Change of the Crystallinity of Heat-sealed PET Film on Laminated Sheet Steel

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In laminated sheet steel for beverage and food cans, the crystallinity of PET film plays a crucial role in revealed properties, such as adhesion to TFS and water permeability, formability through the film. In this study, Laminated specimens were prepared with various conditions such as temperatures, speed and pressure, using a laminating simulator. In order to investigate the crystallinity behavior of PET film, analyses were conducted by XRD, DSC, bi-refringence analyzer, FT-IR. The relationship between crystallinity and property with laminating conditions on the laminated sheet steel was determined. The cystallinity of PET film varied inversely as the temperature increased. It was also affected by treatment speed. Adhesion and water permeability were increased with the decrease of the crystallinity of PET film.

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Introduction

Recently, in Japan and Europe the laminated sheet steel appears before the footlights in beverage and food can stock, which is not coated with lacquer in a standpoint of environmental problems. A lacquer coating, heretofore, has not only induced a emission of volatile organic compounds (VOC) and a large consumption of energy in can maker, but also been a probable extrication of endocrine disrupting chemicals, such as bisphenol A. The laminated sheet steel is attractive because it could be simple to apply, provide long-term protection of a emission of metal ions, and improve the corrosion resistance of can stock.

In the laminating process, as the PET film of crystalline state contacts with heated substrate, tin-free steel plate (TFS), it could be changed into the amorphous state and adhered to the substrate by succeeding heat treatment nearby its melting point. The crystallinity of the film of the laminated sheet steel plays crucial roles for determining its properties, such as adhesion to substrate, and water permeability and formability of the film.

This study has been performed in order to understand basic phenomena concerning the manufacturing process of laminated sheet steel. We had set up a lab-scale laminating simulator, and investigated the effect of laminating variables on the crystallinity of films. Various analytical methods were applied to determine the change of crystallinity, and the relationships between the crystallinity and the physical properties of the film, such as adhesion and water permeability, were also investigated.

Experimental

Laminating Simulator

A schematic representation of the laminating simulator, which is consisted of four major sections, heating, laminating, water quenching, and film feeding, is given in Figure 1. The specimen was installed into heating chamber, and convectively heated by electrical heater and blower. It was dropped between a pair of laminating rolls, and clear and white films are fed to both sides of the specimen. Then the films were able to adhere to the specimen between laminating rolls by thermal melting and nip pressure. The laminated specimen rapidly fell into quench water to minimize recrystallization.

The general operating conditions of the simulator are:

-Heating temperature is max. 300°C.

-Nip pressure range is 0.5 to 6 kg.f/cm^2.

-Speed is max. 68 mpm (miters per minute).

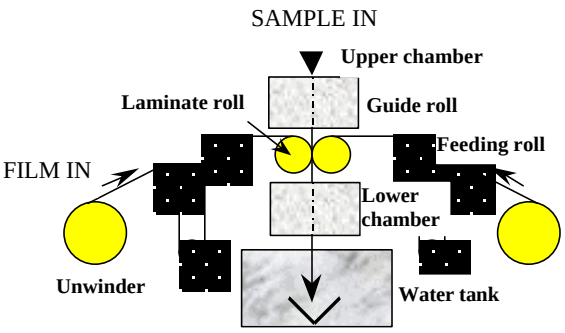

Figure 1 – Schematic Representation of the Laminating Simulator

Preparation of Laminated Specimen

The laminated sheet steel with variation of the laminating variables, such as temperature, nip pressure, speed, and cooling condition, was prepared using the simulator. The substrate was a commercial tin-free steel (TFS) of 0.17 mm thick and 310 × 400 mm.

Mono-layer PET films having thickness of 15μm (white one) and 25μm (clear one) were used. Nip pressure was 4 kg.f/cm^2 and speed was 68 mpm.

Determination of Crystallinity and Evaluation of property

The laminated specimens were determined the crystallinity of the films using various methods as shown in Table 1. The details of the methods will be explained with the results.

Adhesion properties were evaluated by a blister test and a peel test. The peel test[1)] was achieved in 90% of relative humidity at 80°C, and examined by 180° peeled length of the film. The experimental technique[2)] were described in ISO 2528 for permeability to water.

Results and Discussion

Figure 2 shows the change in the crystallinity of the film with laminating temperature. The degree of crystallinity was determined using density-gradient technique by the following equation:

$d_c(d-d_a)/d(d_c-d_a) \subseteq 100(\%)$

Here d_a = density of 100% amorphous PET

d_c = density of 100% crystalline PET
d = density of specimen

As expected, the crystallinity decreases with increasing temperature.

Table 1
Applied Analysis Methods for Evaluating Crystallinity of the Laminated Film

Analysis	Equation
Density-gradient technique	**$d_c(d-d_a)/d(d_c-d_a)$ × 100(%)** d_a = density of 100% amorphous PET d_c = density of 100% crystalline PET d = density of specimen
X-ray diffraction (XRD)	**A/(A+B) × 100(%)** A = crystalline at 17.9°, 22.8°, 26.3° B = armophous area at 24.9°
Differential scanning calorimetry (DSC)	**$(\Delta H_m-\Delta H_c)/\Delta H_{mo}$ × 100(%)** ΔH_m = heats of fusion in crystalline ΔH_c = heats of fusion in recrystallized one ΔH_{mo} = heats of fusion of original film
Bi-refringence	**$R = t(n_1-n_2) = t \cdot \Delta$** R = phase difference, t = thickness of film n_1, n_2 = refractive index, Δ = birefringence index
Fourier transform IR (FT-IR)	**Peak ratio = A/B** A = peak intensity of 1504 cm^{-1} B = peak intensity of 793 cm^{-1}
Polarization microscope	transmittance and cross polarized light

X-ray diffraction patterns of clear films with laminating temperature are shown in Figure 3. At low temperature, sharp peaks (2 = 17.9°, 22.8°, 26.3°, 46.8°, 53.9°) indicate that the PET film has large portion of crystalline region. As increasing the temperature, these peaks are diminished and very broad peaks (2 = 24.9°, 42.3°) are appeared, which indicate the loss of crystallinity.

From figure 3, it is able to calculate the degree of crystallinity as the following:

By assuming that the film is composed of crystalline and amorphous region, the whole diffraction peak could be resolved into two components. The main crystalline component has three peaks at 17.9°, 22.8°, 26.3°, and the amorphous has a broad peak at 24.9°. A proper numeric treatment could calculate the peak area separately, and the degree of crystallinity can be determined by A/(A+B)×100(%); where A is a sum of area of crystalline region and B is that of amorphous region. The variation of crystallinity shows nearly same trends as determined by density-gradient technique.

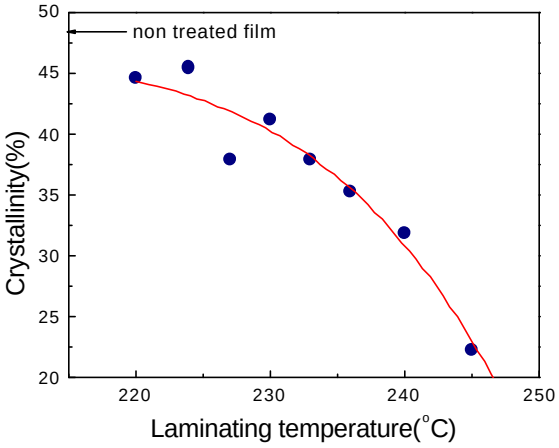

Figure 2 - Change of Crystallinity of Clear Film with Laminating Temperature Determined by Density-Gradient Technique

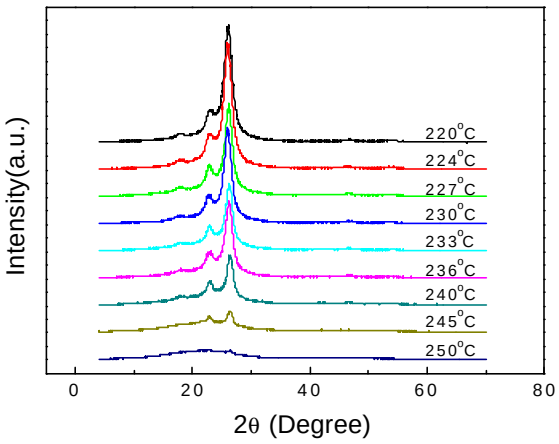

Figure 3 - X-ray Diffraction Spectra of Clear Films with Laminating Temperature

Figure 4 shows the change in crystallinity of white and clear films determined by DSC with variation of laminating temperature. In DSC method, the degree of crystallinity can be calculated by the following equation:

$(\Delta H_m-\Delta H_c)/\Delta H_{mo}\subseteq 100(\%)$

Where, ΔH_m and ΔH_c are heats of fusion in crystalline and recrystallized state after laminating, respectively, and ΔH_{mo} is heats of fusion of original

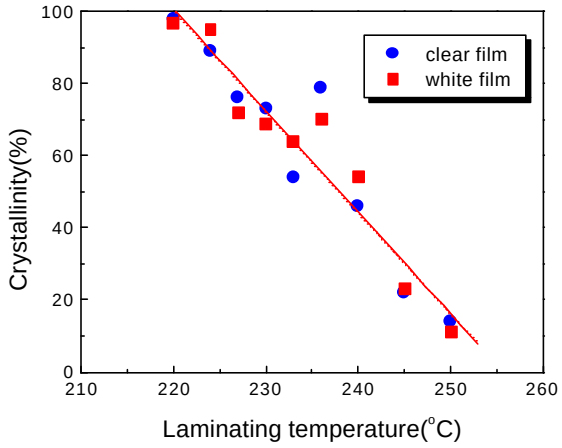

Figure 4 - Change of Crystallinity with Laminating Temperature Determined by DSC

film before laminating.

This trend is also similar to previous results.

Figure 5 shows the variation of birefringence of the clear film, which is a measure of optical anisotropy. Since the polymeric materials have both crystalline and amorphous structure, a phase difference can be occurred when a beam of light is transmitted through the film. The birefringence is defined as the maximum algebraic difference between two refractive indices measured in two perpendicular directions. Because the birefringence is decreased when the portion of amorphous region is increased, the degree of crystallinity of the film can be evaluated in terms of the birefringence.

By measuring the birefringence, it can be noticed that the crystallinity of the film also decreases with laminating temperature.

Figure 6 shows the change in absorption peak ratio from FT-IR spectra with laminating temperature.

In the previous methods, they can only measure the overall average crystallinity of the film regardless of the position along the thickness direction. But the crystallinity could change along the thickness of the film because of the temperature gradient developed through the direction. By the FT-IR method, it would be capable of measuring the crystallinity at the side contacting with substrate and the opposite side of the film separately.

In FT-IR spectrum by a specular reflectance technique, 1504 cm^{-1} represents a reference peak of which the intensity does not changed by heating and 793 cm^{-1} represents a peak of which the intensity can be easily changed by heating. By the intensity ratio of two peaks, it is able to calculate the change of crystallinity at each side of the film.[3)]

At the metal side of the film, the peak ratio drops in low temperature region and remains unchanged. It indicates that the structure of the film becomes amorphous state regardless of laminating temperature in high temperature above melting point. But, at the opposite side, it linearly decreases with increasing temperature, which implies that the crystallinity can be gradually changed by thermal gradient through the film.

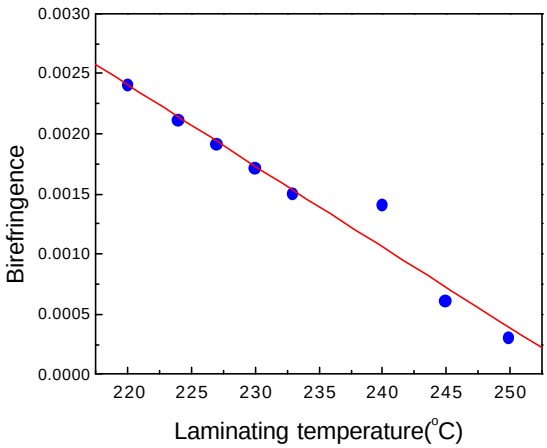

Figure 5 - Change of Crystallinity with Laminating Temperature Determined by Birefringence

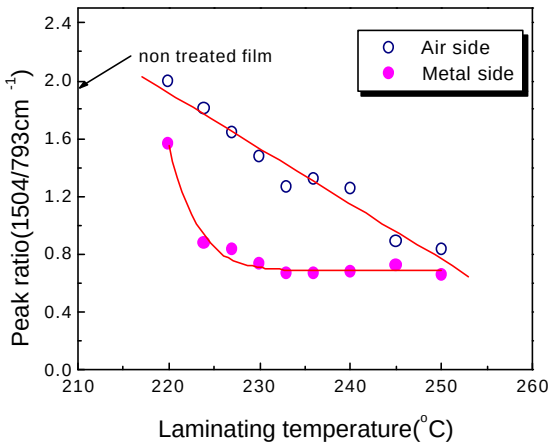

Figure 6 - Change of Absorption Peak Ratio in FT-IR Spectra with Laminating Temperature

It is also possible to distinguish the crystalline region from amorphous one using by a polarization microscope. The cross sections of laminated clear films by a polarization microscope are illustrated in Figure 7. When the cross-polarized light was applied, only the crystalline region can be visualized. At a low temperature, almost all of the crystalline was not transformed into amorphous state, while at high temperature it changed into amorphous state.

Summing up the results from various analytical methods for change of the crystallinty with temperature, it could be noticed that the crystallinity of the film decreases with increasing laminating temperature regardless of the methods applied.

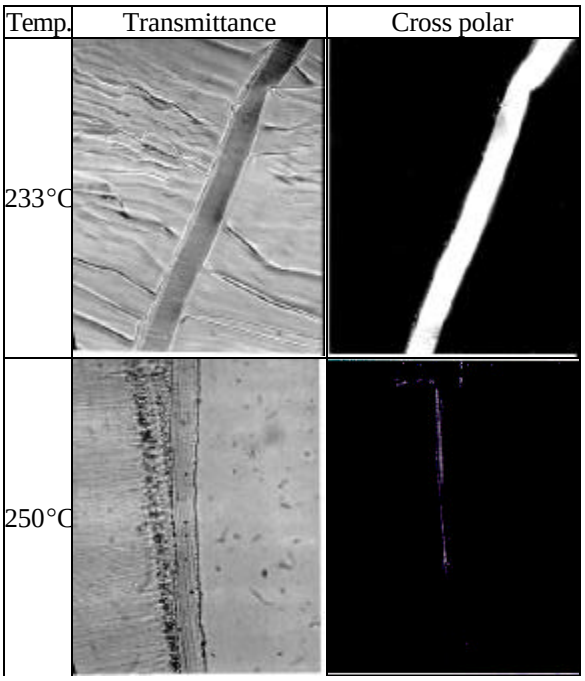

Figure 7 - Cross Section of Laminated Clear Film; Polarization microscope

Figure 8 shows the adhesion strength evaluated by a blister test. In the previous FT-IR result, the amorphous state of the film attached to the substrate reached its saturation value above 230°C, so it was expected that the adhesion strength would be unchanged above that temperature. But as shown in this figure, the film adhesion strength is increased with laminating temperature.

It could be mentioned that the adhesion strength are solely affected by the crystallinity at the substrate side, but the overall crystallinity has something to do

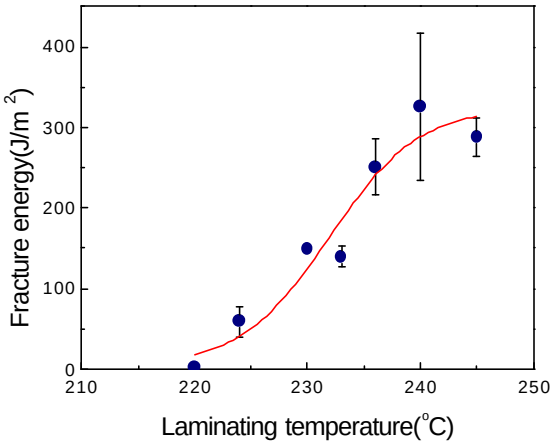

Figure 8 - Adhesion Property Evaluated by Blister Test with Laminating Temperature

with the adhesion properties of the film.

The variation of permeability to water with laminating temperature is shown in Figure 9. It has been known that the crystalline region can restrict water permeation. So, as increasing the laminating temperature, thereby decreasing the crystallinity, the water permeability is increased.

But in the white film due to the existence of titanium oxide and the different film thickness, the permeability properties exhibit different temperature dependency between two kinds of films.

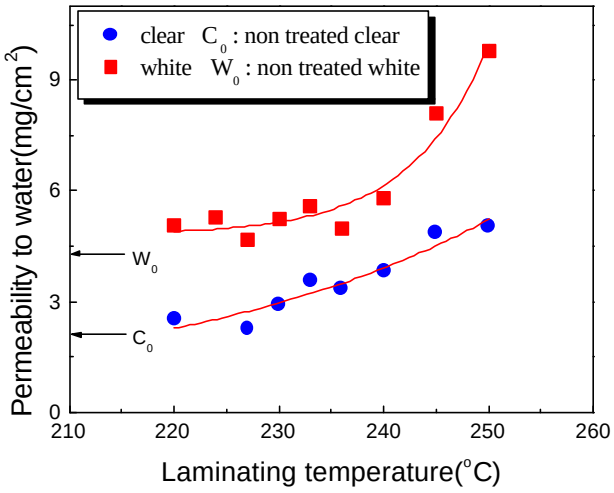

Figure 9 - Water Permeability of Laminated Film with Laminating Temperature

Figure 10 shows the variation of the crystallinity with laminating speed. The laminating speed refers to the specimen moving speed by the rotation of laminating rolls. As increasing the speed, the degree of crystallinity is decreased. It could be explained in terms of recrystallization during a passing time between laminating rolls and quench tank.

If the speed could be very higher, the shorter the time for recrystallization, which makes the portion of amorphous state keep unchanged.

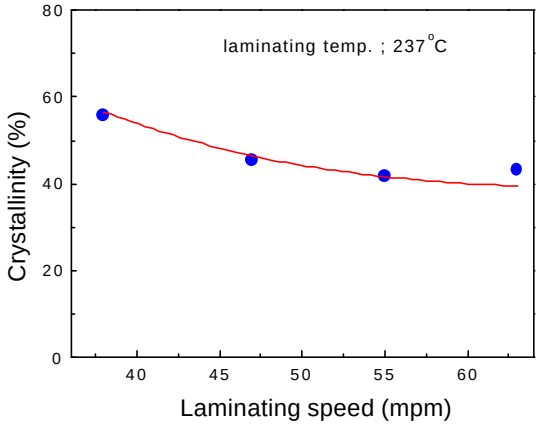

Figure 10 - Change of Crystallinity of Clear film with Laminating Speed Determined by XRD

Figure 11 indicates the degree of crystallinity with cooling conditions. In water quenching the crystallinity was calculated about 50%, while in air-cooling it was appeared about 70 to 80%.

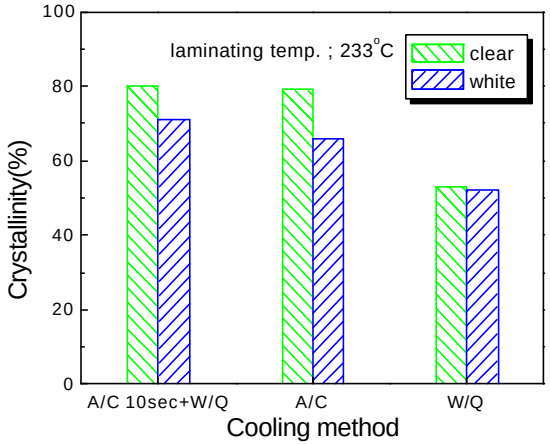

Figure 11 - Comparison of Crystallinity with Cooling Method: A/C = air-cooling; W/Q=water-cooling

Assuming that the air-cooling provided enough time for recrystallization, theses crystallinity will be a saturation value. When the air cooling for 10 seconds were followed by the water quenching, the crystallinity shows little difference with air-cooling, which implies that 10 second was enough for recrystallization.

Summary

1. The crystallization behaviors of laminated films using a lab-scale simulator yielded reliable results for investigating the effect of process variables, such as temperature, speed and cooling condition.
2. Various analytical methods for measuring the crystallinity of the film can inform diverse aspect of crystallization characteristics. Especially by the FT-IR and polarization microscopic method, the variation of the crystallinity through the thickness direction of the film can be examined.
3. Change in crystallinity by laminating speed and cooling condition at constant laminating temperature seems to be caused by recrystallization after laminating, and it needs precise control of heat cycle to maintain the crystallinity to the desired range.

References

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3. S.M. Aharoni, R.K. Sharama, J.S. Szobota, and D.A. Vernick, *Journal of Applied Polymer Science*, **28**, 2177 (1983).