

Mechanisms of Direct Bonding between PET and PVF Induced by Plasma Irradiation

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Introduction

Fluorinated resins are used widely because they have high performances such as heat-resistivity, anti-chemical reaction, high electric resistivity, gas barrier, anti-burning and low friction. A back-sheet of solar cells must have properties as high electrical resistivity, anti-burning and heat-resistivity as well as protecting the solar cell materials and circuits from natural circumstances (rain, moisture, wind). Further, it must be adhesive with packing materials. To satisfy these demands, various materials are under development [1].

Poly vinyl fluoride (PVF) has been used for the back-sheet of solar cells for twenty years. Usually fluorinated resins are difficult to be adhesive with themselves and other materials, then PVF films are used as laminated with polyethylene terephthalate (PET) films using glues. However, people have serious problems in this compound because they have to retrieve and clean up organic solvents included in the glues. People wish to reduce to use the glues in terms of environmental issues and energy consumptions.

Recently we succeeded to bond two sheets of PET films without any glues employing plasma irradiation technique, and proposed the bonding mechanisms such as hydrogen bondings and condensation reactions [2]. This technique was applied to bond PVF and PET films. They were successfully bonded by adjusting the plasma conditions. Here we report results of analyses and discussions on mechanisms.

Experimental

Polymer films: We used PVF films (Tedlar, DuPont) with thickness of 25 μm and area of 100 mm x 100 mm, and PET films (Lumirror, Toray) with thickness of 75 μm and area of 100 mm x 100 mm.

Plasma irradiations: We prepared the plasma generation and irradiation system with Bell-Jar type vacuum chamber [2]. The film sample was attached on a rotating drum-electrode (150 mm diameter and 150 mm width). The chamber was evacuated down to 5 Pa, then a gas (Ar or O₂) was introduced with a rate of 20 cc/min, keeping its partial pressure at 15 Pa. The gas was discharged by applying AC voltages between the drum-electrode and counter electrode to generate each plasma. The rotating

film sample was irradiated by the plasma for 10 sec. PVF films were irradiated by Ar-plasma and PET films were irradiated by O-plasma as shown in Table 1, where rotation rates (m/min), electric powers (W) and irradiation energies ($\text{W}\cdot\text{min}/\text{m}^2$) are shown. Ar-plasma conditions were controlled, while O-plasma conditions were fixed.

Table 1 Plasma irradiation conditions.

Film	Gas	Rotation rate (m/min)	Electric power (W)	E_{PVF} ($\text{W}\cdot\text{min}/\text{m}^2$)
PET	O ₂	2.0	1200	4000
PVF	Ar	0.5~3.0	2.5~1200	5~15000

Pressing: PVF and PET films were pressed at 5 MPa at 150°C for 30 min with their irradiated surfaces faced using a press machine (VH-1.5, Kitagawa Seiki). Their bonding strength S_p (N/cm) was measured by 180°-peel test under JIS-C2151 standard as illustrated in Fig.1 using a pulling machine (E-L, Toyoseiki Seisaku).

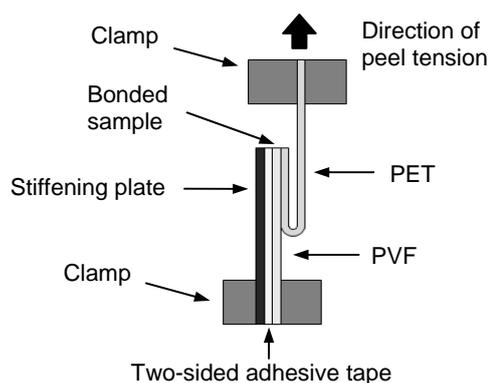


Fig. 1 Illustration of 180°-peel test for two bonded films.

Surface analyses: Surface morphologies of irradiated PVF and PET films were characterized by SEM, their surface roughness R_a was measured by AFM. Their chemical bonding states were analysed by XPS (ESCALB220iXL, VG Scientific). Surface wettability was estimated by contact angle of pure water droplet using a contact angle meter (DM-100, Kyowa Kaimen Kagaku).

Results and Discussion

The results of bonding strength Sp are shown in Fig.2 as a function of E_{PVF} for two categories of the experiments. In the figure, sample-A indicates the pressed films of PVF/PET in which PVF was irradiated by Ar-plasma but PET was not irradiated, while sample-B indicates those of PVF/PET in which each PVF and PET was irradiated by each plasma. The sample-A shows increase in Sp with increasing E_{PVF} , and shows the maximum around $E_{PVF}=200 \text{ W}\cdot\text{min}/\text{m}^2$, then rapid decrease. It indicates that the sample-A has a weak bonding strength ($Sp=0.13 \text{ N}/\text{cm}$) at the optimum irradiation energy for PVF. While the sample-B shows monotonic increase in Sp till $E_{PVF}=4 \times 10^3 \text{ W}\cdot\text{min}/\text{m}^2$, then decrease. The maximum Sp reaches to $0.45 \text{ N}/\text{cm}$, indicating very strong bonding.

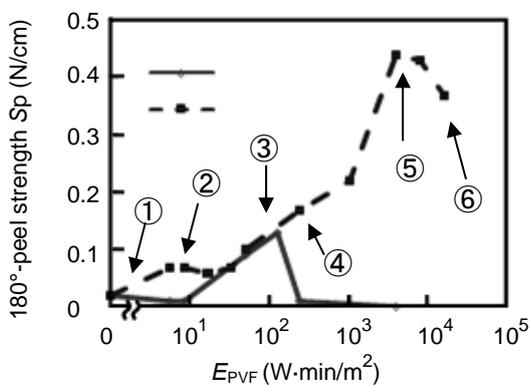


Fig.2 180°-peel strength Sp as a function of plasma energy E_{PVF} for the bonded PVF/PET films.

Table 2 Influence of plasma energy on surface compositions (atomic %) of PVF obtained by XPS.

	E_{PVF} ($\text{W}\cdot\text{min}/\text{m}^2$)	atomic %						
		C	N	O	F	Si	P	Cr
①	0	66.7	-	0.3	33.0	-	-	-
②	8	66.8	-	1.2	32.0	-	-	-
③	125	68.3	0.2	6.9	24.6	-	-	-
④	233	70.3	0.1	9.0	20.5	-	-	-
⑤	3867	79.8	0.2	11.1	8.0	0.2	-	-
⑥	15467	82.2	0.3	12.5	4.3	0.4	0.2	0.1

The results of atomic compositions in the non-irradiated and the irradiated PVF obtained by XPS are shown in Table 2. In this Table, the numbers in circle correspond to those shown in Fig.2, that is, E_{PVF} values as shown in Table 2. Outstanding results are increase of O and decrease of F with increasing E_{PVF} . An increase of C may be caused relatively by the decrease of F. This increase of O must be important for bonding, but a reason why it increases even the film is irradiated by Ar-plasma, is not clear. Probably after taking the sample from the vacuum chamber into the air, the activated surface by Ar-plasma must be oxidized

by the air. An increase of N can be recognized by the same way. The oxygen-related species might be some functional groups like hydroxyl group, carbonyl group, carboxyl group. The decrease of F might be caused by surface destruction of PVF by the plasma irradiation. It was confirmed by its color, changed from transparent to dark color at the stages of ⑤ and ⑥. Increases of Si, P and Cr are not essential, PVF was contaminated by the plasma sputtering of the chamber.

The water contact angle θ is plotted in Fig.3 as a function of E_{PVF} . θ shows minimum at around $E_{PVF}=200 \text{ W}\cdot\text{min}/\text{m}^2$, corresponding to the maximum bonding strength of the sample-A. Then it is thought that the sample-A is activated upto $200 \text{ W}\cdot\text{min}/\text{m}^2$ but it loses its bonding nature beyond $200 \text{ W}\cdot\text{min}/\text{m}^2$ due to the destruction of PVF structure. However, it is strange that the sample-B shows further strong bonding nature even beyond this criterion of $200 \text{ W}\cdot\text{min}/\text{m}^2$ because of the irradiated PET film. Thus the irradiated PET plays more important role for this strong bonding.

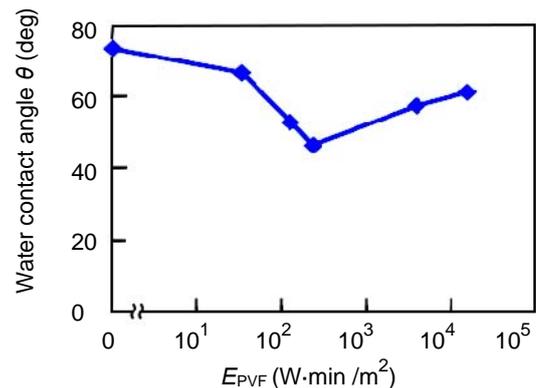


Fig.3 Influence of plasma energy on water contact angle at the surface of PVF .

Summary

The direct bonding is weak between the plasma-irradiated PVF (Ar-plasma) and the nonirradiated PET. It is much stronger between the irradiated PVF and the irradiated PET (O-plasma) even after PVF is partially destroyed by excess irradiation. This indicates the importance of irradiated PET surface, having O-related functional groups [2], for the strong direct bonding. It in turn suggests that the condensation reaction is a possible mechanism for the tight bonding.

References

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2. M. Yokura, T. Hayashi, T. Yoshii, Y. Maeda, and T. Endo, *Transactions of the Material Research Society of Japan*, **35** (2010) 191-194.