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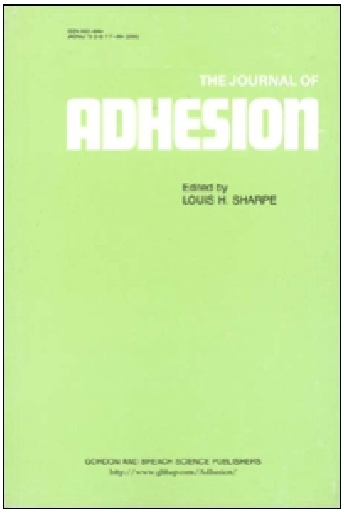

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Adhesion Between Plasma-Treated Polypropylene Films and Thin Aluminum Films*

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(In final form January 16, 1996)

Polypropylene (PP) film was treated with radio-frequency-induced oxygen plasma, followed by the vacuum deposition of aluminum (Al) thin film, and the peel strength of the Al deposited PP film (Al/PP) was examined. The peel strength of plasma-treated PP film varied widely in the range of 6.7 to 157 N/m depending upon the plasma treatment conditions, whereas that of the untreated PP was 5.2 N/m. The peel strength was minimized at oxygen pressure near 13.3 Pa (0.1 Torr), and decreased with increasing discharge power. The peel strength rapidly increased at the initial stage of plasma treatment (~ several seconds), decreased at the second stage, and slightly increased again at the third stage. A good agreement was found between the peel strength of Al/PP and the amounts of oxygen introduced onto the PP surface at the initial stage. A short-time treatment was very effective to improve the adhesion of Al/PP. At the end of the second stage, a large amount of carbon was detected by XPS on the Al layer of the peeled interface of Al/PP, which gave a minimum peel strength. Cohesive failure of PP film might have occurred. SEM photograph showed that PP surface was etched by oxygen plasma at the thrid stage. These peel behaviors of Al/PP were explained by the chemical and physical changes of the PP surface caused by oxygen plasma treatment: (1) introduction of O-functional groups onto the PP surface at the initial stage, (2) formation of weak booundary layers resulting from the partial scission of PP molecules at the second stage, and (3) plasma etching of the PP surface at the third stage.

KEY WORDS: Radio-frequency-induced oxygen plasma; surface treatment; peel strength; adhesion mechanism; X-ray photoelectron spectroscopy (XPS); scanning electron microscopy (SEM); weak boundary layer; surface functionality.

INTRODUCTION

Adhesion to polypropylene (PP) is poor and some kind of surface treatment is indispensable for achieving practically sufficient adhesion to the PP surface.

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The classical surface treatments such as flame-treatment and treatment with chromic-sulfuric acid have been used to improve the adhesion properties of polyolefins.[1-3] A dry process using corona discharge is widely used, and many investigators have reported its effect on the modification of PP surfaces.[4-7] Plasma treatment has been applied to PP surfaces by many researchers,[8-11] and it is revealed that the adhesion properties of PP surfaces can be changed by the plasma treatment process.

Plasma treatment has also been found to be effective for the adhesion between polymer films and vacuum-deposited metallic films. Gerenser[12] found a relationship between the newly-created chemical species on a PE surface treated with nitrogen and oxygen plasmas and the adhesion strength of a silver thin film on the surface. Nakamae *et al.*[13] also reported the improvement of the adhesion of the vacuum-deposited cobalt film on a PET surface by an oxygen plasma treatment.

Aluminum-coated polypropylene film (Al/PP) is widely used as a component of multilaminated films for food packaging. The adhesion strength between Al and PP films is one of the most important performance requirements of the laminated films. *In-situ* deposition of Al onto PP film, which was pretreated with nitrogen plasma, has been studied by Andre *et al.*[14] They found that good adhesion of Al/PP could be obtained with very short time treatments.

In this report, PP film was treated with radio frequency (RF)-induced oxygen plasma, followed by the vacuum deposition of an Al thin film. The peel strength of the obtained Al/PP was measured. We also investigated the effect of plasma treatment conditions on the peel strength of Al/PP. Furthermore, the surfaces of PP film treated with plasma and the interfaces of Al/PP obtained as a result of the peel test were analyzed. The mechanism involved in the adhesion between plasma-treated PP film and Al thin film is discussed.

EXPERIMENTAL

Unoriented PP film ($d = 25\ \mu m$) was used as the substrate film without any pretreatment, because we discovered that there was little difference in peel strength before and after washing with acetone or methanol. PP film was set on the lower electrode, which was cooled with water, and treated with 13.56 MHz RF-induced oxygen plasma using the apparatus shown in Figure 1.

After plasma treatment, the film was transferred to a vacuum deposition system. Aluminum thin film was deposited under a pressure of $6.7 \sim 13 \times 10^{-3}$ Pa, which gave an Al layer 400 ± 50Å in thickness on the PP film.

PET film ($d = 25\ \mu m$) was laminated on the Al side of Al/PP using a two-part type of urethane adhesive. After hardening, the peel strength of the laminate was measured as shown in Figure 2 (sample size $150 \times 15\,mm^2$, peel speed 300 mm/min). The mean of peel strength (N/m) was obtained by averaging 2–6 samples.

As shown in Figure 3, the surfaces of plasma-treated PP film and the peeled interfaces of Al/PP were observed by SEM (HITACHI S-650) and analyzed by XPS (ULVAC-PHI ESCA Model 5400). In addition, the visual appearance of the peeled interfaces gave some valuable information.

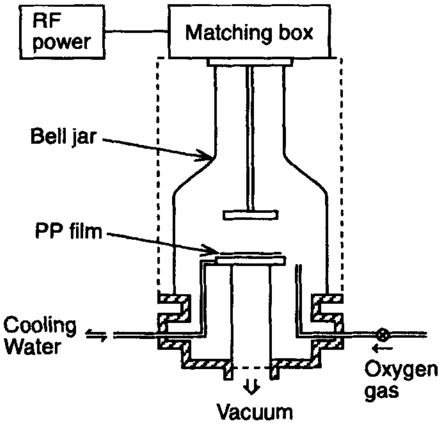


FIGURE 1 Schematic diagram of the apparatus of oxygen plasma treatment. (Flow rate, 10sccm)

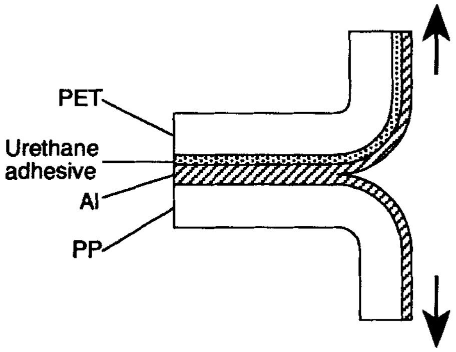


FIGURE 2 Peel test of Al/PP laminated by PET film.

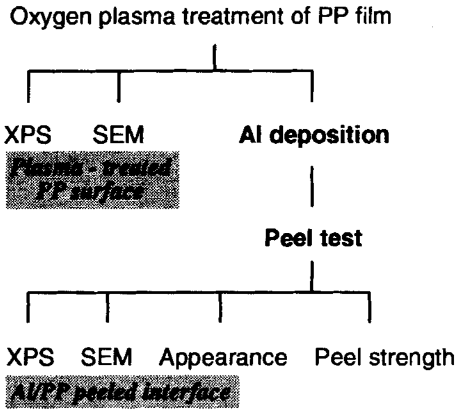


FIGURE 3 Experimental flow chart.

RESULTS AND DISCUSSION

1. Effect of Plasma Treatment Condition on Peel Strength

Figure 4(a) shows the relationship between oxygen pressure and peel strength, and Figure 4(b) shows that between RF power and peel strength, when the PP film was treated for 1 min. At 5 watts, in Figure 4(a), the peel strength showed the minimum value of 70 N/m at about 13.3 Pa (0.1 Torr), while higher peel strength was obtained above and below this pressure. At 10 watts the peel strength also showed a minimum value at the same pressure, but it was extremely low. Significant peel strength was not obtained below 13.3 Pa at 20 watts.

As shown in Figure 4(b), the peel strength apparently decreased with an increase of RF power. The degree of decrease depended on the oxygen gas pressure. It was apparent that lower energy and an optimum pressure are essential to obtain higher peel strength (see Sec. 6).

2. Effect of Plasma Treatment Time on Peel Strength

The peel strength of untreated PP(*UT*) was only 5.2 N/m. The changes of peel strength during plasma treatment under two different conditions are shown in Figure 5. The peel strength of the treated PP varied in the range of 6.7 to 134 N/m under one condition. 13.3 Pa and 20 watts, which was designated as a "strong condition". Under the other, the "weak condition", 133 Pa and 5 watts, the changing pattern of peel strength was similar to that of the strong one, although a higher peel strength of *ca.* 140 N/m was maintained for about 1 min and the succeeding drop in the peel strength was limited to 80 N/m. It is considered that these two conditions gave substantially the same kinds of results even though the effects of treatment time on peel strength differed in magnitude.

For further investigation, we chose the strong condition which gave a pronounced change of the peel strength during the treatment. The peel strength rapidly reached the maximum value with a 1- or 2-second treatment. At the next stage, an abrupt

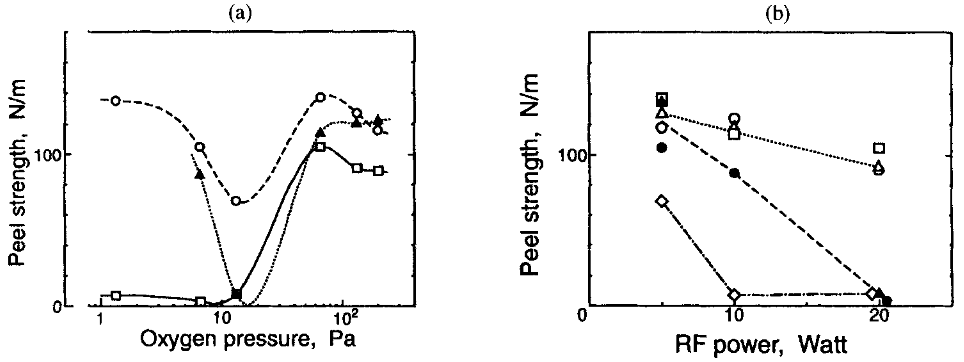


FIGURE 4(a) Effect of the oxygen pressure on the peel strength of Al/PP. (treatment time, 1min) ○ 5 Watt, ▲10 Watt, □ 20 Watt. FIGURE 4(b) Effect of the RF power on the peel strength of Al/PP. (treatment time, 1min) ○ 200 Pa, △133Pa, □ 67Pa, ● 6.7Pa, ▲ 1.3Pa, ◇ 13.3Pa.

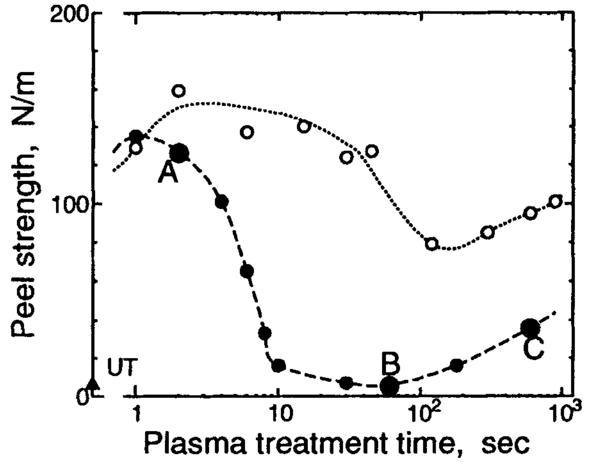


FIGURE 5 Effect of the plasma treatment time on the peel strength of Al/PP. ○ 133Pa and 5W, ● 13.3Pa and 20W, ▲ Untreated. A, B, C see Table I.

decrease of peel strength was observed, and the minimum strength was obtained with a 1-min treatment. Beyond 1 min the peel strength gradually increased again and recovered up to 36 N/m with a 10-min treatment. The process of plasma treatment was thus found to consist of three stages, as follows: the initial stage, which is from very low (untreated PP) to maximum peel strength; the second stage, which is from maximum peel strength to minimum peel strength; and the third stage, which is beyond minimum peel strength.

3. XPS Analysis of Plasma-Treated Surface

The elemental composition of the treated PP surface was examined by XPS. Figure 6 shows the change in the amount of oxygen (relative to carbon) on the PP surface during plasma treatment. The untreated PP surface had a very small amount of oxygen.

At the initial stage, the O/C ratios rapidly increased from 0.006 (*UT*) to 0.17 under both conditions shown in Figure 6. There certainly is a good agreement between the increase of peel strength and the amounts of oxygen introduced onto the PP surface at the initial stage. As the treatment proceeded, the O/C ratio increased under the "strong condition", but it remained unchanged under the weak one. It is difficult to find a simple relationship between the O/C ratio and the peel strength at the second and third stages.

It has been revealed by Nakamae *et al.*[13,15] that the polar groups introduced onto a polymer surface by oxygen plasma closely relate to the adhesion strength of the metal film deposited on the polymer surface. A PP surface treated with oxygen plasma involved some kind of oxygen-containing functional groups. The newly-formed shoulder peaks in the C1s spectra were separated into the typical three groups of O-bound carbons, —C—O—, —C=O, and —COO—, as shown in Figure 7. Some of C—O bonds formed by plasma treatment were found to be very

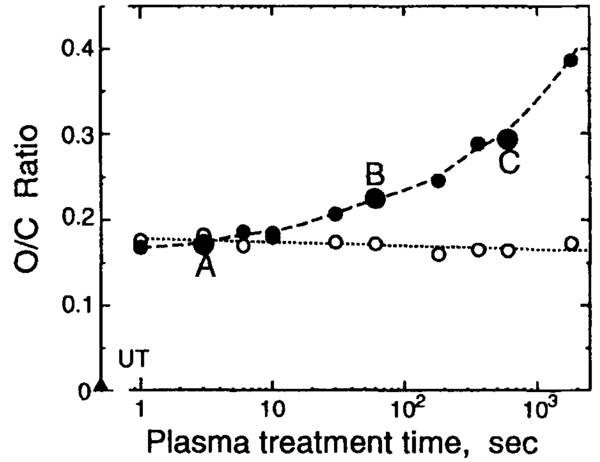


FIGURE 6 Effect of the plasma treatment time on the O/C ratios of PP surface. ○ 133Pa and 5W, ● 13.3Pa and 20W, ▲ Untreated. A, B, C see Table I.

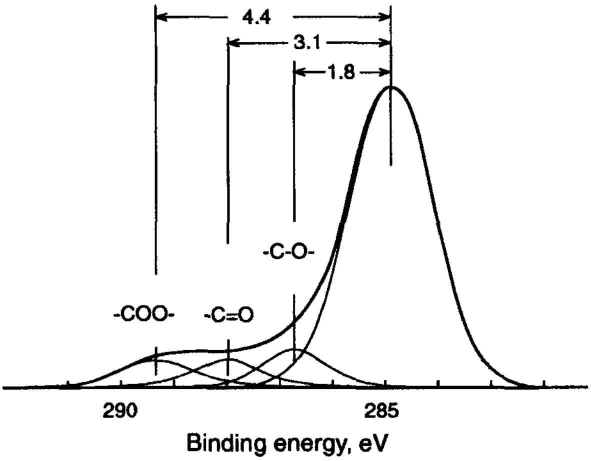


FIGURE 7 Peak separation of C1s spectra for PP surface treated with oxygen plasma.

unstable to X-ray irradiation and/or its generated heat. The decline in the O/C ratio during XPS measurement is shown in Figure 8. Therefore, the percentage of each group was estimated roughly by curve fitting to the C1s spectra acquired within 1 minute. Figure 9 shows the changes in the percentage of each O-bound carbon with respect to the total carbon. It was difficult to determine the composition of these carbons accurately because of their instability. However, it has become known that the increase of total of O-bound carbon under the strong condition is mainly dependent on both —C—O— and —COO— groups. The increasing pattern of the ratio of O-bound carbon/total carbon in Figure 9 is in fair agreement with that of the O/C ratio shown in Figure 6.

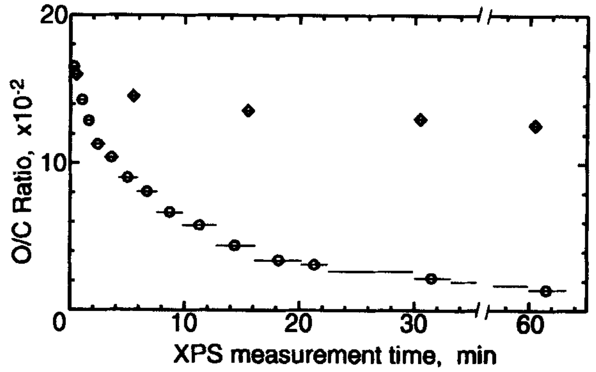


FIGURE 8 Decrease of oxygen on the plasma-treated PP surface during X-ray irradiation of XPS. ⊖ Continuous irradiation, ◇ Discontinuous irradiation. Each line shows the period of X-ray irradiation, and the average O/C ratio over the period is plotted as ○ or ◇.

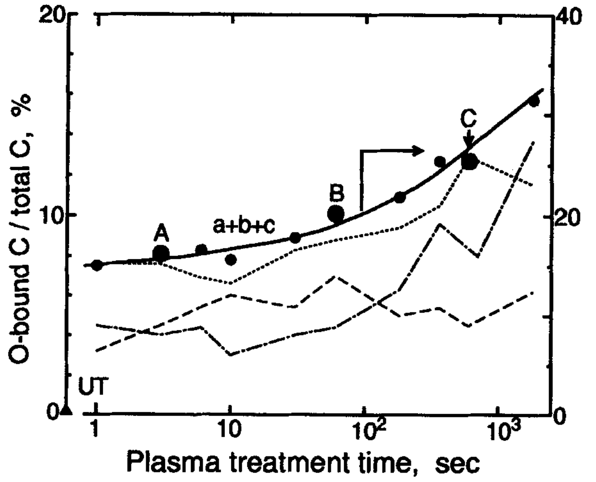


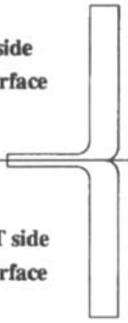
FIGURE 9 Changes of the O-functional groups in C1s peak during plasma treatment at 13.3Pa and 20 Watt. ----------a,—C—O—; – – – – b, —C=O; ————c, —COO—. A, B, C see Table I.

At the initial stage, the O-functional groups generated on the PP surface are considered to be responsible for the rapid increase of peel strength. At the second and third stages, however, peel strength became very low in spite of proceeding oxidation.

4. Appearance of Peeled Interface

Table I shows the interfaces revealed by peel testing some of the PP/Al/urethane/PET laminates, in which the PP films were treated under the strong condition for 2 sec(*A*), 1 min(*B*) and 10 min(*C*), respectively. Each side of the peeled interface was

TABLE I
Interfaces revealed by peel testing of PP/Al/urethane/ PET laminates

	UT	A	B	C
Treatment time (sec)	0	2	60	600
Peel strength (N/m)	5.2	131	6.5	36
PP side interface 				
PET side interface				

UT;Untreated
A, B, C ; Treated at 13.3Pa and 20 Watt.
PP or PET side interface, see text

designated as a "PP side interface" or a "PET side interface". In sample *A*, giving the nearly-highest peel strength, a large amount of Al was found on the PP side interface. Some Al was also found on the PET side interface of *A*. It is supposed that cohesive failure of Al layer might have occurred because of the existence of Al on both peeled interfaces.

Furthermore, these facts mean that the true adhesion force just at the Al/PP interface is larger than the peel strength of 131N/m obtained for *A* which is peeled at the Al layer.

On the other hand, no Al was found on the PP side interface in *UT*, *B*, and even in *C* which showed the recovered peel strength. These facts suggest that there is no substantial adhesion between PP film and Al layers.

5. XPS Analysis of Peeled Interface

The appearance of *B* and *C* in Table I shows that all of the peeled Al layer is found on the PET side interface. Unexpectedly, however, about 90% of carbon, instead of Al, was detected on these interfaces of *B* and *C* by XPS (Table II). The existence of some organic layers on the peeled Al layer indicates that the weakest part against the peeling is located in the PP film rather than at the Al/PP interface. The cohesive

TABLE II
XPS analysis of peeled interfaces of Al/PP

		UT	A	B	C
Treatment time (sec)		**0**	**2**	**60**	**600**
Peel strength (N/m)		**5.2**	**131**	**6.5**	**36**
PP side interface	**C**	**99**	**43**	**97**	**97**
	O	**1.4**	**35**	**2.8**	**2.8**
	Al	**-**	**22**	**-**	**-**
PET side interface	**C**	**41**	**74**	**88**	**92**
	O	**33**	**20**	**8.4**	**5.3**
	Al	**26**	**3.4**	**4.0**	**2.2**
	N	**-**	**2.1**	**-**	**-**

(atm %)

UT;Untreated.
A, B, C ; Treated at 13.3Pa and 20 Watt.
PP or PET side interface, see text and Table I.

failure of the PP film suggests the formation of "weak boundary layers (WBLs)" on the intensively-treated PP surface. It is thought that the outermost surface of oxidized PP film is strongly attached to the surface of the Al layer and the decomposed inner parts of the PP film function as WBLs when the laminate is peeled. The formation of WBLs on the PP surface is considered to be responsible for the decreased peel strength in *B* and *C*.

In sample *A*, the amount of Al on the PP side interface was larger than that on the PET side interface. (Both metallic Al and aluminum oxide were detected in the Al2p spectra.) The difference of the amounts of Al on both interfaces agreed well with the different appearances of the interfaces in *A* (Table I). Additionally, a very small amount of nitrogen was detected on the PET side interface, which means that the cohesive failure of the Al layer is partially accompanied by interfacial failure at the Al/urethane adhesive interface.

On the PET side interface of *UT*, the largest amount of Al (26%) was detected by XPS, as expected from the appearance. The completely different or unsymmetrical compositions between PP and PET side interfaces of *UT* suggest interfacial failure at the Al/PP interface. In *B* and *C*, on the other hand, both PP and PET side interfaces show rather similar compositions, again supporting cohesive failure of the PP film.

It is noticed that there are differences between the O/C ratios of the peeled interfaces of *B*(or *C*) shown in Table II and that of the plasma-treated surface of *B*(or *C*) shown in Figure 6. The cause of the differences is under investigation.

6. SEM Observation of Plasma-Treated Surface

Photo 1 shows the morphological changes in the PP surface treated with oxygen plasma under the strong condition. Compared with *UT*, obvious morphological changes were not found on the surface of *A* having the nearly-highest peel strength. Consequently, chemical changes such as the introduction of O-functional groups are supposed to be responsible for the steep rise of peel strength at the initial stage.

At the second stage, the partial decomposition of PP molecules and the subsequent formation of WBLs were proposed for the decrease of peel strength. As seen in *B*, a certain change or a limited etching is observed at the end of this stage. Most of the results of 1-min treatment in Figure 4 are involved in the second stage, as seen in Figure 5. At the second stage, the activated oxygen species lead the PP surface to decomposition rather than to adhesion improvement. As mentioned in Sec. 1, lower energy and optimum pressure (lower pressure where smaller numbers of the activated species exist, and higher pressure where it is difficult for the activated species to reach the PP surface because of the higher density of molecules) are preferable for higher adhesion.

At the third stage, the PP surface was remarkably roughened as seen in *C*. Plasma etching of PP film has been reported by Garton *et al.*[16] and others. In spite of the recovery of peel strength by 30 N/m, sample *C* did not show any adhesion between the Al layer and the PP film because of the total lack of Al on the PP side interface.

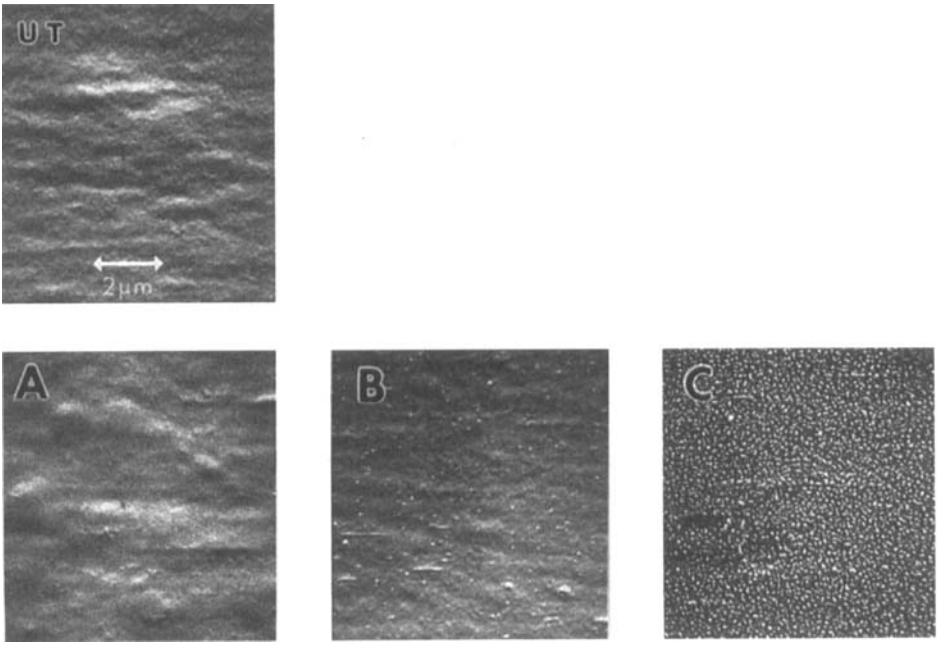


PHOTO 1 SEM photographs of PP surfaces treated with oxygen plasma at 13.3 Pa and 20Watt. UT; Untreated. A, B, C ; Treated for 2sec, 60sec and 600sec, respectively.

This apparent increase of strength is considered to reflect merely the peel resistance created by the roughened surface. The highly oxidized and etched surface of *C* suggests that PP molecules near the surface are oxidatively degraded to low molecular weight fractions,[5] which are easily removed during plasma treatment. This excessive treatment is continuously generating the oxygen-containing WBLs on the etched surface.

CONCLUSIONS

From the results mentioned above, we propose the adhesion mechanism involved in the vacuum-deposited Al/PP film as follows (see Fig. 10):

1) At the initial stage, from untreated PP to the maximum of peel strength, the increase of peel strength depends primarily on the O-functional groups introduced onto the PP surface. Cohesive failure of the Al layer was observed at the maximum.
2) At the second stage, from the maximum peel strength to the minimum, the effect of WBLs formed by the partial chain scission of PP molecules becomes progressively greater and results in the decrease of peel strength. Cohesive failure of (degraded) PP film was recognized at the minimum.
3) At the third stage, beyond the minimum peel strength, the strength slightly recovered presumably because of the etched surface. However, substantial adhesion between the PP surface and the Al layer was not observed at all. This

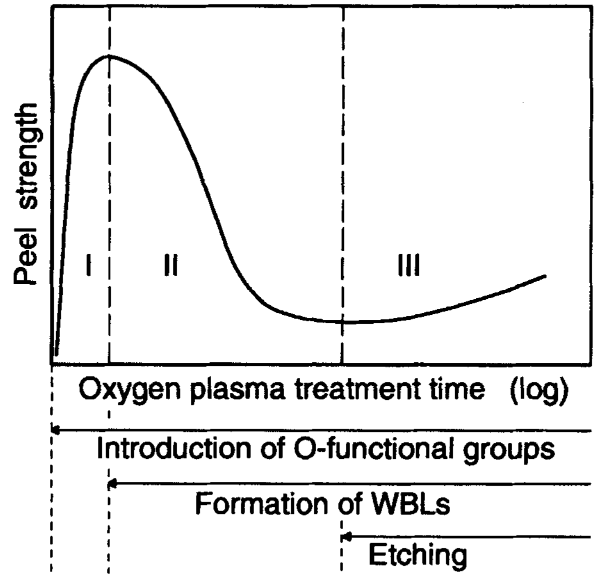


FIGURE 10 Treatment time-dependence of the peel strength of Al/PP and its relation to the changes of PP surface by oxygen plasma.

"non-adhesion" is also explained by the cohesive failure of PP film which is caused by WBLs (degraded PP) present on the roughened PP surface.

4) PP film is easily oxidized and decomposed by oxygen plasma compared with polyimide and PET films.[13,15] Higher reactivity of PP with the plasma might be explained by the fact that tertiary radicals are easily formed on PP molecules by plasma,[17] which is followed by the oxidation and scission of the PP main chain. Especially the latter mechanism induces the formation of WBLs on the PP surface, the characteristics of which are being investigated.

Acknowledgements

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