of the steel plate in a vise, bending it 180º at a pressure of 1 kgf, and then tightening it until it is flat (0T-bending). When the scotch tape was attached to the bent coating film and the coating film was peeled off, the occurrence of cracks on the surface peeled off the tape and the presence or absence of coating peeling were evaluated. Chemical resistance was determined as the number of times until the coating film was peeled off when the gauze wetted with MEK (Methylethylketone) was rubbed back and forth with a force of 1 kgf. Both acid and alkaline resistance evaluation were performed by leaving a 5% H_2SO_4 and NaOH solution on the surface of the steel sheet at a temperature of 20 ºC for 24 hours respectively and then evaluating whether blister or rust occurred on the surface.

2.2 Antiviral properties

The antiviral properties of color-coated steel plates (50 × 50 mm) were evaluated by ISO 21702 standard at Chonbuk National University. The undiluted solution of COVID-19 (2.15×10^7 TCID50/mL) virus cultured in monkey cells (Vero E6) was dropped to 100 mL on the control and coated steel sheet specimens, covered with cover film (polyethylene) at room temperature, washed and recovered with 10 ml of SCDLP medium, and diluted the virus solution of $10^{-1} \sim 10^{-5}$ step by step. Each well was infected with a monkey host cell (Vero E6 Cell) and then cultured at 37 ºC for 72 hours. After dropping MTT staining solution (triazolium) in each cultured well, color changes were observed to determine the survival of the host cell. The concentration value (TCID50/mL) of living cells in the well was calculated by the Spearman-Karber method, and the virus mortality rate was quantified compared to the uncoated galvanized steel plate as a control group.

2.3 Antibacterial properties

Korea Conformity Laboratories evaluated four types of bacteria (E. coli, staphylococcus aureus, staphylococcus aureus, and pneumococcus) in JIS Z 2801:2012 standard for antibacterial evaluation of color coated steel sheets. Both control and a color-coated steel sheet (50 × 50 mm) were put into a petri dish, and inoculated bacteria (2.5×10^5 to 10^6 CFU/ml) were cultured in an NB medium, and 300 μL of the bacterial solution was dropped to act. At this time, the sample was covered with a stomacher film (40×40 mm) and the bacterial solution and the sample were closely adhered to each other to test the contact area constantly. The inoculation specimen was treated at temperature (35 ºC) and relative humidity (92.9%) for 24 hours, washed with 10 mL of SCDLP medium, collected

bacteria, and diluted stepwise to prepare a sample solution until it reached 10^{-1} to 10^{-5}. The sample solution (1 mL) was divided into a petri dish, and 1.5 % agar medium was added and mixed. The inoculated petri dish was placed in an incubator at 37 ºC for 72 hours to incubate bacteria, then count colony units, calculate the number of bacteria, and quantitatively evaluate the mortality rate of bacteria compared to the uncoated galvanized steel plate as a control group.

2.4 Anti-fungal properties

The anti-fungal properties evaluation was conducted by the Korea Conformity Laboratories on five types of fungi (*Aspergillus niger, Penicillium pinophilum, Chaetomium globosum, Gliocladiumvirens, Aureobasidium pullulans*) in accordance with the standard test method (KCL FIR-1003:2011). After inoculating the fungal strain on the surface of the steel sheet (50 × 50 mm in size), the growth area of the fungal mycelium was evaluated after 4 weeks to evaluate the anti-microbial properties.

3. Results and Discussion

Since the harmfulness to bacteria and viruses is a function that is more needed inside the building than outdoors, it was developed as a color steel plate for building materials for application. The developed product uses PosMAC1.5 material instead of commonly used GI because it has excellent corrosion resistance and is suitable for construction materials. However, it is possible to expand the application to GI and EG materials according to the customer's needs. For application purposes, it can be applied to negative pressure rooms in hospitals, school classrooms and toilet walls, and inside food factories. It is expected to be applicable to refrigerators and air conditioners for home appliances. This product was developed by coating a top layer having antiviral performance after pretreatment and primer coating of existing color steel sheets. The upper coating film was developed by adding color pigments, anti-corrosive pigments, and antiviral additives to a conventional polymer-hardener system. Color coated steel sheets typically require antiviral (COVID-19) and antibacterial (bacteria), which are unique functions of this product, as well as properties such as appearance aesthetics, processability required for processing, corrosion resistance and durability (heat resistance, weather resistance), and chemical resistance to pollutants (acid, base resistance). In addition, viscosity, solid content, and curing temperature were generally optimized for stable roll coating of the top coating film, and operation of line speed 80 mpm suitable for mass production of building materials was secured.

3.1 Development of new products

The eco-friendly inorganic composite, MX (M, metal ion; X, non-metal ion) is a strong basic material and has a problem of inhibiting the polymer crosslinking reaction by reacting with an acid catalyst when applying the existing polyester polymer-melamine curing system. In order to solve this problem, a urethane modified polymer and isocyanate that do not use an acid catalyst were introduced to cause a polymer crosslinking reaction, thereby ensuring coating properties. The MX material is an eco-friendly low-cost basic material and has excellent metal ion release properties when forming a film, but Y (Y = metal cation) material is added to ensure stable performance by making an MX-Y composite. In particular, MX-Y compounds manufactured through wet reactions using natural materials are not only harmless to the human body, but also have the advantage of being able to supply and demand stable raw materials. Fig. 1 shows a schematic diagram of antiviral-antibacterial expression

Table 1. Evaluation of three color-coated steel sheets

Color	Code	Thickness (μm)	Line speed (mpm)	Gloss (%)	Surface quality for building application			
					Formability	Solvent resistance	Acid & alkaline resistance	Surface appearance
Beige	EC6	18 ± 2	80	15 ± 5	Good	Good	Good	Good
Ivory	EC9	18 ± 2	80	30 ± 5	Good	Good	Good	Good
Gray	GTNJ9A	18 ± 2	80	20 ± 5	Good	Good	Good	Good

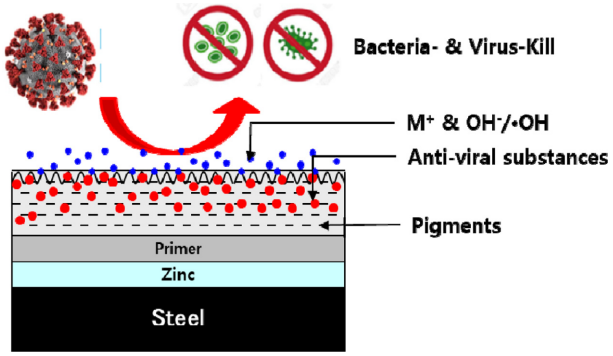

Fig. 1. Schematic diagram of anti-viral functionality

for MX-Y. The development of the developed product was completed by verifying mass production by promoting test production at the POSCO STEELEON CCL line.

3.2 Antivirus mechanism

In the coating film containing antiviral substances, metal ions (M^{2+}) and hydroxide ions (OH^-) are released when viral droplets contact, and metal ions react with dissolved oxygen to form reactive oxygen species, killing viruses and bacteria. However, a sufficient ion concentration (dissociation rate) is required for virus (~nm) death, which is very small in size compared to bacteria (~mm). The antiviral substance MX-Y is estimated to exhibit antibacterial and antiviral properties due to the rapid release of M^{2+} and Y^+ ions and X^- anions and easy hydroxy radical production. In particular, MX-Y composites exhibited better properties than when MX and Y materials were used alone. In addition, the MX material is manufactured in a nano-size by wet process from nature, and it is judged to have excellent ion release. In general, if antiviral properties for small viruses are excellent, it was experimentally evaluated as excellent antibacterial properties.

3.3 Antimicrobial-antiviral performance

① **Antiviral Performance**: The COVID-19 virus is defined as the highest risk rating and can only be handled in laboratories above biosafty level-3. For the development of new products, it was evaluated by Chonbuk National University. In addition, the evaluation of similar coronaviruses, Feline and Influenza-A viruses, was conducted by the Korea Research Institute of Bio Science (KRIBS). The evaluation was evaluated by ISO 21702 standard. However, in the standard, the virus contact time is defined as 2 to 24 hr, and in this study, the optimal contact time was set as 2 hr and evaluated. The goal of the mortality rate for COVID-19 was determined to be excellent when it was 99.0% (active value 2) or higher in accordance with the antibacterial evaluation standard. ② **Antiviral long-term reliability evaluation**: Antiviral maintenance was verified during the product life cycle (~10 years). There are no international standards for this, but color steel sheets are usually evaluated accordingly because they are conducted as ultraviolet promotion tests (weather resistance tests) to evaluate the durability of the coating film. In other words, it was determined that the life of the product could be guaranteed for about 10 years if the accelerated weathering test (Q-UV Test) was conducted for 1000hr. ③ **Anti-microbial evaluation**: Anti-bacteria evaluation is internationally specified in ISO 22196 standard. In this study, it was commissioned and evaluated by the Korea Conformity Laboratories (KCL), an authorized certification institution. The mortality rate for bacteria is determined to be excellent when it was 99.9% (active value 3) or higher according to the antibacterial steel plate currently sold. In addition, when mold proliferation experiments were conducted on five mixed strains on the developed product, very

Table 2. Evaluation of microbicidal activities

Microbe		Efficiency	Evaluation	Standards
Virus	COVID-19	99.9% *Long-term 98.0%	Chonbuk National Univ.	ISO 21702
	Influenza A	99.98%	KRIBS	ISO 21702
	Feline	99.9%	KRIBS	ISO 21702
Bacteria (4 types)		99.999%	KCL	ISO 22196
Fungi (mixed strain)		0%	KCL	ASTM G21-15

Fig. 2. Application of (a) interior panels for modular school and (b) toilet, and (c) duct panel for air conditioning system

good results were obtained with a growth rate of 0%. Table 2 summarizes the anti-viral and anti-microbial evaluation results.

3.4 Application of customers

The developed products produced by POSCO STEELEON CGL were applied for the first time in the world through domestic building materials customers (Yoochang Co., Ltd. and Hanshin Color Steel), shown in Fig. 2. For use, ivory (code EC9) and beige (code EC6) colored panels were applied for walls of elementary school modular classrooms and toilets. In addition, the new gray (code GTNJ9A) colored product was also applied to the duct part of air conditioning system and received favorable reviews. It is expected to be mass-produced at the request of customers in the future.

4. Conclusion

In this paper, a color steel sheet with excellent antiviral and antimicrobial properties was developed as follows.

First, by combining eco-friendly antiviral substances with the top layer of PCM color coated steel sheet, the world's first color steel sheets for construction and home appliances with antiviral and antimicrobial properties was developed. The developed product is judged to kill viruses or microorganisms by extremely small amounts of metal ions, anions, and reactive oxygen species released from inorganic composites in the coating film, and has excellent antiviral performance at a lower cost than existing commercial products as well as has secured long-term durability (about 10 years) during the product's life cycle. (mortality rate of 99.0% for COVID-19 and 99.999% for bacteria) Second, the mass productivity and quality of coating films of three types of colors were secured using the POSCO STEELEON CCL line. Third, it was applied to interior panels for school classrooms and toilets, and duct panel for air conditioning system through customers specializing in building materials. Developed products will be mass-produced and applied to customers as part of POSCO's corporate citizenship activities in the future.

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