Effects of Glass Transition Temperatures of Films on the Corrosion Resistance after Forming of Pre-Coated Aluminum Sheets

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Aluminum sheets with superior surface functions have been increasingly used in electrical fields. In this paper, the effects of the glass transition temperatures of the films on the corrosion resistance of pre-coated aluminum sheets before and after forming were investigated. The corrosion resistance after forming of polyester type pre-coated aluminum sheets with three different glass transition temperatures were investigated by salt spray test. It was found that corrosion resistances of the film with glass transition temperatures higher than the forming temperature were low. In the cups with low corrosion resistance after forming, whitening phenomena were observed. This whitening behavior was also investigated by the stretching test. Results showed that whitening was only caused in areas where lubricants were applied, and micro-cracks were only observed in the areas where whitening occurred. In addition, whitening was observed only in films with high glass transition temperatures. As films with high glass transition temperatures are hard, excessive internal stress (cause of cracks) tend to concentrate on local area. It is considered that the adsorbed lubricant on the polyester films acts to decrease the mechanical strength of the films. As a result of the lubricant adsorption, the film can not withstand internal stress in stress-concentrated regions, which in turn causes micro-cracks to develop. It can be thought that the corrosion resistance was deteriorated by the sodium chloride solution that penetrated into these micro-cracks.

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1. Introduction

Aluminum materials have been used for wide applications because of lighter weight, higher specific strength, and higher heat conductivity than steel materials. In recent years, pre-coated aluminum sheets provided with various surface functions have been increasingly used. In the case of heat exchangers of air conditioners, for example, the surface is coated with hydrophilic treatment so as to insure smooth flow of condensation water. In the case of optical disc drive covers for notebook computers, the covers are coated with such a treatment that scratched marks and finger marks are made invisible. In addition to these, aluminum sheets with surface functions such as radiation performance, antibiotic property, high reflectivity, and antifouling property have been developed and put into practical use.

The cost for the process to coat aluminum sheets with these functional films before forming is remarkably lower than that for the process to coat after forming. However, these surface functions should not be damaged after forming. In this study, the function of corrosion resistance was taken up among these surface functions. And the effects of the glass transition temperatures of the films on the corrosion resistance of pre-coated aluminum sheets before and after forming were investigated. The difference between the films with excellent corrosion resistance after forming and those with poor corrosion resistance was made clear. And the mechanism for this phenomenon was discussed.

2. Experimental

2.1 Preparation of pre-coated aluminum sheets

The preparation process for the pre-coated aluminum sheets is as follows. The material of substrates used pure aluminum sheets (1.2 \times 10^{-3} m thick A1100-O).

The substrate was degreased with a mild alkaline degreasing agent and treated with chromium phosphate treatment\textsuperscript{1)} a typical conversion coating for aluminum. The chromium deposit per unit area was 2 \times 10^{-5} kg/m\textsuperscript{2} in terms of metallic chromium. On the one surface of aluminum substrate after chromium phosphate treatment, three kinds of polyester coating materials with different glass transition temperatures were coated so that the dry film thickness would be 5 \times 10^{-6} m, and cured at a temperature of 523 K. The glass transition temperatures of these coating materials were 273 K, 313 K, and 353 K. The baking time was 40 seconds.

2.2 Drawing test

Three kinds of pre-coated aluminum sheets were drawn to cylindrical cup of 5 \times 10^{-2} m diameter \times 2.5 \times 10^{-2} m long (Fig. 1). Drawing was performed in such a way that the surfaces with polyester films of pre-coated aluminum sheets would be the outside of drawn cups. Quick-drying type oil was used as lubricant. The composition of lubricant was paraffinic hydrocarbon and the viscosity was 1.4 \times 10^{-7} m\textsuperscript{2}/s. The temperature at the time of drawing was 313 K.

2.3 Stretching test

Deep drawing test is a realistic method because it reproduces the products in a simulated way. However, it is
difficult to quantitatively evaluate the strain produced in the pre-coated aluminum sheets by forming. So, stretching test which possible to strain the specimens quantitatively was also performed (Fig. 2). The same quick-drying type oil was applied to the film surface. The strain in these test were 0% (no stretching), 10%, and 20% stretching.

2.4 Corrosion test

Tests were performed in accordance with ISO 9227 neutral salt spray test. Namely, sodium chloride solution of 5 mass% was used as the spray solution, the temperature was 308 K, and the amount of spray in one hour per an area of $8 \times 10^{-3}$ m$^2$ was $1.5 \times 10^{-6}$ m$^3$. The time of tests was 3000 hours. The tests were performed both for the drawn cups and stretched specimens.

As for the stretched specimens, the test results were quantified in accordance with the rating number method in which the degree of corrosion is quantified by the corrosion area ratio.

2.5 Observation of film surface

The surface of the film were observed by SEM.

3. Results

3.1 Corrosion test

3.1.1 Drawn cups

Figure 3 shows the appearances of the drawn cups after neutral salt spray test of 3000 hours. While corrosion was not observed in the cups with the glass transition temperatures, $T_g$, of 273 K and 313 K, corrosion was observed in the cup of 353 K. And, only the cup with the glass transition temperature of 353 K was observed whitened appearance. As whitening was observed before starting of salt spray test, it was not caused by corrosion test but by the drawing test.

3.1.2 Stretching test specimens

Figure 4 shows the appearance of the specimen with 0%, 10% and 20% stretching before neutral salt spray test. Only in the specimen with the glass transition temperature, $T_g$, of 353 K, whitening was observed on the surface just after stretching of more than 10%. It was the same case as after drawing test.

Figure 5 shows the appearance of the specimen with 0%, 10% and 20% stretching after neutral salt spray test of 3000 hours. As for the specimens with the glass transition temperatures, $T_g$, of 273 K and 313 K, corrosion is limited only to the specimen edges and the neighborhood of cross cuts. As for the specimens with $T_g$ of 353 K without stretching, corrosion is also limited only to the specimen edges and the neighborhood of cross cuts. However, as for

<table>
<thead>
<tr>
<th>$T_g = 273$ K</th>
<th>$T_g = 313$ K</th>
<th>$T_g = 353$ K</th>
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</thead>
<tbody>
<tr>
<td>Good (No corrosion)</td>
<td>Good (No corrosion)</td>
<td>Poor (Corrosion)</td>
</tr>
</tbody>
</table>

Fig. 3 Appearance of the drawn cup after 3000 hours neutral salt spray test. $T_g$ means the glass transition temperature of pre-coated film.
the $T_g$ of 353 K with stretching more than 10%, corrosion is caused not just at the specimen edges and the neighborhood of cross cuts but at any positions of the surface.

The corrosion level of every specimen after neutral salt spray test of 3000 hours was quantified in accordance with the rating number method. Figure 6 shows the results as plotted against stretching strain. The rating numbers which show corrosion area ratio for the specimens with the glass transition temperatures, $T_g$, of 273 K and 313 K showed high value of more than 9. This is because the positions of corrosion are limited as mentioned in the above. As for the glass transition temperature of 353 K, the rating number of 0% stretched specimen showed a high value of 9 because the corroded positions are limited. However, the rating numbers of 10% and 20% stretched specimens showed remarkably low values of less than 7 because corrosion has taken place at

<table>
<thead>
<tr>
<th>Stretch</th>
<th>$T_g$ = 273 K</th>
<th>$T_g$ = 313 K</th>
<th>$T_g$ = 353 K</th>
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<tbody>
<tr>
<td>0%</td>
<td>Good</td>
<td>Good</td>
<td>Good</td>
</tr>
<tr>
<td>10%</td>
<td>Good</td>
<td>Good</td>
<td>Whitening</td>
</tr>
<tr>
<td>20%</td>
<td>Good</td>
<td>Good</td>
<td>Whitening</td>
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Fig. 4 Appearance of the stretched specimens before neutral salt spray test. $T_g$ means the glass transition temperature of pre-coated film.

<table>
<thead>
<tr>
<th>Stretch</th>
<th>$T_g$ = 273 K</th>
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</tr>
</thead>
<tbody>
<tr>
<td>0%</td>
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</tr>
<tr>
<td>10%</td>
<td>Good</td>
<td>Good</td>
<td>Poor</td>
</tr>
<tr>
<td>20%</td>
<td>Good</td>
<td>Good</td>
<td>Poor</td>
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</tbody>
</table>

Fig. 5 Appearance of the stretched specimens after 3000 hours neutral salt spray test. $T_g$ means the glass transition temperature of pre-coated film.
any positions of the specimens. As the rating numbers decrease with the increase in the stretching strain, it is suggested that strain is one of the factors which deteriorate corrosion resistance.

3.2 Surface observation

Figure 7 shows the film surface of the drawn cups with the glass transition temperatures of 273 K and 353 K. Numerous micro cracks are observed in the film with the glass transition temperature of 353 K. As for this cup, whitening was already observed in the as-drawn state. This implies that the surface seems to be whitened as observed visually because light is scattered by these observed micro cracks. On the other hand, for the drawn cup with the glass transition temperature of 273 K in which whitening is not observed, micro cracks were not observed. The cup of 313 K which didn’t show whitening was also observed no micro cracks. Consequently, film whitening is a phenomenon characteristic only to the film with the glass transition temperature of 353 K among the films used in this study.

Also in the stretched specimens of 10% and 20% with the glass transition temperature of 353 K in which whitening was observed, micro cracks of the film were observed. In the specimen of 0% stretching, no cracks were observed and no whitening was observed visually. From these results, it is clear that the whitening of the film is a phenomenon caused when strain is applied to the film.

3.3 Factors affecting whitening

From the above results, the specimens with low corrosion resistance were already whitened before salt spray test. In the whitened area, numerous micro cracks were observed in the film. Therefore, it is considered that sodium chloride solution penetrates through the film cracks to cause corrosion. In order to insure corrosion resistance after forming, it is necessary to clarify the mechanism of crack generation. Stretching tests were performed to make clear the conditions for the occurrence of whitening.

The specimen of 353 K was examined in 5% stretching test. Lubricant was applied only partially. Figure 8 shows the results. In the state of (a) before stretching, whitening was not observed. In the state of (b) after stretching, whitening was caused only in the region where lubricant was applied. This implies that factors causing whitening include lubricant as well as before mentioned glass transition temperature and stretching.

4. Discussion

The temperature at the time of this drawing test was 313 K. At this temperature, the film with the glass transition temperature of 273 K is soft rubbery state and the film with the glass transition temperature of 353 K is hard glassy state. Generally, the mechanical properties of polymer materials are changed remarkably above and below the glass transition temperature. An example is known in which the elastic modulus of one resin is changed by three-digit above and below the glass transition temperature.3,4)

In this study, polyester coating films were selected for all of the pre-coated aluminum sheets. Therefore, it can be presumed that the elastic modulus of the polyester film with the glass transition temperature of 353 K at the time of drawing test was about three-digit higher than that of the
film with the glass transition temperature of 273 K. Glassy state film with such a high elastic modulus is susceptible to high internal stress even by small strain. Even though the elastic modulus is three-digit higher, the fracture strength can not be higher about three-digit. Therefore, it is considered that the fracture strength of such a film can not endure the stress due to only small amount of strain and the film is susceptible to brittle fracture.

In the case of such a material that is susceptible to brittle fracture, local concentration of internal stress should be taken into consideration. Polymer materials such as films are not completely uniform when considered from the standpoint of molecular configuration. Consequently film should be considered to include mechanically weak regions and strong regions because of structural non-uniformity. If there exist portions of stress concentration, the portions are considered to become the starting points of local fracture to cause cracks in the films.5–7)

In the case of the rubbery state film with low elastic modulus, as the internal stress in the film caused when strained is extremely low, it can hardly exceed the fracture strength of the film. As the deformable strain range including elastic strain and plastic strain is very wide, the film itself can deform even when subjected to some strain. From the above reason, fracture of the film can hardly take place.

As the glass transition temperature of the specimen of 313 K was in accord with the drawing test temperature, it is considered that the film was in the state of transition region between glassy and rubbery state. While the properties of metallic materials are changed sharply at the transition temperatures, the properties of polymer materials are generally changed gradually in the temperature range above and below the transition temperature. Therefore, it is considered that the elastic modulus of this film must be the value between the value of glassy state and that of rubbery state. The elastic modulus was one-digit or two-digit lower than that of the glassy state, therefore local cracks of the film could not take place.

In this study, whitening of the films was affected by the existence of lubricant. It is known that micro cracks called stress-cracking are generated when some kinds of organic solvents or interfacial active agents act on the hard polymer materials including internal stress. As whitening of the films took place only when the internal stress caused by strain and lubricant coexisted, the characteristics of stress-cracking are clearly observed in this whitening phenomenon.

The mechanism of brittle fracture in which cracks are generated in a hard film by the action of solvents can be explained with the Theory of Griffith.8) Accordingly, the fracture strength of a brittle material proportional to the square root of its surface energy which is decreased by the action of agents such as solvents.9–11) When assumed that the role of lubricant in this study is the same as this action of solvents, micro cracks caused in the film can be explained the brittle fracture occurred by lubricant.

From the results of above discussions, the generation mechanism of whitening will be explained schematically in the following. When the glass transition temperature of the film is higher than the temperature at the time of forming, the film is glassy and hard. As the film with high elastic modulus is deformed, high internal stress is likely to be occurred in the film. Polymer materials are non-uniform at microscopic level. Therefore, portions with and without local stress concentration are produced.

The surface energy of the film is decreased by the penetration of lubricant and, as a result, the fracture strength

![Fig. 8 Appearance of the local area lubricated specimens before (a) and after (b) stretching.](image-url)
Whitening of coated film is the cause of decrease of the corrosion resistance of pre-coated aluminum sheet after forming. Adequacy of glass transition temperature is necessary to keep the corrosion resistance superior of more than 9 of rating number after forming.

5. Conclusion

The corrosion resistance after forming of polyester pre-coated aluminum sheets with different glass transition temperatures was investigated by salt spray test. It was found that corrosion resistance of the film with a glass transition temperature higher than the forming temperature is low.

In the specimens with low corrosion resistance after forming, whitening was caused by strain. As numerous micro cracks were observed in the region of whitening, it can be thought that the corrosion resistance was deteriorated by the sodium chloride solution that penetrated into these micro cracks.

The mechanism of whitening of the film was discussed. In the case where the glass transition temperature of the film is higher than the forming temperature, the regions with high concentrated internal stress are occurred in the film because a glassy film with high elastic modulus is deformed. When lubricant acts on these regions, the fracture strength of the film is decreased, the film strength can not endure the internal stress and brittle fracture is caused.

From the above results, in order to improve the corrosion resistance of formed pre-coated aluminum sheets, means to prevent the generation of whitening due to forming are effective.

REFERENCES