

Improvement of Adhesion and Long-Term Adhesive Reliability of Liquid Crystalline Polyester Film by Plasma Treatment

Yasuhiro Kurihara,^{1,2} Hiroyuki Ohata,² Masahiko Kawaguchi,² Shinichi Yamazaki,¹ Kunio Kimura¹

¹Graduate School of Environmental Science, Okayama University, 3-1-1 Tsushima-naka, Okayama 700-8530, Japan

²Japan Gore-Tex Inc., 1102-4 Mitsu Kouchi, Okayama 709-2123, Japan

Received 22 July 2007; accepted 8 October 2007

DOI 10.1002/app.27537

Published online 21 December 2007 in Wiley InterScience (www.interscience.wiley.com).

ABSTRACT: Surface modification of thermotropic liquid crystalline aromatic polyester (LCP) films was examined by low-pressure plasma treatment to improve initial adhesion and long-term adhesive reliability between the LCP film and an epoxy bonding sheet for printed circuit boards. Plasma irradiation was carried out in various plasma gases with different plasma modes as reactive-ion-etching (RIE), direct-plasma (DP) with pressures ranging from 4.0 to 26.6 Pa. Although the initial adhesion of the DP-treated film increased, the long-term adhesive reliability estimated by pressure cooker test (PCT) decreased with decreasing the plasma gas pressure in every gas. The higher concentration of the generated polar groups such as phenolic hydroxyl group and carboxyl group enhanced the initial adhesion by

the increase in the chemical interaction; however, it damaged the long-term adhesive reliability due to the acceleration of the penetration of water molecules into the interface. The large surface roughness was effective to enhance the initial adhesion and the long-term adhesive reliability. The RIE-treatment generated the polar groups and the larger surface roughness than the DP-treatment. The RIE-treatment in the O₂ atmosphere at the gas pressure of 13.3 Pa was the best plasma condition for both the initial adhesion and the long-term adhesive reliability. © 2007 Wiley Periodicals, Inc. *J Appl Polym Sci* 108: 85–92, 2008

Key words: liquid-crystalline polymers; cold plasma; adhesion; surfaces; printed circuit board

INTRODUCTION

Advanced printed circuit boards (PCB) for information and communication such as personal computers, cellular phones, and the automobile applications need high speed signal, fine lines, and multilayer formability. Therefore, excellent high frequency performance, highly accurate thickness, dimension stability during the process, and multilayering processability are necessary for the substrates of the recent PCB. LCP films have been paid much attention because of the highly satisfactions against these serious requirements^{1–5} and they have been used as PCB stiffeners. Although LCP possesses a unique combination of properties including heat resistance, lower moisture absorption, good electrical performance, and chemical resistance, it shows anisotropy of mechanical strength, coefficient of thermal expansion, and dielectric constant between the machine and transverse directions. Significant improvement on anisotropic properties is required for LCP films. Additionally, LCP films have the serious disadvan-

age on the poor adhesive force with other materials because of nonpolar surface and low surface energy. For example, copper clad LCP films are prepared by direct vacuum metalization or heat-lamination with copper foil to enhance the adhesive force.^{3,4} On the other hand, patterning LCP films and PCB stiffener LCP films are bonded to epoxy glass substrates and other circuit boards with thermosetting adhesives. When LCP films are used as PCB, the long-term adhesive reliability is quite important as well as the initial adhesion, and it is usually evaluated by PCT. In regard to the adhesion with thermosetting adhesives, it have been reported that the surface modification of LCP by plasma irradiation, excimer laser irradiation, and corona treatment is effective to strengthen the adhesive force.^{6–11} Among them, plasma irradiation treatment is known as an excellent method for surface modification to generate polar groups.^{5,12–14} Plasma contains ions and electrons, excited neutrals, radicals and so on, and they can react with a polymer film surface resulting in to remove contamination, to introduce chemical functional group, and to induce chain scission and crosslinking.¹⁵ In particular, cold plasma by radio-frequency (RF) glow discharge is more suitable for the surface modification, because the sample temperature does not become

Correspondence to: K. Kimura (polykim@cc.okayama-u.ac.jp).

Journal of Applied Polymer Science, Vol. 108, 85–92 (2008)
© 2007 Wiley Periodicals, Inc.

 **WILEY**
InterScience®
DISCOVER SOMETHING GREAT

high and the plasma is generated uniformly. Both the plasma modes including DP and RIE, and the working conditions including plasma gas, pressure, gas flow, RF power, and exposure time strongly influence the generation of the polar groups and the surface roughness.^{5,12,13,16} However, few studies on the adhesion of the surface modified LCP films with thermosetting adhesives has been previously reported.

In this work, the surface modification of LCP films was examined by low-pressure plasma treatment to improve the initial adhesion and long-term adhesive reliability with epoxy bonding sheet as thermosetting adhesives, focusing on the effects of the gas pressure, the plasma mode, and the plasma gas in plasma conditions.

EXPERIMENTAL

Materials

LCP used in this study was type II wholly aromatic copolyester mainly comprised of 4-oxybenzoyl moiety. LCP films (STABIAX[®]; 175 μm thick) were obtained from Japan Gore-Tex (Okayama, Japan). The film was cut to 250 mm \times 250 mm and used. Epoxy bonding sheets (NIKAFLEX[®] SAF; 40- μm thick) were obtained from Nikkan Industries Co (Tokyo, Japan).

Plasma treatment

Plasma Dry-cleaning System Model PX-1000 (SAMCO, Kyoto, Japan) was used as parallel-plate-electrode type plasma equipment. The electrode area was 350 mm \times 428 mm, the distance between electrodes was 40 mm, and the capacity of the chamber was 129 L. The powered electrode generated DC bias by cathode fall and the ground electrode were assembled in the chamber and connected to RF generator providing a field of 13.56 MHz. In the case of RIE mode, a film was placed directly on the powered electrode. In the case of DP mode, a film was placed directly on the ground electrode.

The LCP film was placed on the electrode and then the pressure was reduced to less than 2.7 Pa by using a vacuum pump. Four different gases such as O₂, N₂, mixed gas of N₂ and H₂ (N₂/H₂, the content of H₂ gas was 30%), and H₂ were then fed into the plasma equipment, and the pressure was maintained between 4.0 and 26.6 Pa by adjusting the gas flow. Then, high-frequency voltage of 13.56 MHz was applied between the electrodes to generate plasma. The plasma treatment was conducted with an RF power of 0.3 W cm⁻² for 60 s.

Wettability and surface energy

Contact angles (θ) of water and methylene iodide on the LCP film surface were measured by the sessile drop method with a contact-angle meter DM500 (Kyowa Interface Science Co., Niiza, Japan). An average contact angle was determined from five measurements with a standard deviation 1–3°. The surface energy (r_s) was evaluated using the geometric mean equation.^{17–20}

$$(1 + \cos \theta)r_l/2 = \left(r_s^d \times r_l^d\right)^{1/2} + \left(r_s^p \times r_l^p\right)^{1/2}$$

where r_l is the surface tension of the test liquid and r_s is the surface energy of the LCP film.

The superscripts d and p stand for the dispersive and polar (nondispersive) contributions to the surface energy, respectively. The total surface free energy is given by the following equation.

$$r_s = r_s^d + r_s^p$$

The interfacial free energies r_{s1s2} between the LCP film irradiated with the plasma-treatment (s_1) and the epoxy bonding sheet (s_2) can be calculated according to the following equation.

$$r_{s1s2} = r_s + r_l - 2\left(r_{s1}^d \times r_{s2}^d\right)^{1/2} - 2\left(r_{s1}^p \times r_{s2}^p\right)^{1/2}$$

Surface analyses of the film

X-ray photoelectron spectroscopy measurement (XPS) was carried out with a JPS-90MXS Micro X-ray photoelectron spectroscope (JEOL, Tokyo, Japan) to identify the chemical structures of the LCP film surfaces. The monochromatic Mg K α X-ray source was operated at 10 kV and 10 mA. A photoelectron take-off angle was 90°. The peak resolution was performed by using a JEOL System Spec XPS software after Shirley baseline background subtraction. The C1s spectrum was resolved to seven components assigned to the carbon atoms in the phenyl rings at 285.0 eV, CN bonds (C–N) at 285.7 eV, ether/phenolic hydroxyl groups (C–O) at 286.6 eV, ketone groups (C=O) at 287.7 eV, ester/carboxyl groups (C(=O)–O) at 289.4 eV, carbonate groups (O–C(=O)–O) at 290.0 eV, and a very low-intensity shake-up satellite at 291.9 eV according to the previous reports.^{5,8,12,13,20,21} The O/C atomic ratios were calculated from the O1s and C1s intensities.

Surface topography of the film was evaluated on a JSPM-4200 atomic force microscope (AFM) (JEOL, Tokyo, Japan). AFM images were obtained on a contact mode. Surface roughness of the samples was evaluated in terms of the root-means-square (RMS)

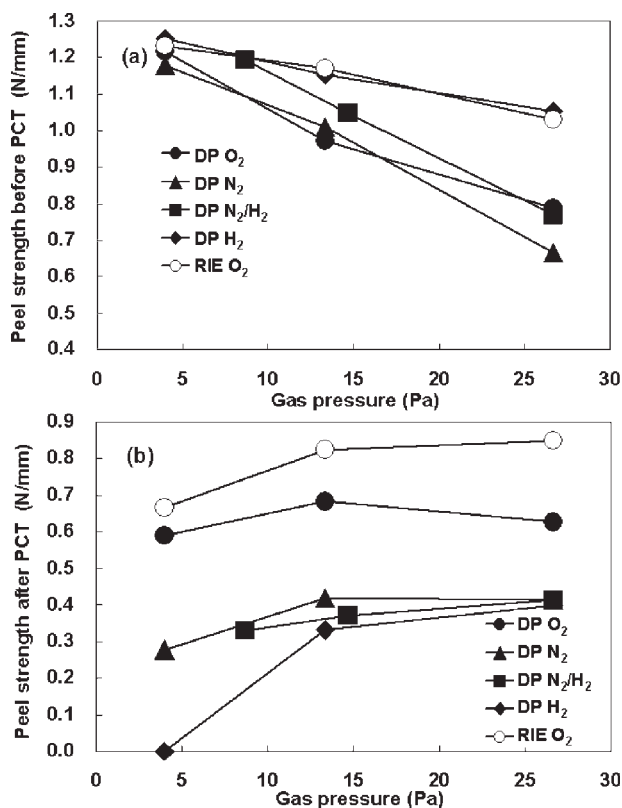


Figure 1 Peel strength of DP and RIE treated LCP films (a) before PCT and (b) after PCT as a function of pressure of various gases.

of the roughness. The LCP film surface topography of peeled-off layers was measured on a scanning electron microscope S-3500N (Hitachi High-Technologies Co., Tokyo, Japan).

Adhesive property of between the LCP film and the epoxy bonding sheet

The test sample was prepared by placing the epoxy bonding sheet on the plasma-treated surface of the LCP film and then a 35- μm -thick electrolytic copper foil GTS-STD-35 (Furukawa Circuit Foil Co., Nikko, Japan) on the top of them. The layered films were heat-pressed at 160°C and 4MPa for 40 min. PCT was carried out at 120°C under 100%RH for 12 h. Adhesive strength between the LCP film and the epoxy bonding sheet was measured before and after PCT as T-type peeling strength at a peel rate of 50 mm min⁻¹ on an Instron type tensile tester Strogaph E5D (TOYO Seiki Co., Tokyo, Japan).

RESULTS AND DISCUSSION

Comparison of plasma gas

The epoxy bonding sheets contained reactive groups such as glycidyl groups. These groups reacted with

polar groups like phenolic hydroxyl group, carboxyl group, amino group, and so on generated on the surface of the LCP film leading to the adhesion, when the epoxy bonding sheet and the LCP films were heated. It is generally known that the DP-treatment improves the surface more effectively by chemical reactions with radicals.⁵ Therefore, the effects of the plasma gas on the adhesion and the long-term adhesive reliability were examined by the DP-treatment in the O₂, N₂, N₂/H₂, and H₂ atmospheres with various pressures ranging from 4.0 to 26.6 Pa. Plasma-treated films are abbreviated as follows; O₂ DP-treated film (DP O₂) stands for the film irradiated by the DP mode in O₂ gas. The peel strength before PCT increased and the peel strength after PCT decreased with decreasing the pressure in every gas as shown in Figure 1. The peel strength after PCT remained practically constant above 13.3 Pa. The peel strength of the O₂ DP-treated film was the highest. Surface conditions of the LCP films irradiated by the plasma were analyzed with XPS and AFM. Figure 2 shows XPS C1s spectra and peak resolution of the untreated and the O₂ DP-treated LCP film surfaces as examples. The C1s spectrum significantly changed after irradiation. A peak C3 attributed to C=O ketone group newly appeared at 287.7 eV, and the peak intensity of C2 attributed to ether/phenolic hydroxyl C—O group at 286.6eV and C4 attributed to ester/carboxyl C(=O)—O group at

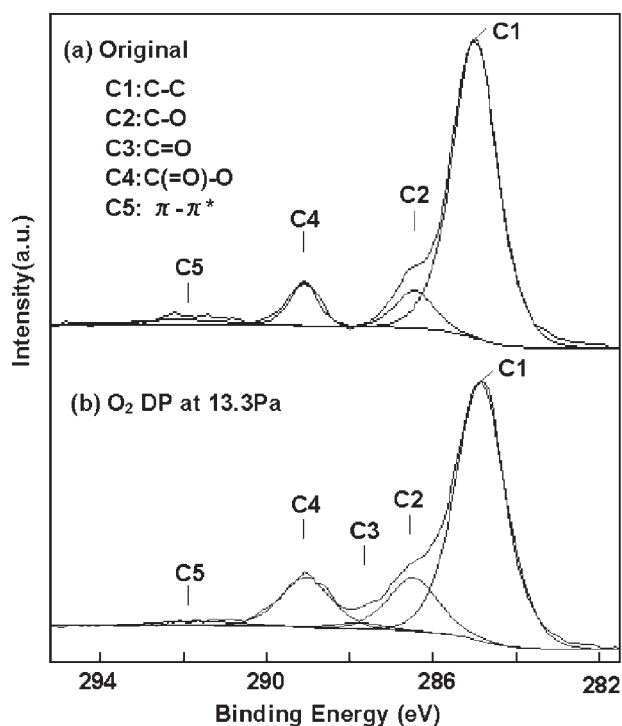
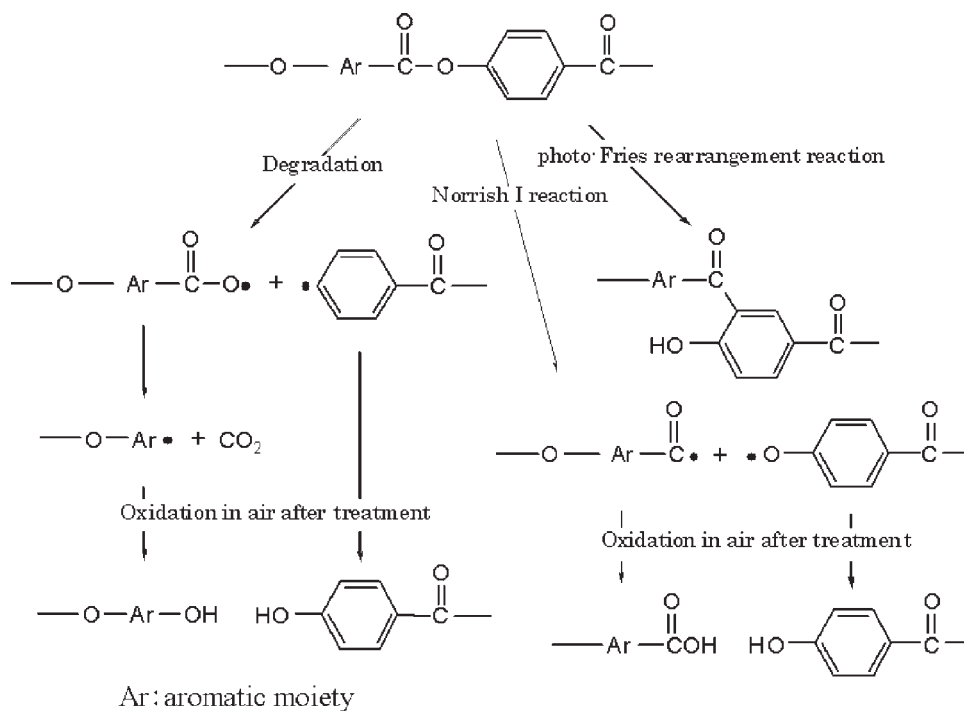


Figure 2 XPS C1s spectra and peak fitting of LCP film surfaces: (a) original LCP and (b) LCP treated with O₂ DP at 13.3 Pa.



Scheme 1 Possible reactions occurring on the LCP film surface in the oxygen plasma.

289.4 eV increased. Surface is modified by the chemical interactions between the polymer surface and plasma active ions, excited neutrals, and radicals as well as UV radiation.²² It has been proposed that many complicated reactions such as photo-Fries rearrangement reaction, photo-oxidation, chain scissions by radical and Norrish I reaction, and destruction of the aromatic rings lead to the formation of ketones, aldehydes, phenols, peroxides, carboxyl groups, and other products.^{23,24} It is well known that an oxygen plasma can react with a wide range of polymers to produce a variety of oxygen functional groups on the polyester film surfaces.^{12,25} Oxygen atoms in oxygen plasma have the possibility of reacting with aromatic rings in polymers to form phenolic hydroxyl groups. Furthermore, the primary radicals formed by Norrish I reaction processes recombine before or after decomposition through decarbonylation or decarboxylation under conditions of vacuum photolysis.²⁴ Scheme 1 shows typical possible reactions to produce phenolic hydroxyl groups and the carboxyl group on the surface in oxygen plasma including degradation. The concentration of polar groups such as the phenolic hydroxyl group and the carboxyl group influences the adhesion. The ratios of the C2 peak area to the C4 peak area (C2/C4) seem highly related to the peel strength as summarized in Table I indicating that the hydroxyl group is more effective to adhere. The concentration of the hydroxyl and carboxyl group per unit area on the LCP film surfaces could not be accurately determined but the

values of $C2/C4 \times O/C$ can be adapted as a criterion to compare the concentration of phenolic hydroxyl group and carboxyl group. Figure 3 is a plot of the peel strength before and after PCT as a function of the $C2/C4 \times O/C$. The peel strength before PCT increased with increasing the value of $C2/C4 \times O/C$ in every plasma gas. The N_2 and N_2/H_2 DP-treated films exhibited higher peel strength

TABLE I
Surface Compositions (C2, C3, C4), C2/C4 Ratio, and Atomic Ratio of Original LCP and DP-Treated LCP Films

Gas	Pressure (Pa)	Components (%)			C2/C4	Atomic ratio of plasma-treated surfaces	
		C2	C3	C4		O/C	N/C
—	—	10	—	11	0.9	0.27	—
O ₂	4.0	17	1	11	1.6	0.47	—
	13.3	14	2	13	1.1	0.45	—
	26.6	12	3	13	0.9	0.44	—
N ₂	4.0	12	6	11	1.1	0.41	0.17
	13.3	12	3	13	0.9	0.35	0.16
	26.6	10	3	12	0.8	0.37	0.19
N ₂ /H ₂	8.7	12	4	8	1.4	0.27	0.19
	14.7	12	1	10	1.2	0.29	0.17
	26.6	10	1	9	1.1	0.29	0.16
H ₂	4.0	16	2	5	2.9	0.35	—
	13.3	13	0	6	2.4	0.28	—
	26.6	12	1	7	1.8	0.26	—

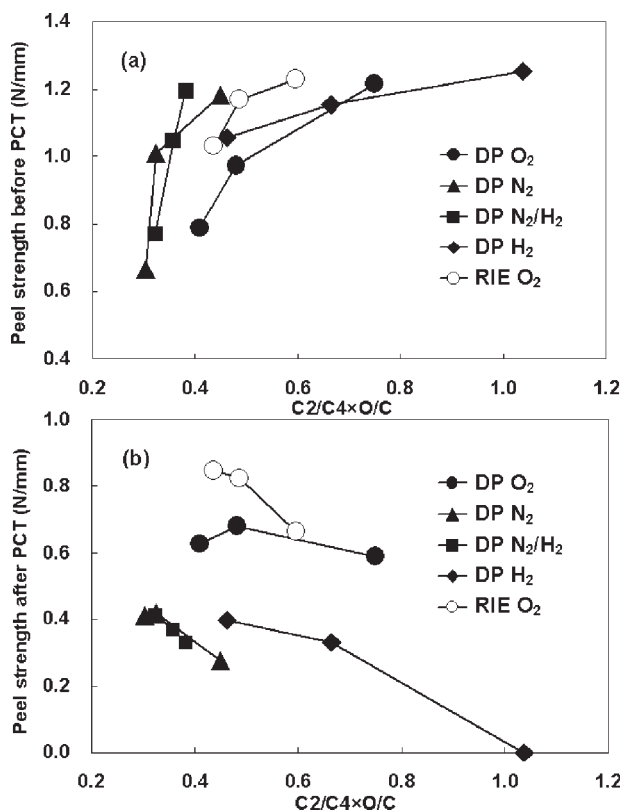


Figure 3 Peel strength of DP and RIE treated LCP films (a) before PCT and (b) after PCT as a function of $C2/C4 \times O/C$ in various gases.

than the O₂ and H₂ DP-treated films compared with the same value of $C2/C4 \times O/C$. The higher peel strength of the N₂, N₂/H₂ DP treated LCP film was attributed to the additional introduction of nitrogen polar groups expecting amino group, amide group, urethane group and so on.¹³ In contrast to the peel strength before PCT, that after PCT decreased with increasing the value of $C2/C4 \times O/C$ in every plasma gas as also shown in Figure 3. The O₂ DP-treated film exhibited higher peel strength and the N₂ and N₂/H₂ DP-treated films showed lower peel strength than the H₂ DP-treated film. The tendency of the peel strength after PCT on the value of $C2/C4 \times O/C$ is also attributed to the higher concentration of the phenolic hydroxyl group. The surface roughness also affects the adhesion and therefore the roughness was examined by AFM as shown in Figures 4 and 5. The O₂ DP-treated film has the largest RMS and its film surface is the most rough among the various treated films. This roughness might enhance the higher peel strength of the O₂ DP-treated film by physical anchor effect. The lower peel strength of the N₂, N₂/H₂ DP treated LCP film compared at the same value of $C2/C4 \times O/C$ is explained by the additional introduction of nitrogen polar groups.

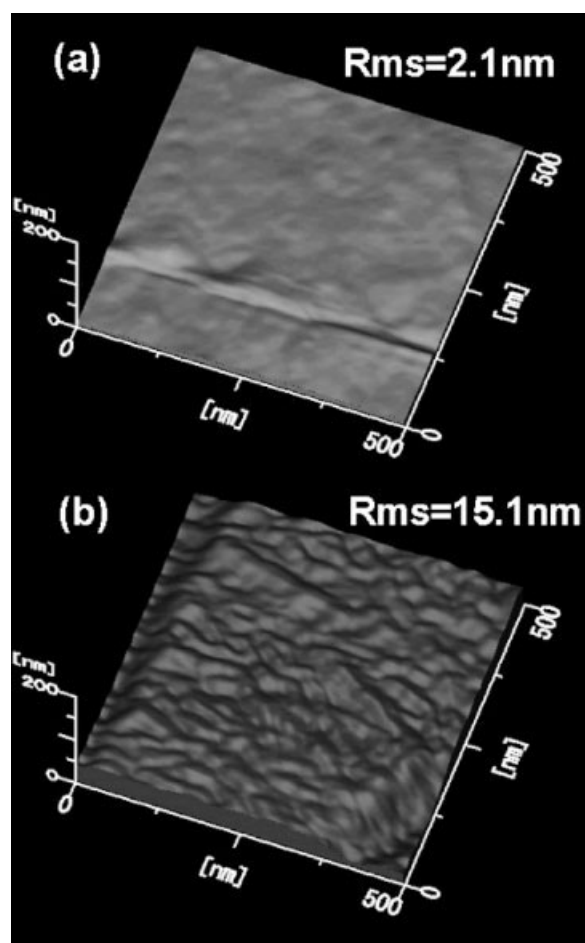


Figure 4 AFM images of (a) original LCP film surface and (b) LCP film surface DP-treated in O₂ at 4.0 Pa.

The surface free energy of the DP-treated LCP films and the interfacial free energies between the epoxy bonding sheet and those LCP films were estimated as presented in Table II. The r_s of the film surfaces irradiated with DP-treatment in each plasma

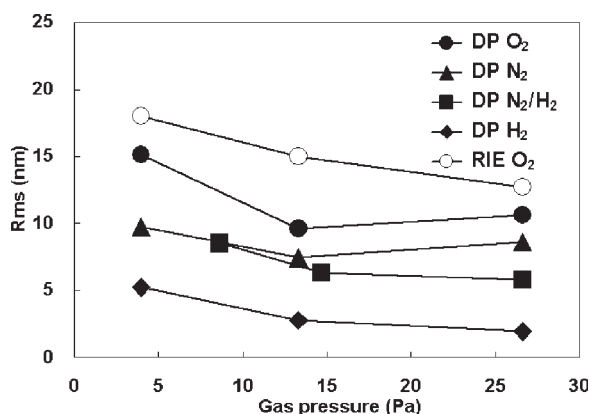


Figure 5 Surface roughness (RMS) of DP and RIE-treated LCP film surfaces as a function of pressure of various gases.

TABLE II
Contact Angles and Surface Free Energies of Original LCP and DP-Treated LCP Films and Interfacial Free Energies Between DP-Treated LCP Films and Epoxy Bonding Sheet

Gas	Pressure (Pa)	Contact angle (°)		r_s^d (mN/m)	r_s^p (mN/m)	r_s (mN/m)	r_{s1s2} (mN/m)
		Water	Methylene iodide				
–	–	79	29	41.4	3.6	45.0	–
O ₂	4.0	6	3	35.0	39.6	74.6	24.5
	13.3	16	20	32.6	39.2	71.8	24.3
	26.6	19	20	32.8	38.1	70.9	23.4
N ₂	4.0	7	7	34.7	39.8	74.5	24.7
	13.3	17	10	34.9	37.4	72.3	22.8
	26.6	17	12	34.6	37.4	72.0	22.8
H ₂	4.0	20	7	35.6	35.7	71.3	21.5
	13.3	54	28	35.5	17.5	53.0	8.1
	26.6	63	32	35.9	12.0	47.9	4.5

gas increased with decreasing the gas pressure. This result is consistent with the fact that an increase in the concentration of polar groups gave rise to an increase in the peel strength before PCT. On the other hand, the r_{s1s2} between the epoxy bonding sheet and the films increased with decreasing the pressure as well as the r_s . The interfacial free energies increased with increasing the concentration of the polar groups. The increase in the interfacial free energies promotes the permeation of the moisture to the interface leading to the decrease in the peel strength. In the comparison between plasma gases, both the surface free energies and the interfacial free energies did not highly relate to the peel strength before and after PCT, respectively. The contact angles are quite sensitive to the surface roughness of the film²⁶ and the discrepancy between the plasma gases is presumably due to the surface roughness.

The peeled LCP film surfaces in LCP film/epoxy bonding sheet systems before and after PCT were observed to identify the failure modes and to understand a change in the peel strength during PCT. The failure modes are summarized in Table III and the peeled LCP film surfaces are shown in Figure 6. The LCP films were treated by DP mode in O₂ at 26.6 Pa and H₂ at 4.0 Pa. When the peel strength was higher, fibrillar morphology was clearly observed and the failure mode was mainly cohesive mode within the LCP film. On the other hand, the failure mode after PCT was changed to interface mode between the LCP film and the epoxy bonding sheet. This result indicated that the water molecules penetrated into the interface between the LCP film and the epoxy bonding sheet and this caused to decrease the peel strength.

Comparison of plasma mode

It is well known that RIE-treatment exhibits a high etching effect by ion bombardment.⁵ Since it became

clear so far that the surface roughness increased the peel strength before PCT and did not decrease the peel strength after PCT, the RIE-treatment was used in the O₂ with pressures ranging from 4.0 to 26.6 Pa to modify the surface of the LCP films. The changes in the peel strength before and after PCT of the RIE-treated films showed the same tendency as the DP-treated films as also shown in Figures 1 and 3, and the peel strength before and after PCT of the RIE-treated films were always higher. As shown in Figure 5, the surface roughness of the RIE-treated films was always larger than those of the DP-treated films and the large surface roughness brought about the higher peel strength before and after PCT. The RIE-treatment in the O₂ atmosphere at the gas pressure of 13.3 Pa is the best plasma conditions for both the initial adhesion and the long-term adhesive reliability between the LCP film and the epoxy bonding sheet system.

CONCLUSIONS

The peel strength of the DP-treated films before PCT increased with decreasing the pressure in every

TABLE III
Failure Modes of LCP Film Surfaces Peeled Off from Adhesive Joints of Epoxy Bonding Sheet and DP-Treated LCP Films Before and After PCT

Gas	Pressure (Pa)	Failure mode	
		Before PCT	After PCT
O ₂	4.0	Cohesive	Cohesive/interface
	13.3	Cohesive	Cohesive/interface
	26.6	Cohesive	Cohesive/interface
N ₂	4.0	Cohesive	Interface
	13.3	Cohesive	Interface
	26.6	Cohesive	Interface
H ₂	4.0	Cohesive	Interface
	13.3	Cohesive	Interface
	26.6	Cohesive	Interface

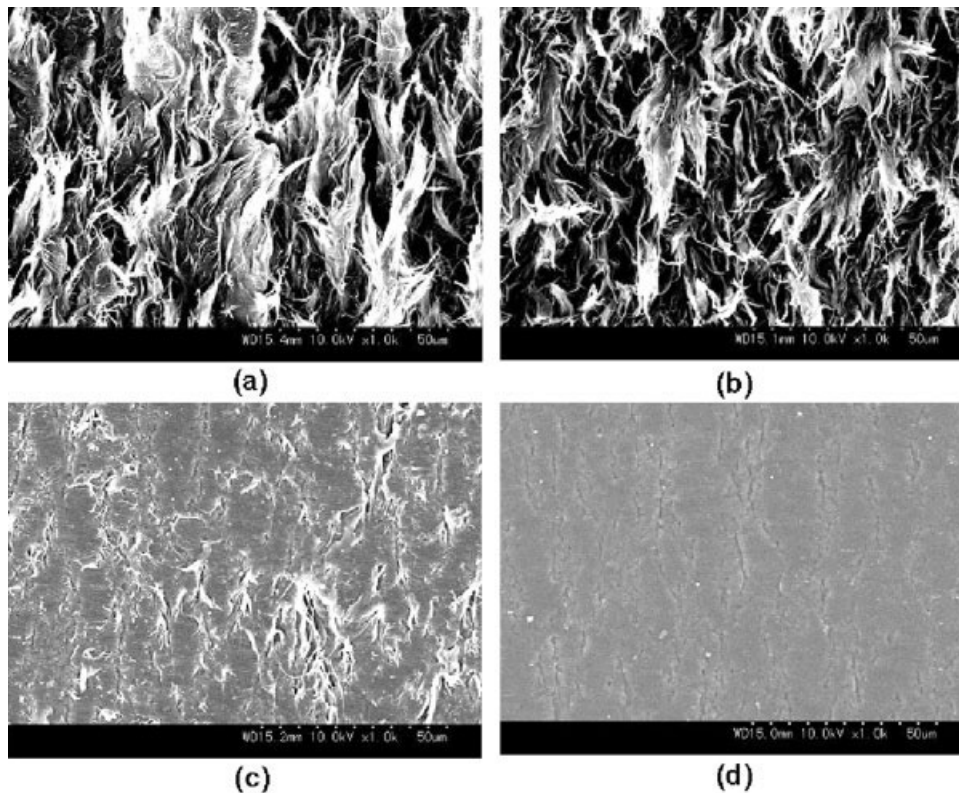


Figure 6 SEM micrographs of LCP film surfaces peeled off from adhesive joints of epoxy bonding sheet and (a) LCP film surface DP-treated in O_2 at 26.6 Pa before PCT, (b) LCP film surface DP-treated in H_2 at 4.0 Pa before PCT, (c) LCP film surface DP-treated in O_2 at 26.6 Pa after PCT, and (d) LCP film surface DP-treated in H_2 at 4.0 Pa after PCT.

plasma gas. In contrast to this, the peel strength after PCT decreased with decreasing the pressure in every plasma gas and it became practically constant above 13.3 Pa. The peel strength of the films DP-treated in the O_2 was the highest. These tendencies were highly related with the concentration of the polar groups such as phenolic hydroxyl and carboxyl groups generated by plasma treatment on the surface and the surface roughness. The higher concentration of the polar groups enhanced the adhesion before PCT by the increase in the chemical interaction; however, it damaged the long-term adhesive reliability corresponding to the peel strength after PCT due to the acceleration of the penetration of water molecules into the interface between the LCP film and the epoxy bonding sheet. The large surface roughness was effective to enhance the peel strength before and after PCT. In the comparison of the plasma mode, the RIE-treatment could induced the polar groups on the surface of the LCP film as well as DP-treatment and the surface roughness by the RIE-treatment was larger than the DP-treatment. Hence, the peel strength before and after PCT of the RIE-treated LCP films was higher. The RIE-treatment in the O_2 atmosphere at the gas pressure of 13.3 Pa was the best plasma conditions for both the initial

adhesion and the long-term adhesive reliability between the LCP film and the epoxy bonding sheet system.

References

1. Culbertson, E. C. In Proceedings of the 45th Electronic Components and Technology Conference; IEEE: Piscataway, NJ, 1995; p 520.
2. Khoo, C. G. L.; Brox, B.; Norrhede, R.; Maurer, F. H. J. IEEE Trans Compon Packag Manuf Technol C 1997, 20, 219.
3. Yang, R. Adv Packag 2002, March, 17.
4. Koide, N. New Development of Liquid Crystal Polymers; CMC books: Tokyo, Japan, 2004.
5. Ge, J.; Turunen, M. P. K.; Kivilahti, J. K. J Polym Sci Part B: Polym Phys 2003, 41, 623.
6. Gleich, H.; Criens, R. M.; Mosle, H. G.; Leute, U. Int J Adhes Adhes 1989, 9, 88.
7. Osterndorf, J.; Rosty, R.; Bodnar, M. J. Int SAMPE Symp Exhib 1989, 34, 613.
8. Teramoto, K. Mater Technol 1996, 14, 283.
9. Man, H. C.; Li, M.; Yue, T. M. J Adhes Sci Technol 1997, 11, 183.
10. Tavakoli, S. M.; Riches, S. T. SPE ANTEC 2000, 58, 1248.
11. Kogoma, M. Converttech 2005, 33, 95.
12. Lim, S. K.; Inagaki, N. J Appl Polym Sci 2003, 88, 2400.
13. Inagaki, N.; Park, Y. W.; Narushima, K.; Miyazaki, K. J Adhes Sci Technol 2004, 18, 1427.

14. Tanigawa, S.; Ishikawa, M.; Nakamae, K. *J Adhes Sci Technol* 1991, 5, 543.
15. Powell, H. M.; Lannutti, J. J. *Langmuir* 2003, 19, 9071.
16. Shi, M. K.; Clouet, F. *J Appl Polym Sci* 1992, 46, 2063.
17. Kasemura, T.; Ozawa, S.; Hattori, K. *J Adhes* 1990, 33, 33.
18. Lugsceider, E.; Bobzin, K.; Moller, M. *Thin Solid Films* 1999, 355, 367.
19. Schuman, T.; Karlsson, A.; Larsson, J.; Wikstrom, M.; Rigdahl, M. *Prog Org Coat* 2005, 54, 360.
20. Cueff, R.; Baud, G.; Besse, J. P.; Jacquet, M. *J Adhes* 1993, 42, 249.
21. Le, Q. T.; Pireaux, J. J.; Caudano, R.; Leclere, P.; Lazzaroni, R. *J Adhes Sci Technol* 1998, 12, 999.
22. Shi, M. K.; Christoud, J.; Holl, Y.; Clouet, F. *J Macromol Sci Pure Appl Chem* 1993, A30, 219.
23. Friedrich, J.; Loeschcke, I.; Frommelt, H. *Polym Degrad Stab* 1991, 31, 97.
24. Rivaton, A.; Gardette, J.-L. *Angew Makromol Chem* 1998, 261/262, 173.
25. Inagaki, N.; Narushima, K.; Lim, S. K. *J Appl Polym Sci* 2003, 89, 96.
26. Onda, T.; Shibuichi, S.; Satoh, N.; Tsujii, K. *Langmuir* 1996, 12, 2125.