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Polypropylene Laminated Steel Sheet Usable without Painting

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Abstract

Painting with organic solvents is shunned due to its environmental problems, and the lamination of steel with thermoplastic resins is being pursued in the canmaking industry. To meet this demand, Nippon Steel developed polypropylene laminated steel sheet by the T-die lamination process that melt-extrudes polypropylene directly on steel sheet. Since the crystallization of polypropylene is controlled by optimizing the cooling conditions, a film with excellent formability and corrosion resistance is obtained. The polypropylene laminated steel sheet is now commercially used for 18-liter cans. Their economy is expected to expand the application of T-die laminated steel sheets to include polyethylene and polyethylene terephthalate as laminating resins.

1. Preface

Painting processes involving organic solvents became unwelcome these days because of the growing consciousness of the global environmental issues and the concern about labor environment during the painting work, and switching to water-soluble resin paints and use of thermoplastic resin-laminated steel sheet are in progress in the canmaking industry. With such a background a new kind of steel sheet product is being developed and commercialized wherein a film of resin such as polyethylene (PE), polypropylene (PP) or polyethylene terephthalate (PET) is formed on the surface of steel sheet, making it possible to eliminate the painting process after canning[1].

There are two processes for producing plastic-laminated steel sheets: one called the thermal lamination process, consists of thermally bonding pre-manufactured plastic film to steel strip, and the other called the T-die lamination process, consists of forming a film from melted resin (melt-extrusion) and laminating it onto the steel strip immediately. Most of the laminated sheet cans presently commercialized are made by the thermal lamination method. The T-die lamination method, which is employed mainly for paper packages[2], is also used for production of pre-coated sheet of galvanized steel with PE resin[3], and for coating steel pipes with PE or PP resin[4].

Since the melt-extrusion lamination process (T-die lamination process) applies melted resin directly onto the steel sheet surface and eliminates the film-manufacturing step, it is expected to be more widely used as an economical process.

2. Development of PP-laminated Steel Sheet by T-die Lamination Process[5, 6]

Development work was commenced envisaging to develop a new PP-laminated steel sheet by the T-die lamination process, which product would offer a new container to substitute the so-called *atron-can*, a container composed of an 18-liter steel can containing a plastic bag, widely used for packaging industrial chemicals which require high corrosion resistance.

Fig. 1 shows structure of the developed product. A PP layer is formed on one surface of steel sheet with a modified PP layer

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in-between acting as a bond. This side will be the inner surface when formed into cans. The other surface is pre-coated with a water-soluble paint as a standard specification.

Fig. 2 is a schematic illustration of a production line of the PP-laminated steel sheet based on the T-die melted resin extrusion process, and **Fig. 3** shows an outline of a two-layer T-die resin extrusion equipment used in the line. The process is quite simple, comprising, (1) the painting one side of coated steel sheet for can use such as electro chromium coated steel sheet (ECCS) or tinplate with water-soluble resin, (2) the application of layers of PP and modified PP directly onto the other side by the two-layer T-die extrusion equipment taking advantage of the heat of the preceding paint drying process, (3) then finally, crystallinity of the resin layers is controlled in the cooling stage that follows. As the T-die extrusion equipment is capable of forming multiple resin layers easily, it is possible to manufacture products meeting widely varying requirements by adequately combining a variety of resins of different characteristics. **Fig. 4** shows a heat pattern for manufacturing PP-laminated steel sheet.

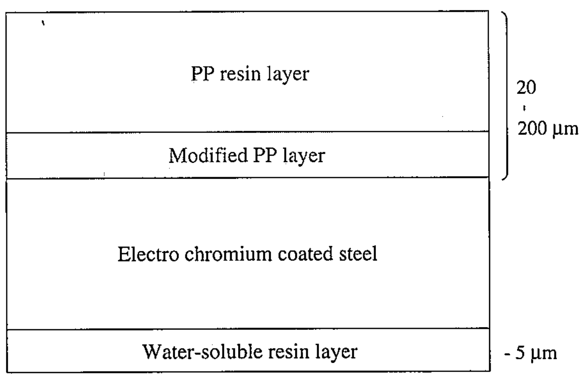


Fig. 1 Structure of PP-laminated steel sheet

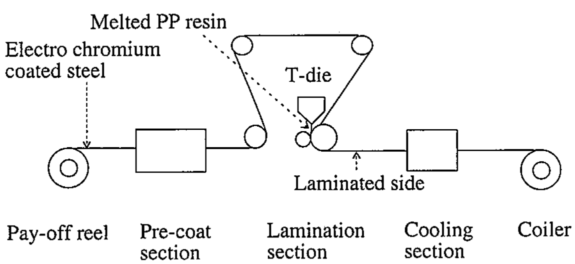


Fig. 2 Outline of PP-laminated steel sheet production line

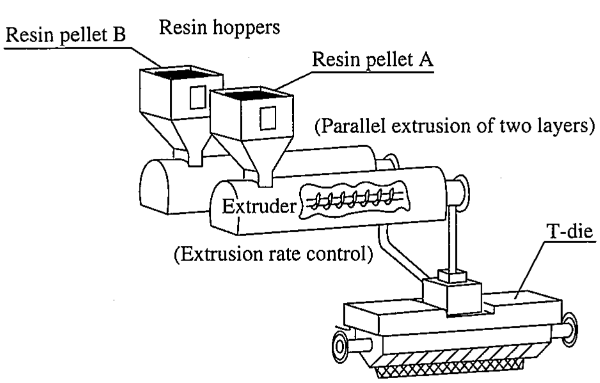


Fig. 3 Outline of two-layer T-die resin extrusion equipment

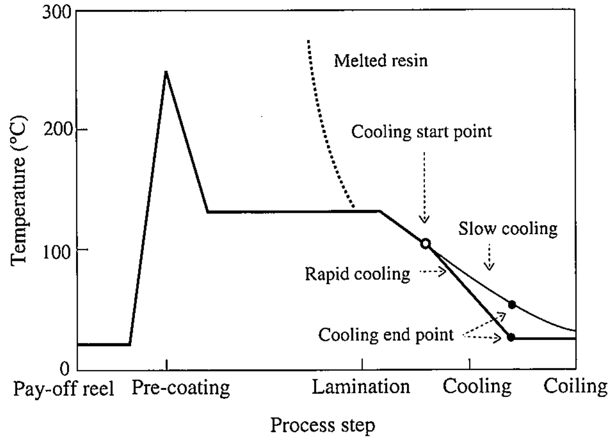


Fig. 4 Heat cycle of PP-laminated steel sheet manufacturing

3. Quality Characteristics of PP-laminated Steel Sheet by T-die Lamination Process

3.1 Crystallization of PP Resin Film

Fig. 5 shows a comparison of X-ray diffraction patterns of two PP-laminated steel sheets, one cooled at 2°C/s in the atmosphere immediately after the T-die lamination and the other at 100°C/s by water spray. The peaks between 10° and 30° of the slowly cooled sample show a higher diffraction intensity in the (100) and (040) planes than the rapidly cooled one, meaning that the crystallization of the former is more advanced than the latter. Crystallinity of the rapid-cooled sample proved to be approximately 28% while that of the slow-cooled one was around 60%.

Fig. 6 shows the relationship between cooling rate and crystallinity of the resin. As seen in **Fig. 5** crystallization can be controlled at a cooling rate of 100°C/s, but at 2°C/s crystallization is too advanced. Then, the authors investigated the effects of cooling rates between these two figures, and it was confirmed that crystallinity

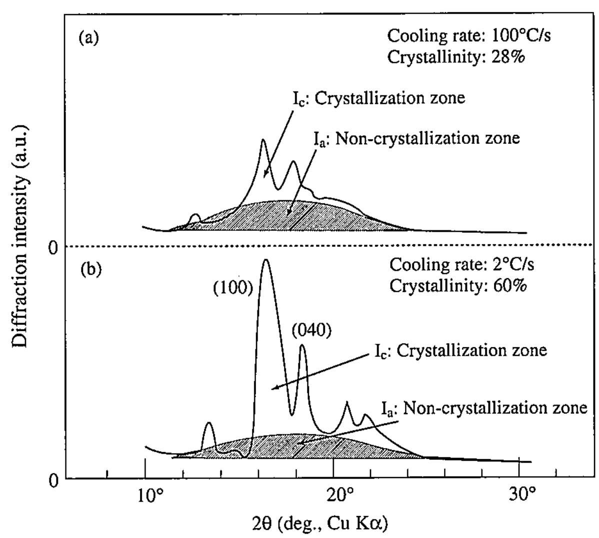


Fig. 5 Comparison of resin crystallinity of PP laminate film under different cooling rate

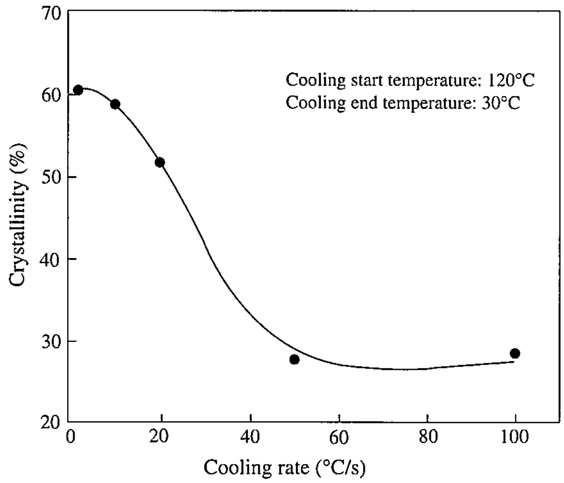


Fig. 6 Relationship between crystallinity and cooling rate of PP film

fell remarkably at cooling rates above 20°C/s, and at 40 - 50°C/s crystallinity was nearly the same as 100°C/s.

Effects of the temperatures at the start and the end of the cooling process were also studied. It was found out that for controlling the crystallinity of the resin to about 30% or less the forced cooling should start while the temperature of the resin and the steel was above 110°C and continue till the temperature fell to 30°C or below.

3.2 Formability and adhesion

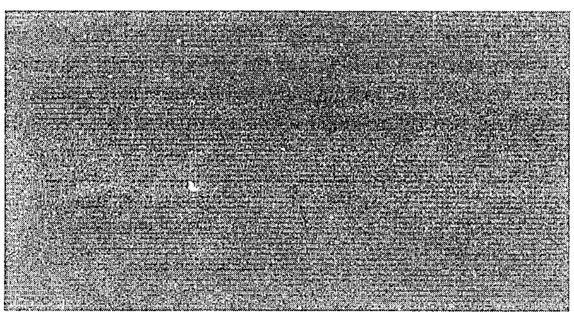
Formability of the slow-cooled and rapid-cooled sheets was studied by impact forming test (Du Pont impact test) and drawing test (Erichsen test). As a result, a whitening of the resin layer at the convex portion of the impact forming was observed in the slow-cooled samples, while no such whitening was seen in the rapid-cooled samples. **Photo 1** shows observations of the convex portion surfaces by scanning electron microscope (SEM). The whitening seen in the slow-cooled sheets was suspected to have been caused by light scattered by microscopic cracks formed in the resin layer, and small cracks were actually observed on the surface of the convex portion, but the rapid-cooled sheets showed no such cracks. In the Erichsen test the whitening of the convex portion was not as conspicuous as it was in the Du Pont test but SEM revealed micro cracks of the slow-cooled samples after the work.

Thus, it has been made clear that the rapid-cooled PP-laminated steel sheet has a good formability under forming works such as pressing, without developing minute cracks in the resin layer, whereas the slow-cooled samples, which has a higher crystallinity, shows cracks or poor appearance after working.

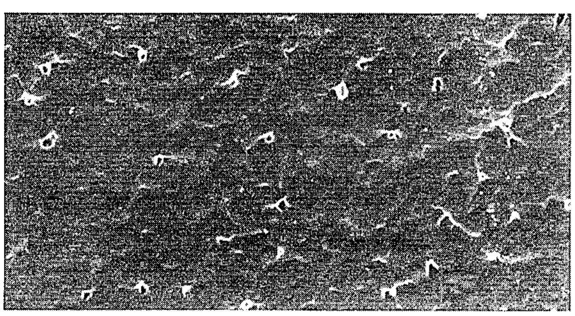
Adhesion of the resin layer before and after the works was also investigated. It was confirmed that the peeling strength of the rapid-cooled resin layer was 190 - 200 g/mm, and that of the slow-cooled resin 250 - 280 g/mm either before or after working, and no deterioration of adhesion by working was observed. The higher adhesion of the slow-cooled resin is accounted for by the longer time it was kept at high temperatures.

3.3 Corrosion resistance

As described above, there is a clear difference in formability between the slow-cooled and rapid-cooled samples, the former developing micro cracks in the worked portions. For the purpose of studying the effects of this difference on corrosion resistance, the samples were tested by immersion in surface-active agent. **Photo 2** shows the result. Whereas no change was observed on the resin

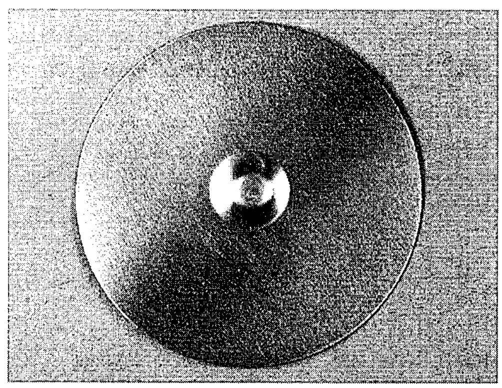


(a) Rapid-cooled sample (100°C/s)

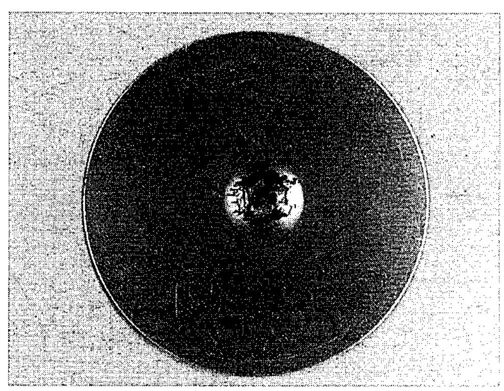


(b) Slow-cooled sample (2°C/s) 100μm

Photo 1 SEM photographs of worked portion of laminated PP film



(a) Rapid-cooled sample (100°C/s)



(b) Slow-cooled sample (2°C/s) 10mm

Photo 2 Surface active agent immersion test

surface of the rapid-cooled sample after the immersion test, occurrence of steel corrosion of the slow-cooled sample was confirmed by rust formation on the surface of the Du Pont-drawn portion. This is suspected to result from penetration of the detergent through the micro cracks of the slow-cooled resin layer and slow propagation of the crack due to a combined effect of the detergent penetration and stress by the drawing work.

As products packaged by 18-liter cans or the like often include surface-active agents, poor stress crack resistance against these matters sometimes cause problems to containers such as plastic containers using PE[7]. The corrosion of the steel substrate of the slow-cooled sample was, presumably, caused by poor stress crack resistance of the resin layer due to its crystallization.

As discussed above, it became clear that the slow-cooled laminated steel sheet, the resin layer of which is well crystallized, is inferior to the rapid-cooled sample in appearance and corrosion resistance after forming, and it is essential to rapidly cool the resin layer immediately after the lamination in order to obtain good formability and corrosion resistance. With respect to the difference

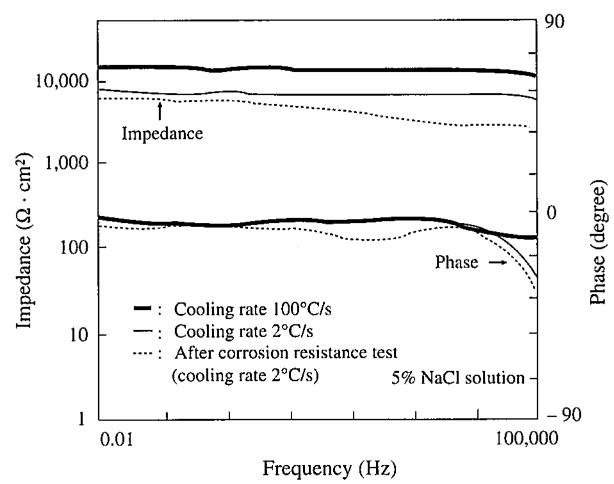


Fig. 7 AC impedance measurement of PP-laminated steel sheets

in corrosion resistance between the rapidly cooled and slowly cooled samples, the authors carried out impedance measurements of the Du Pont-formed portion as a means to electrochemically evaluate integrity of the resin layer. The result is shown in **Fig. 7**. There is a difference between impedance before the corrosion test of the slow-cooled sample and that of the rapid-cooled sample as shown by continuous lines in the figure, and the slow-cooled sample showed lower impedance than the rapid-cooled sample. Further, as indicated by dotted lines, the impedance of the slow-cooled resin layer falls yet deeper after the corrosion resistance test.

Table 2 Properties of PP-laminated steel sheet (Part 2)

Test item		Test method	Result
Corrosion resistance		5% salt spray for 1 month after a 5 mm Erichsen forming	No rust
Corrosion resistance against chemicals and food filled as contents after can forming (cup drawing 50 mmφ × 30 mm high)	Chemical	①5% acetic acid (40°C, 1 month) ②10% hydrochloric acid (40°C, 1 month) ③10% sulfuric acid (40°C, 1 month) ④10% caustic soda (40°C, 1 month) ⑤Detergent (40°C, 1 month) ⑥Chloric bleach (40°C, 1 month)	①No change ②No change ③No change ④No change ⑤No change ⑥Little change
	Paint	①Water-soluble acrylic parint (40°C, 1 month) ②Water-soluble polyvinyl acetate paint (40°C, 1 month)	①No change ②No change
	Solvent	①Ethanol (25°C, 1 month) ②Methyl ethyl ketone (25°C, 1 month) ③Trichloro-ethylene (25°C, 1 month) ④Benzene (25°C, 1 month) ⑤Toluene (25°C, 1 month) ⑥Acetone (25°C, 1 month) ⑦Gasoline (25°C, 1 month) ⑧Kerosene (25°C, 1 month)	①No chnage ②No change ③No change ④No change ⑤No change ⑥No change ⑦No change ⑧No change
	Food	①Vinegar (40°C, 1 month) ②Soy source (40°C, 1 month) ③Spirit (40°C, 1 month)	①Little change ②No change ③No change

Table 1 Properties of PP-laminated steel sheet (Part 1)

Test item	Test method	Result
Adhesion	①180° T-peel test ②180° T-peel test after fusion of PP layer ③2 mm cross hatch adhesion ④2 mm cross hatch adhesion (after 90 min retort in 3% NaCl solution at 125°C)	①Good (PP film fractured.) ②20 kg/25 mm ③No peeling ④No peeling
Adhesion after aging	①1 h immersion in boiling water ②1 month exposure to 100% RH atmosphere at 50°C ③1 month immersion in water at room temperature	①No peeling ②No change ③No change
Formability (room temperature)	①180° bend ②90° impact bend ③Du Pont impact forming (1/2 inch hemisphere, 500g, 30 cm) ④Cylindrical drawing	①No cracks ②No cracks ③No whitening of resin layer ④No whitening and cracks
Stain resistance	Stain (marking ink, lipstick, etc) left at 20°C for 25 h, then cleaned with neutral detergent and observed.	No remaining stains
Food noxiousness	Notification No.20 of Ministry of Health & Welfare, FDA (non-retort)	Compliance confirmed

3.4 Properties of PP-laminated sheet

It was made clear that, in order to secure good product quality of the PP-laminated steel sheet, control of crystallization of the resin layer was important for preventing deterioration of corrosion resistance caused by the micro cracks formed during press forming of the can-making process. **Tables 1** and **2** show product properties of the PP-laminated steel sheet by the T-die process.

4. Conclusion

It has been made clear that formability and corrosion resistance of the PP-laminated steel sheet depend largely on crystallization of the resin layer and that it is possible to manufacture a product having good formability and corrosion resistance by controlling crystallization of the resin layer. As the T-die lamination process consists of directly applying melted resin onto the steel sheet it allows for widely varied cooling conditions and stably manufacturing high performance PP resin layer having low crystallinity.

The PP-laminated steel sheet manufactured by the T-die process is being used for 18-liter cans as a highly formable and corrosion resistant material.

5. Future Development

The economic advantages offered by the laminated steel sheet products by the T-die process will expand their applications and, in view of the possibility, laminated steel sheets with PE and PET are being developed besides the above discussed PP-laminated sheet. Not only the containers such as 18-liter cans, aerosol cans, food and drink cans are considered as applications of these products but studies have been made on their applications also to construction, electric appliances, etc., for cultivating possibilities of eliminating painting process at the users' plants. Their demands are expected to rapidly expand as environment-friendly materials.

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