

Adhesion Behavior of Different Annealed Polyphenylquinoxaline Foils Treated Using Low Pressure Plasma

Nabil Anagreh, Radwan Dweiri

Materials Engineering Department, Al-Balqa Applied University, Al-Salt 19117, Jordan

Correspondence to: N. Anagreh (E-mail: anagreh1961@hotmail.com)

ABSTRACT: The aim of this study was to investigate the adhesion behavior of polyphenylquinoxaline (PPQ) foils. PPQ foils were initially produced and then annealed in vacuum furnace at different temperatures. The surface of PPQ was activated with GHz-low pressure plasma (lp-plasma) using oxidative (O_2) and noble (Ar, Ar/He) gases. An epoxy adhesive was used to glue the PPQ foil with a sheet of steel. The adhesions of foils were examined using 90°-peel test. Observations from scanning electron microscopy (SEM) and atomic force microscopy (AFM) in addition to the gravimetry measurements were used to interpretate the effects of plasma treatment of adhesion of foils. The results showed that the peeling resistance values were significantly dependent on plasma treatment time and power as well as annealing conditions. In case of PPQ foils where the adhesion was significantly enhanced, it was observed that the fracture changed from adhesion mode at the interface between the adhesive layer and the PPQ foil to cohesive mode, which was seen either in the layer nearby the PPQ surfaces or in the foil itself. Furthermore, furrowed structures were observed at the fracture surface and they were oriented transversely to the peeling direction. SEM and AFM graphs showed that the surface roughness of PPQ foils increased significantly with increasing plasma treatment time and it was more pronounced when using oxidative than noble gas. © 2013 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* **2014**, *131*, 39949.

KEYWORDS: adhesives; thermoplastics; structure-property relations; microscopy; surfaces and interfaces

Received 26 May 2013; accepted 22 August 2013

DOI: 10.1002/app.39949

INTRODUCTION

The bonding technology is the only possible joining technology to join high performance plastics. For optimal adhesion of adhesives to plastic surfaces, obtaining surfaces free of antiadhesive materials is not sufficient, but a chemical and physical activation of the surfaces is absolutely necessary. Harmful or environmental friendly procedures are usually used to activate the surfaces of plastic materials. Plasma treatments are environmental friendly methods, which are industrially assigned already for pretreating components and foils of automotive and other industrial areas. The optimum treatment parameters are empirically found to a large extent, because the interpretation of the obtained adhesion strengths on the basis of changes in chemical and physical surface character as well as the topographic structure are uncompleted. This study aimed to correlate the ascertained adhesion strengths with surface modifications using lp-plasma.

Extensive investigations of adhesion improvement were reported with conventional technical plastics.^{1–31} In previous studies, the enhancement of the adhesion of lp-plasma (H_2 , NH_3) treated poly(tetrafluoroethylene (PTFE))³ and the adhesion of PTFE and

tetrafluoroethylene perfluorovinyl ether copolymer (PFA) both treated with TMB(trimethoxyborane)/ H_2 /He plasma¹³ have been related to the removal of fluorine atoms from the polymer surface rather than to the presence of polar functions at the surface. On the other hand, the improvement of bonding strength of treated poly(ethyleneterephthalate (PET), polyamide (PA6), high density polyethylene (HDPE), and polypropylene (PP) surface with lp-plasma and atmospheric-pressure plasma (APP) was mainly ascribed to increased surface oxygen and nitrogen contents and to increased surface roughness.¹² Similar phenomenon was observed when treating ultra-high-modulus polyethylene (UHMPE) with APP.²⁰ Other studies reported that APP treatment of polycarbonate (PC), acrylonitrile butadiene styrene copolymer (ABS), low density polyethylene (LDPE), HDPE, PP, and PFA surfaces introduced new polar functional groups (carbonyl, amine, or hydroxyl) and enhanced the total and polar components of the surface energy.^{14,18,28,31} Cepeda-Jiménez et al.¹⁹ reported that the formation of polar groups on ethylene vinyl acetate (EVA) copolymers was more noticeable by treatment with nonoxidizing plasma gases (Ar, N_2) than with oxidizing gases (air, N_2/O_2 , O_2/CO_2). The surface etching with the nonoxidizing plasmas giving rise to a higher roughness. The

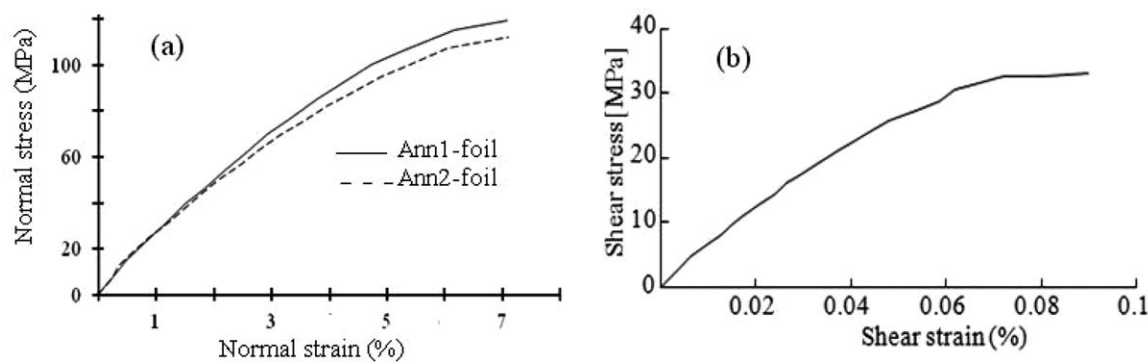


Figure 1. (a) Tensile stress–strain diagram of Ann1- and Ann2-PPQ foils and (b) shear stress–shear strain diagram of Eupox adhesive.

high peel strength values of EVAs treated with oxidizing gases due to increased roughness causing a mechanical interlocking of the adhesive.

Meanwhile, the gluing of thermally stable plastics polyimide (PI), polyether ether ketone (PEEK), polyphenylene sulfide (PPS), and polyetherimid (PEI) and their adhesion improvement by means of environmental friendly surface treatments were previously studied.^{22,32–37} The higher bonding strength of PPS, PEI, PEEK after treatment with lp-plasma or APP was found to be caused by the higher polar surface energy and the increase of surface roughness.^{22,32,34,35,37} Comyn et al.³² and Seidel et al.³⁷ attributed the increase of the surface energy of lp-plasma treated PEEK to the increase of the amounts of oxygen and nitrogen, and to the creation of new surface groups (carbonyl and hydroxyl). Other researchers found that the increase of surface energy of PEI after treated with lp-plasma resulted from the removal of release agent and carbon and from the creation of polar species, esters, or carboxylic acid groups.²²

PPQ is a thermoplastic material with a linear chain structure, soluble in common organic solvents like chloroform and fusible. PPQ is produced by polycondensation of tetraamine and tetraketone at a reaction temperature of 50°C in chloroform as a solvent. Because of the high content of aromatic structural components in the macromolecule, the segment mobility is strongly reduced. This explains the high glass transition temperature of ~250°C as well as the high operating temperature of PPQ. Variation of composition and structure of parent compounds (i.e., tetraketone and tetraamine) can affect strongly the thermal and mechanical behavior of PPQ. Therefore, PPQ is recommended for products where good mechanical characteristics are demanded at high temperatures.³⁸

The aim of this study was to investigate the effect of annealing conditions (temperature and time) on the adhesion behavior of PPQ foils. Furthermore, the influence of lp-plasma parameters (plasma power, treatment time, and plasma process gas) on the topography, physical, and chemical properties of PPQ surfaces was also investigated.

EXPERIMENTAL

Materials

The test material used in this study was PPQ. The PPQ foils were produced in the laboratory as described in a previous

study³⁸ and Figure 1(a) shows the tensile stress–strain diagram of PPQ foils annealed at two different conditions. Sheets of steel of type St-1403 with a thickness of 1 mm were selected according to DIN EN 10130 to be adhered with PPQ foils. A glue system consists of epoxy (Eupox 720/783) and a hardener (Versamid 145) was supplied by Witco Company, Germany. The shear stress–shear strain diagram of the glue system is shown in Figure 1(b).³⁸

In this experiment, PPQ foils were annealed in vacuum at two different conditions. Samples denoted as Ann1-foils were initially annealed at 120°C for 3 h, and then at 180°C for 8 h. Samples denoted as Ann2-foils were initially annealed at 120°C for 3 h, and then at 230°C for 3 h. It was found, in case of Ann1-foils, that thermally induced structural changes could be avoided, but a little amount of solvents still remains in the foils. In contrast, in case of Ann2-foils, thermally induced structural changes of PPQ foil were caused, while the residual of solvent was completely removed.³⁸

Surface Modification

The preliminary peeling tests³⁸ showed that the lp-plasma treatment led to a strong adhesion between the PPQ foils and steel sheets. For this reason, the lp-plasma treatment was selected to explain the context between structural changes and adhesion. The treatment of PPQ foils (200 μm thick) was performed using GHz-lp-plasma type G 200 supplied by Technics Plasma Company, Germany. O₂-, Ar-, and Ar-He-gas mixture (mix ratio 1 : 1) were used to treat PPQ foils.

To obtain optimal adhesion of adhesive to steel sheets, the steel sheets were immersed in a cold cleaning fluid hydrocarbon-based (Cleaner NA 09) for 5 min in an ultrasonic bath to remove grease and contamination. Thereafter, the steel sheets were rinsed with a cold cleaning fluid to remove the residues and dried using degreased-compressed air. Clean steel surfaces were then sandblasted with corundum (grain size 0.25–0.5 mm) at a pressure of 0.6 MPa. The sheet metals were again degreased to remove the residual of the corundum particles from the treated surfaces.

Preparation of Samples for Peeling Test

Initially, the epoxy and the hardener were carefully weighed and manually mixed by a wood spatula with a mixing ratio of 2 : 1.

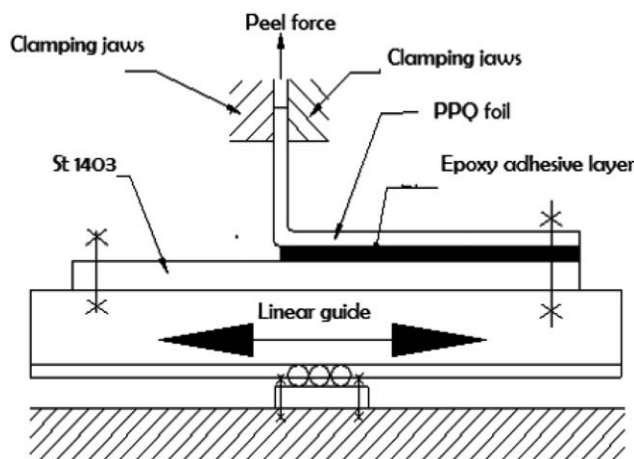


Figure 2. Arrangement of 90° peeling test.

The mixed glue was then degassed in vacuum for some minutes to avoid the formation of bubbles. The steel sheet was initially inserted in a mold and the adhesive was then spread out on the steel sheet by means of a spatula. The PPQ foils were next placed on the steel sheet above the adhesive and the excess material of the foils above the height of the mold level was then rolled. So, an adhesive layer of 200 μm thickness was produced. The samples were hardened at room temperature for 7 h and tested after 7 days. For each peeling test, three samples were prepared.

Characterization of Samples

For the determination of the adhesion strength of PPQ foil glued to steel sheet, the peel test of 90° was implemented and further modified according to EN 1464:2010 (Figure 2). The samples were peeled at a test speed of 100 mm/min using Instron tensile testing machine. A Hitachi HD-2700 SEM microscope (USA) with an electron beam energy of 20 kV was used to provide the analysis of the physical modification of PPQ foil. Specimens were gold coated prior to obtaining the SEM micrographs. The AFM investigations were carried out using Topometrix (Germany) TMX 1000 in contact mode and TMX 2000 in noncontact mode at normal atmosphere. The AFM in contact mode was used in order to scan a larger surface area, whereas for small scan areas the noncontact mode was preferred. The operating mode in the first type was a constant force, while for the second type it was the constant excitation frequency.

RESULTS AND DISCUSSION

Gravimetry Measurements

Table I shows the weight losses of Ann1- and Ann2-PPQ foils treated using GHz-lp-plasma. As seen from Table I, the weight losses of Ann1- and Ann2-foils increased with increasing the treatment time either the foils treated using O₂- or Ar-gas. The percentages of weight losses were almost the same after a short treating time of 6 s when compared the O₂-treated Ann1-foils (~0.07%) with the Ar-treated ones (~0.06%). Similar trend was observed for O₂- or Ar-treated Ann2-foils. However, with increasing treatment time up to 1086 s, the weight loss of O₂-treated Ann1-foils increased to ~1.5%, while O₂-treated Ann2-foils reached ~8.1%. For Ar-treated Ann1- and Ann2-foils, the losses were almost the same; 0.25% and 0.28%, respectively at

1086 s. It could be concluded that the weight loss of O₂-treated Ann2-foils at 1086 s was more pronounced than that of O₂-treated Ann1-foils. The weight losses were also more pronounced using O₂- than Ar-gas for both Ann1- and Ann2-foils. This might be due to the strong oxidation of the PPQ foils in case of treating using O₂-gas.

A dipping of O₂-plasma treated PPQ foils into acetone or wiping them with a spatula rubber caused no substantial change in weight. It was clearly seen, after O₂-plasma treatment, that a film of reaction products was deposited on the lower surface of PPQ foil, which exhibited a good adhesion to the base material. The lower surface of PPQ foil was referred to the surface, which contacts the mold during the production process of PPQ foil. A storage of the treated samples either in the desiccator or under normal conditions for 24 h caused no significant change in weight. The unchanged weight was attributed to that a diffusion and/or an adsorption of the air humidity as well as attracting of dust particles of environment; resulting from electrostatic charging on the surfaces, were not found after surface treatment.

Adhesion Strength

It was worth to be mentioned at the beginning of this section that the PPQ was produced in the laboratory in very small quantities and it is not commercially available. The peeling test results of the untreated and treated PPQ foils are shown in Table II. The missing values in Table II were not recorded because the produced PPQ quantity was insufficient to run all the peeling tests. Table II shows that the untreated PPQ foils exhibited small peeling resistance value (0.03 N/mm), which was found to be independent of the annealing conditions (Ann1 or Ann2). It could be also noticed from Table II that the peeling resistances of treated PPQ foils were generally improved with different trends as a function of process gas, plasma power, and annealing conditions of the foils. On the one hand, it was found that the process gas played a main role in improving the adhesion in case of Ann1-foils. In general, it could be reported that the peeling resistance of Ann1-foils treated using O₂-gas increased with increasing treatment time and for example it reached at 300 s a value higher than 2 N/mm with a plasma

Table I. Weight Losses of Ann1- and Ann2-PPQ Foils Treated Using GHz-lp-Plasma Based on Process Gas and Treatment Time

Treatment time (s)	Weight losses (%)			
	O ₂ -gas		Ar-gas	
	Ann1	Ann2	Ann1	Ann2
6	0.0717	0.107	0.0637	0.1065
66	0.1434	0.1783	0.1101	0.1065
120	0.2672	0.2578	0.1321	0.1234
186	0.3227	0.321	0.1468	0.1419
300	0.4361	0.4465	0.1634	0.1586
486	0.6454	0.7133	0.1836	0.1774
600	1.2855	1.7534	0.2013	0.2034
1086	1.5418	8.1312	0.256	0.2839

Table II. Influence of GHz-Ip- Plasma Power and Process Gas on the Peeling Resistance Values of Different Annealed PPQ Foils

Treatment time, plasma power (s, W)	Peeling resistance values (N/mm)					
	Ann1			Ann2		
	O ₂	Ar	Ar-He	O ₂	Ar	Ar-He
Untreated PPQ	0.03 ± 0.00	0.03 ± 0.00	0.03 ± 0.00	0.03 ± 0.00	0.03 ± 0.00	0.03 ± 0.00
6, 100	0.2 ± 0.10	1.0 ± 0.30	3.33 ± 0.45	-	0.5 ± 0.25	1.93 ± 0.35
6, 200	0.6 ± 0.30	0.82 ± 0.24	2.4 ± 0.39	0.08 ± 0.00	0.5 ± 0.19	1.8 ± 0.28
6, 300	-	0.63 ± 0.28	2.46 ± 0.40	-	0.53 ± 0.20	0.9 ± 0.15
6, 400	0.28 ± 0.17	0.98 ± 0.16	0.61 ± 0.27	0.195 ± 0.09	0.53 ± 0.16	1.4 ± 0.22
60, 100	-	0.2 ± 0.19	-	-	0.062 ± 0.0	-
60, 200	0.36 ± 0.15	-	-	0.156 ± 0.01	-	-
60, 400	0.46 ± 0.09	0.63 ± 0.23	0.54 ± 0.20	0.16 ± 0.08	0.62 ± 0.12	0.52 ± 0.13
120, 100	-	0.29 ± 0.12	-	-	0.07 ± 0.05	-
120, 200	1.28 ± 0.52	-	-	0.156 ± 0.3	-	-
300, 100	-	0.47 ± 0.17	-	-	-	-
300, 200	2.33 ± 0.43	-	-	-	-	-
600, 100	-	-	-	-	0.27 ± 0.11	-
600, 200	-	-	-	0.2 ± 0.05	-	-

power of 200 W as compared to 0.6 N/mm at 6 s, 200 W (Table II). The fracture mode was initially observed to be at the boundary layer between adhesive/PPQ foil and after 120 s, it changed to cohesive fracture in the PPQ foil itself. In contrast, the peeling resistance of Ann1-foils increased noticeably (~1.0 N/mm) after 6 s at 100 W using Ar-gas as compared to the untreated PPQ (0.03 N/mm), and then it dropped to a value of 0.47 N/mm after 300 s at 100 W. One of the three samples, which tested in this group (i.e., for 6 s at 100 W) was fractured cohesively in the PPQ foil itself, while the other two samples were fractured at the boundary layer between the PPQ foil and the adhesive layer. A similar fracture mode was observed after a longer treatment time. On the other hand, there was no significant improvement in the adhesion strength with increasing the treating time for Ann2-foils treated using either O₂- or Ar-gas at the same plasma power. The plasma power had also a slight effect on the peeling values at the same treating time. The peeling values for Ann1-foils treated using O₂- or Ar-gas were

found to be higher than those of their counterparts for Ann2-foils when they were compared at the same treating time and power plasma. The fracture in these samples took place adhesively along the boundary layer between the PPQ foil and the adhesive layer.

For PPQ foils treated using Ar-He mixture, the peeling resistances for 6 s rose significantly (3.33 N/mm for Ann1-foils and 1.93 N/mm for Ann2-foils at 100 W) as compared with the untreated PPQ (0.03 N/mm) and the values were higher in the case of Ann1- than Ann2-foils. Increasing the plasma power e.g., from 100 to 400 W for a treating time of 6 s resulted in a decrease in the peeling values from 3.33 to 0.61 N/mm for Ann1-foils and from 1.93 to 1.4 N/mm for Ann2-foils (Table II). The samples were ruptured cohesively in Ann1- and Ann2-foils. The peeling values of both Ann1- and Ann2-foils using Ar-He-mixture were clearly higher than those of their counterparts using either Ar- or O₂-gas (Table II). The Ann1- and Ann2-foils treated using Ar- or O₂-gas for 6 s were fractured at

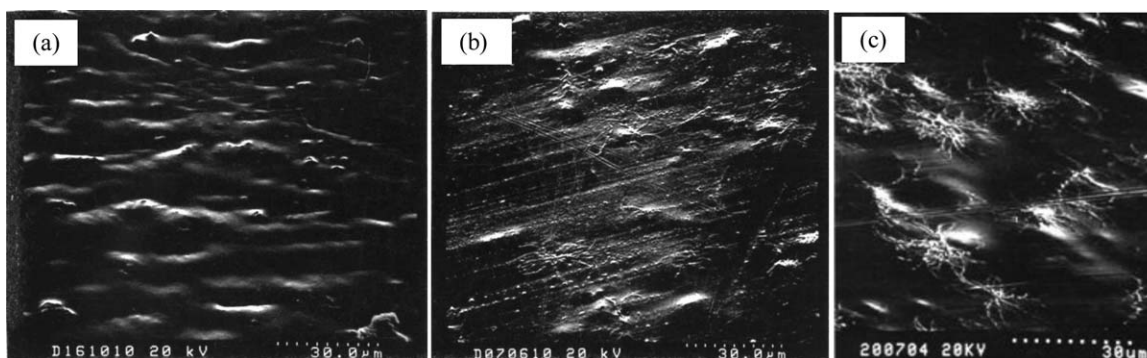


Figure 3. SEM photographs of (a) surface of untreated PPQ foil (unannealed), (b) surface of untreated Ann1-PPQ foil (annealed), and (c) fracture surface of a glued joint of untreated Ann1-PPQ foil.

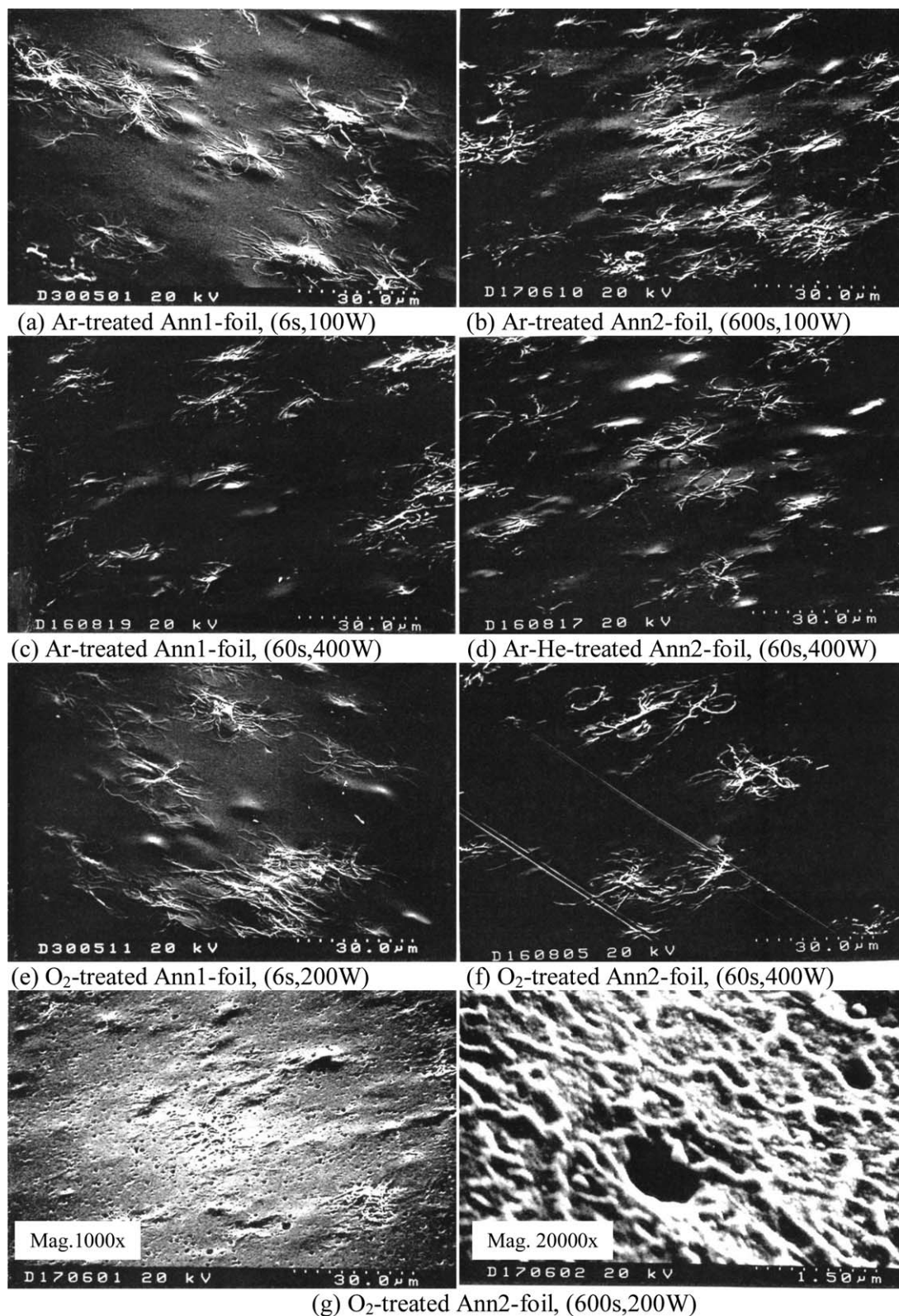


Figure 4. SEM surface photographs of different treated Ann1- and Ann2-foils using GHz-lp- plasma.

the boundary layer between the adhesive layer and the PPQ foil. Independent on the gas used, no significant difference in adhesion strength values of Ann1- and Ann2-foils (ranging from 0.5

to 0.6 N/mm) was observed at a longer treatment time of 60 s and a plasma power of 400 W and the fracture mode took place at the boundary layer between the adhesive layer and the PPQ

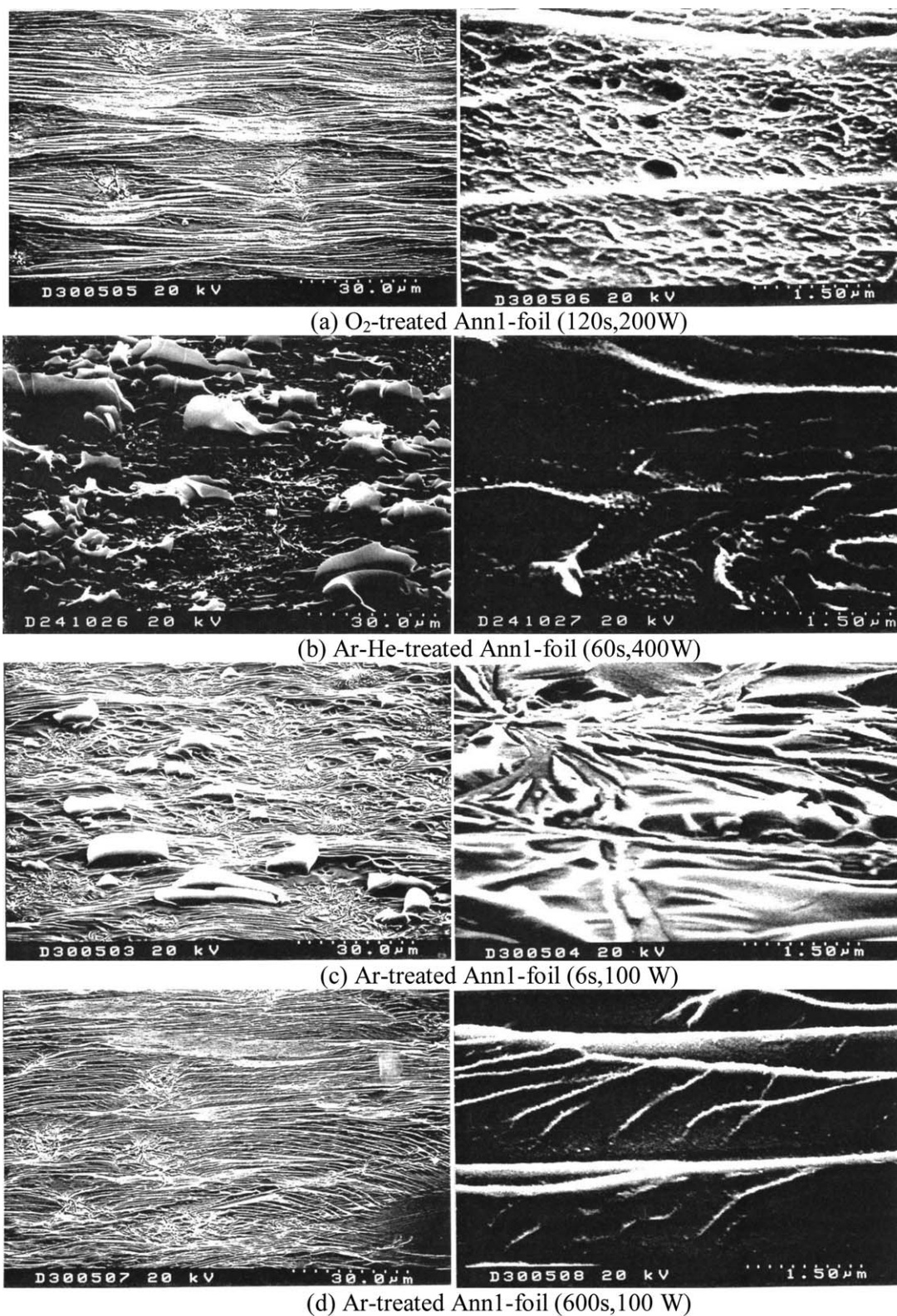


Figure 5. SEM Fracture surfaces photographs of different treated Ann1-foils using GHz-Ip plasma. Graphs to left at $\times 1000$ magnification and graphs to the right at $\times 20,000$ magnification.

foil. On the contrary, a significant difference was noticed at shorter treating time of 6 s (ranging from 0.2 to 3.33 N/mm).

Finally, it could be reported that the peeling resistance values of PPQ foils treated using O₂-gas depended strongly on the plasma power at long treating times, and it was found that with

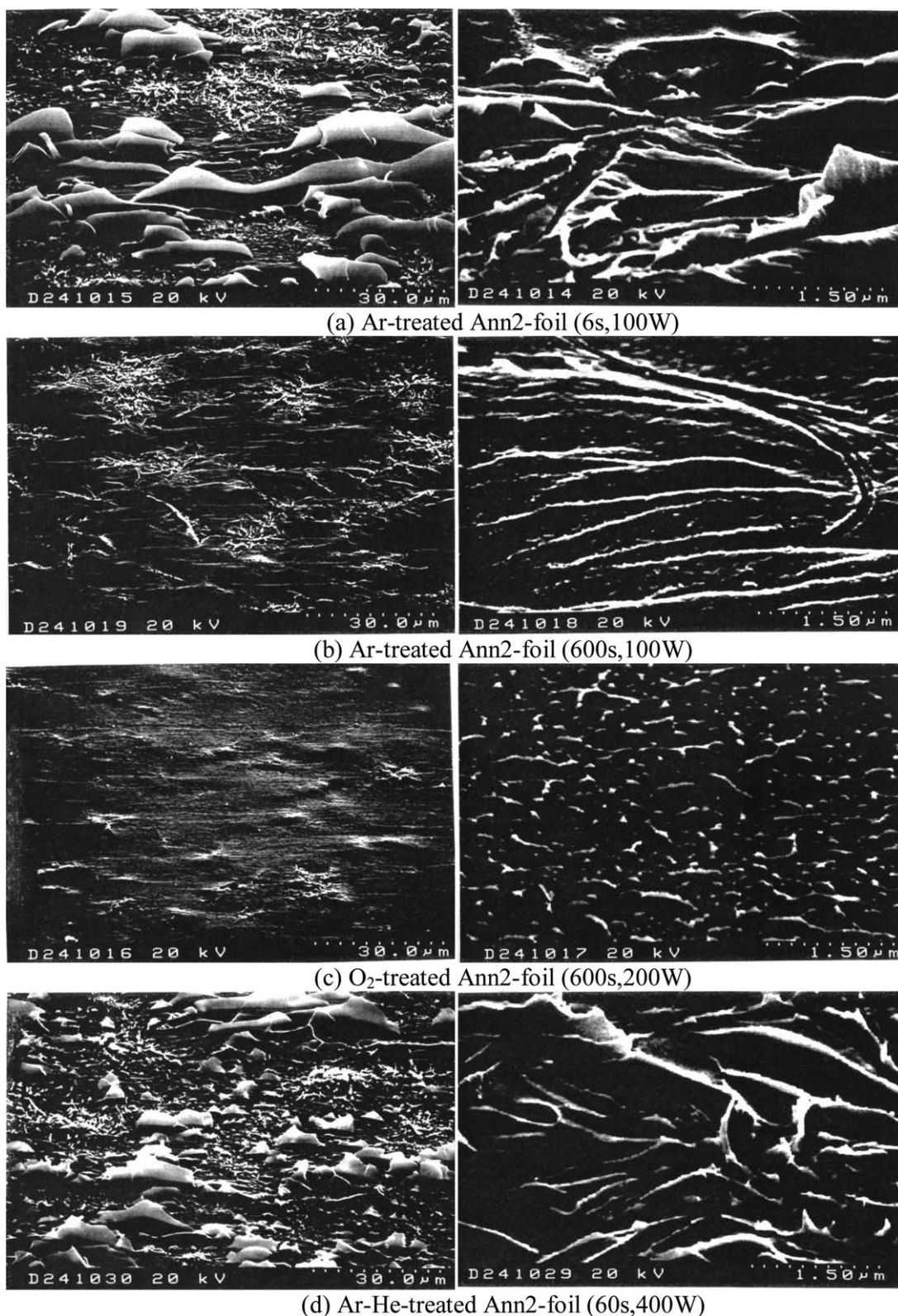


Figure 6. SEM Fracture surfaces photographs of different treated Ann2-foils using GHz-lp plasma. Graphs to left at $\times 1000$ magnification and graphs to the right at $\times 20,000$ magnification.

increasing plasma power, the temperature of the chamber increased sharply,³⁹ which led to increase the mobility of the surface molecules.

Scanning Electron Microscopy (SEM)

Untreated PPQ Foils. SEM micrographs in Figure 3(a,b) showed that the surface roughness of the Ann1-foils increased

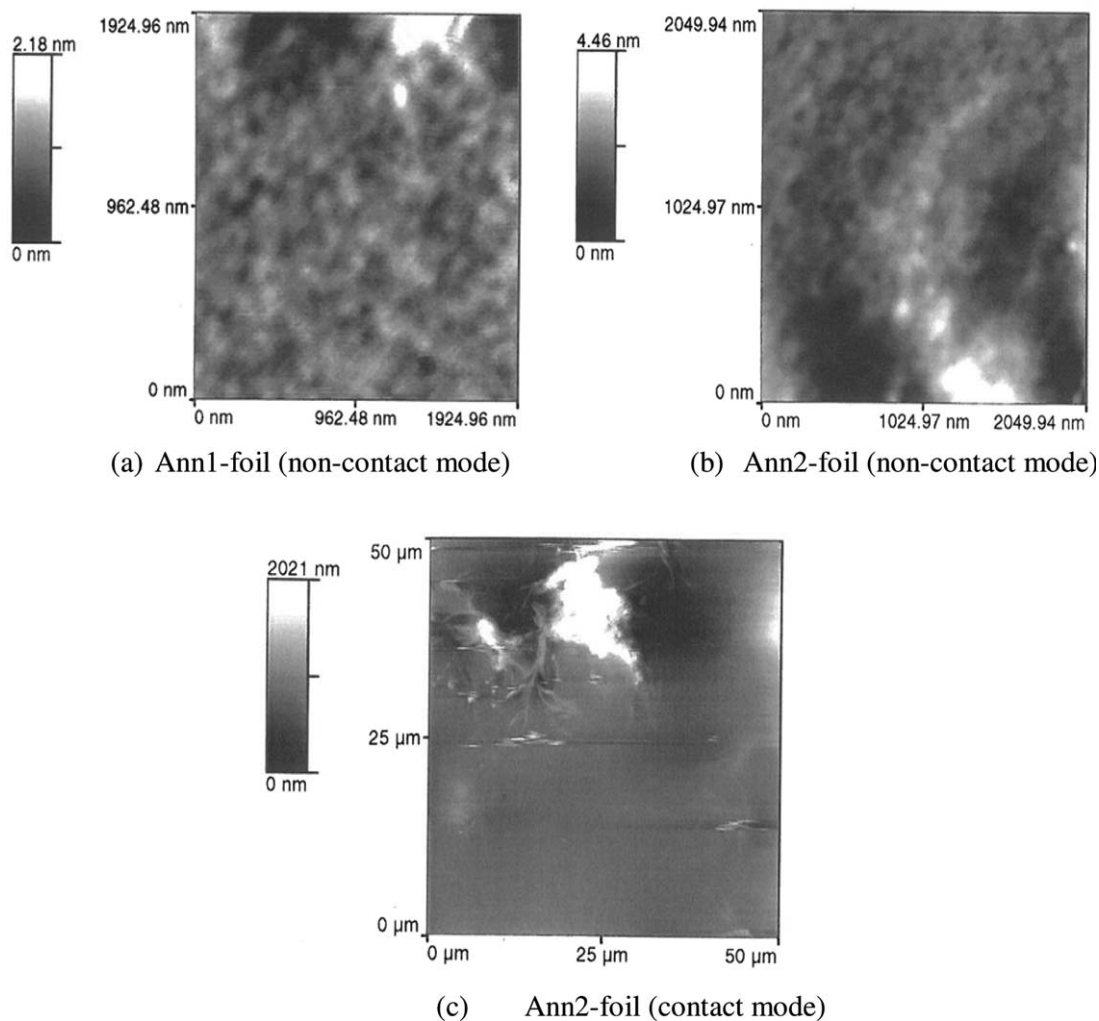


Figure 7. AFM photographs of untreated Ann-1 and Ann2-PPQ foils.

as compared to unannealed foils. A recognizable blisters of the solvent were enclosed in the unannealed samples. Furthermore, the SEM micrographs of annealed foils appeared similar to a large extent for different annealing conditions. The unannealed foils were self-rolled, while the annealed ones were not and this could be attributed to the removal of solvent from the PPQ foils after annealing and to the enhancement of strength of the annealed PPQ foils. SEM micrograph of fracture surface of a glued joint of untreated Ann1-PPQ foils indicated that there was an adhesion fracture at the PPQ surface [Figure 3(c)], where low peeling resistance values (0.03 N/mm) was also reported (see Table II).

GHz-Ip Plasma Treated PPQ Foils. Some SEM surface micrographs for different Ann1- and Ann2-foils are shown in Figure 4(a–g) at different plasma treatment time and power. In general and as it can be seen from the micrographs in Figure 4, there were no significant changes on surface topography of Ann1- and Ann2-foils regardless the plasma treatment time and power and they were similar to some extent to the surface fracture of untreated PPQ foils shown in Figure 3(c). A slight stronger roughening of the surface of Ar-treated Ann2-foils occurred in Figure 4(b) as compared to that of either Ar-treated Ann1-foils

[Figure 4(a,c)] or O₂-treated Ann2-foils [Figure 4(f)]. Practically, the solvents removal during the foil production took place at the edge faster than at the center, which may result on different morphologies. The surface topographies of O₂-treated Ann1-foils at the edge were slightly different from those at the center as seen in Figure 4(e). However, in some cases, higher peeling resistance values were measured at the edge of the foils. A selective etching appeared on the surface of O₂-treated Ann1-foils at 600 s [Figure 4(e,g)] and moreover, the most upper PPQ layers were unevenly removed away from the surfaces as can be observed at a higher magnification of 20,000× in Figure 4(g).

On the other hand, the fracture surface of the Ann1-foils was macroscopically seen covered with a thin layer of the adhesive and this usually occurred when the fracture took place at the boundary layer (PPQ foil/adhesive layer) and as the adhesion of the Ann1-foils increased. The foil after separation from the adhesive layer was strongly deformed and was self-rolled. At low magnifications, the SEM graphs of the fracture surfaces of Ann1-foils were seen to be similar to a great extent when using either O₂- or Ar-gas [see Figure 5(a,c,d) left]. These fracture surface graphs indicated the presence of a furrowed structure

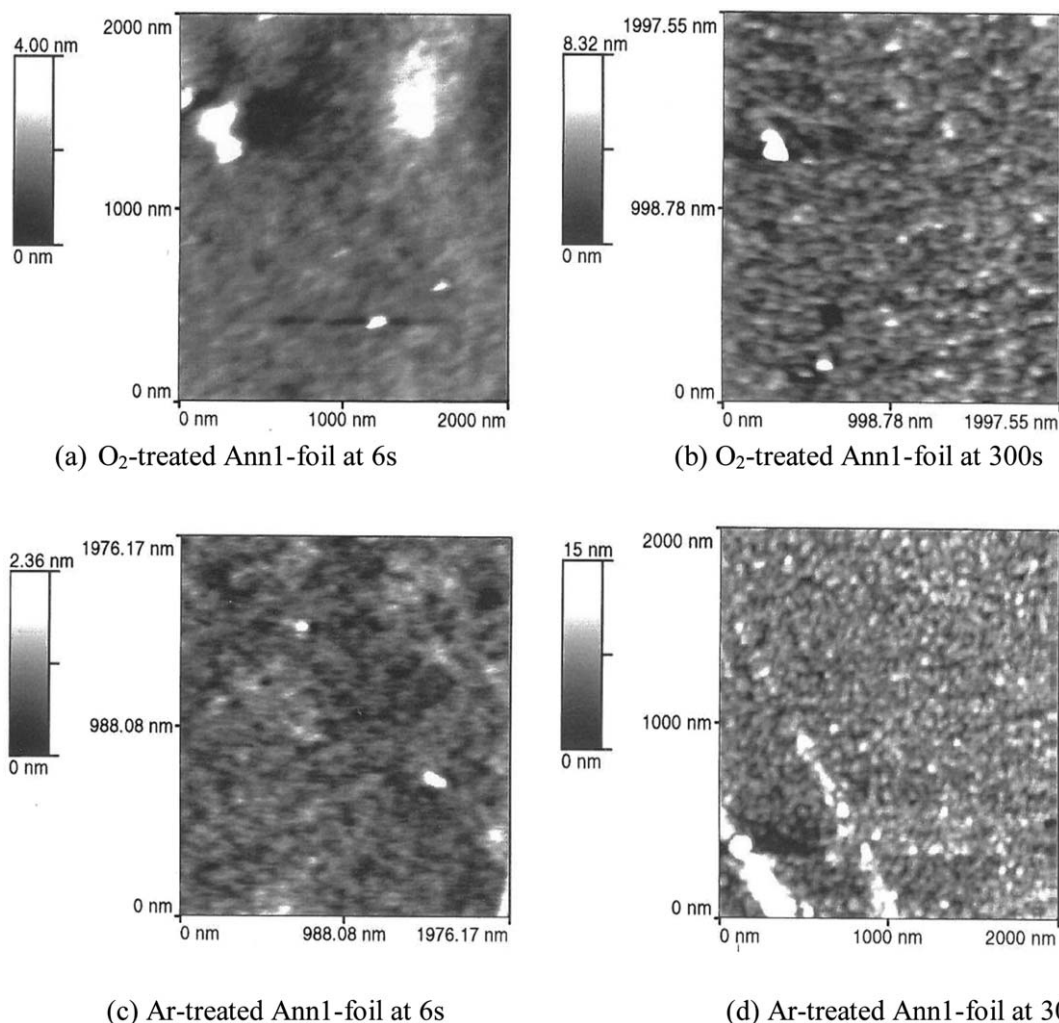


Figure 8. AFM photographs (noncontact mode) of different treated Ann1-PPQ foils using GHz-lp plasma.

oriented transversely to the peeling direction. At high magnification, the fracture surfaces between furrows were smooth for Ar-treated Ann1-foils [Figure 5(c,d) right], while the surface was rough between furrows for O₂-treated Ann1-foils [Figure 5(a), right] and particularly, this occurred when higher values of peeling resistance was achieved (~ 1.0 N/mm for Ar-treated Ann1-foils at 6 s, 100 W, and ~ 1.28 N/mm for O₂-treated Ann1-foils at 120 s, 200 W). On the other hand, fracture surface graphs showed that the fracture of O₂-treated Ann2-foils took place adhesively on the surface of the foils after 600 s, 200 W [Figure 6(c)]; however, the adhesion was greatly improved (~ 0.2 N/mm) as compared to its value at 6 s, 200 W (~ 0.08 N/mm) and it slightly improved as compared to that at 6 s, 400 W (~ 0.19 N/mm). In contrast, the presence of mixed fractures (i.e., adhesively and cohesively) were observed in Ar-treated Ann2-foils at 6 s [Figure 6(a)] and Ar-He-treated Ann2-foils at 60 s [Figure 6(d)], i.e., strips of the residual glue remained on the PPQ surfaces, which were oriented transversely to the peeling direction. At higher magnification in Figure 6(a), a strong roughening of the fracture surface was detected, which probably occurred either as a fracture in the weak boundary layer or as a fracture in the foil-itself, and in fact in a level

parallel to the adhesive layer. The fracture took place at 600 s, 100 W mainly adhesively at the surface of Ar-treated Ann2-foil [Figure 6(b)]; however, the measured adhesion values were small (~ 0.27 N/mm) in this case as compared to its value at 6 s, 100 W (~ 0.5 N/mm) and compared to that at 6 s, 400 W (~ 0.53 N/mm).

Finally, the SEM graphs of fracture surfaces after activation of the Ann1- and Ann2-foils using Ar-He-mixture at 60 s, 400 W in Figures 5(b) and 6(d), respectively, were, on one hand, similar to each other and, on the other hand, similar to that of Ar-treated Ann2 at 6 s, 100 W [Figure 6(a)]. Their peeling values were almost the same (~ 0.5 N/mm) as seen in Table II.

Atomic Force Microscopy (AFM)

The AFM surface topography of untreated Ann1- and Ann2-PPQ foils, which are shown in Figure 7, illustrated that the surfaces exhibited different roughness values at close neighboring scan areas. In addition, the surface at some places was scratched and these scratches were impressions of those which may be originally existed on the glass disks during the pouring of PPQ/chloroform solution on the glass disks. Besides the presence of these scratches, pits were also formed and they were

observed clearly when scanning PPQ foil surface near its edge. The pits were not recognized in the SEM micrographs because of the coating of the surface with a thin layer of gold.

AFM photographs in Figure 8(a–d) showed a strong roughening of the surface of Ann1-foils treated with GHz-plasma using O₂-gas or using Ar-gas as compared to untreated foils. This surface roughness increased with increasing the treatment time. However, upper layers were uniformly removed. It can be concluded that the increase of peeling resistance values after plasma treatments can be attributed to the removal of weak boundary layer (contamination and reactions product that deposited on the surface as a result of plasma etching), and to the increase of the surface roughness. The surface roughness caused a mechanical interlocking between the adhesive and the PPQ surface. Other researchers reported that the increase of adhesion strength of treated high performance plastics (PPS, PEI, PI, and PEEK) using lp-plasma besides the removal of weak boundary layer, the increase of surface roughness were also attributed to the increase of surface energy, especially the polar parts.^{22,32,35,37}

CONCLUSIONS

The peeling resistance values of PPQ foils were related to different annealing conditions and plasma treatment parameters in this work and the following conclusions were drawn:

- In general, the peeling resistances of treated PPQ foils were improved as a function of process gas, plasma power, and annealing conditions as compared to the untreated ones.
- Among all the peeling values of different foils, the maximum values can be achieved at 6 s, 100 W for both Ar- and Ar-He-treated Ann1- and Ann2- foils, where the O₂-treated Ann1- and Ann2- foils had the minimum peeling values at these parameters and its maximum value appeared at longer treating times.
- The peeling values for Ann1-foils treated using O₂- or Ar-gas were found to be higher than those of their counterparts for Ann2-foils and this was true when they were compared at the same treating time and power plasma and the peeling values of both Ann1- and Ann2-foils using Ar-He-mixture were clearly higher than those of their counterparts using either Ar- or O₂-gas.
- For a short treating time of 6 s, increasing the plasma power resulted in a noticeable decrease in the peeling values for Ar-He-treated Ann1- and Ann2-foils and a slight decrease for Ar-treated Ann1- and Ann2-foils, while it resulted in a slight increase for O₂-treated Ann1- and Ann2-foils.
- At 6 s and by increasing plasma power, the values of peeling of Ann1-foils can be arranged in the order of Ar-He-treated foils > Ar-treated foils > O₂-treated foils. Similar trend was valid for the values of peeling of Ann2-foils.
- Regardless of the treatment time and power, two modes of fracture were observed macroscopically depending on the degree of improvement in adhesion: when the adhesion slightly improved, the samples fractured adhesively at the boundary layer between the PPQ foil and the adhesive layer, whereas they fractured cohesively in the PPQ foil itself, when the adhesion highly improved. SEM graphs of fracture

surfaces showed another type of fracture mode when the adhesion increased and that is a furrowed structure oriented transversely to the peeling direction.

- Finally, a future work is recommended to further explain the relationship between the annealing conditions and plasma treatment parameters on the adhesion of PPQ foils. It is also recommended in the future to do the chemical analysis of plasma treated PPQ foils e.g., FTIR and XPS to provide chemical/surface analysis results.

REFERENCES

1. Anagreh, N.; Dorn, L. *Int. J. Adhes. Adhes.* **2005**, *25*, 165.
2. Mahlberg, R.; Niemi, H. E.-M.; Denes, F.; Rowell, R. M. *Int. J. Adhes. Adhes.* **1998**, *18*, 283.
3. Badey, J. P.; Espuche, E.; Jugnet, Y.; Chabert, B.; Tran Minh Duc. *Int. J. Adhes. Adhes.* **1996**, *16*, 173.
4. Sanchis, R.; Fenollar, O.; García, D.; Sánchez, L.; Balart, R. *Int. J. Adhes. Adhes.* **2008**, *28*, 445.
5. Guedes Pinto, A. M.; Magalhães, A. G.; Gomes da Silva, F.; Monteiro Baptista, A.P. *J. Adhes. Adhes.* **2008**, *28*, 452.
6. Martínez-García, A.; Sánchez-Reche, A.; Gisbert-Soler, S.; Landete-Ruiz, M. D.; Torregrosa-Maciá, R.; Martín-Martínez, J. M. *Int. J. Adhes. Adhes.* **2008**, *28*, 38.
7. Zhu, X. L.; Liu, S. B.; Man, B. Y.; Xie, C. Q.; Chen, D. P.; Wang, D. Q.; Ye, T. C.; Liu, M. *Appl. Surf. Sci.* **2007**, *253*, 3122.
8. Romero-Sánchez, M. D.; Martín-Martínez, J. M. *Int. J. Adhes. Adhes.* **2006**, *26*, 345.
9. Stewart, R.; Goodship, V.; Guild, F.; Green, M.; Farrow, J. *Int. J. Adhes. Adhes.* **2005**, *25*, 93.
10. Żenkiewicz, M. *Int. J. Adhes. Adhes.* **2005**, *25*, 61.
11. Krump, H.; Hudec, I.; Luyt, A. S. *Int. J. Adhes. Adhes.* **2005**, *25*, 269.
12. Noeske, M.; Degenhardt, J.; Strudthoff, S.; Lommatzsch, U. *Int. J. Adhes. Adhes.* **2004**, *24*, 171.
13. Tanaka, K.; Kogoma, M. *Int. J. Adhes. Adhes.* **2003**, *23*, 515.
14. Tsuchiya, Y.; Akutu, K.; Iwata, A. *Prog. Org. Coat.* **1997**, *34*, 100.
15. Mühlhan, C.; Nowack, H. *Surf. Coat. Technol.* **1998**, *98*, 1107.
16. Kühn, G.; Weidner, St.; Decker, R.; Ghode, A.; Friedrich, J. *Surf. Coat. Technol.* **1999**, *116–119*, 796.
17. Nihlstrand, A.; Hjertberg, T.; Johansson, K. *Polymer* **1997**, *38*, 1557.
18. Abenojar, J.; Torregrosa-Coque, R.; Martínez, M. A.; Martín-Martínez, J. M. *Surf. Coat. Technol.* **2009**, *203*, 2173.
19. Cepeda-Jiménez, C. M.; Torregrosa-Maciá, R.; Martín-Martínez, J. M. *J. Adhes. Sci. Technol.* **2003**, *17*, 1145.
20. Liu, Y.; Xu, H.; Ge, L.; Wang, C.; Han, L.; Yu, H.; Qiu, Y. *J. Adhes. Sci. Technol.* **2007**, *21*, 663.
21. Liston, E. M.; Martinu, L.; Wertheimer, M. R. *J. Adhes. Sci. Technol.* **1993**, *7*, 1091.
22. Evieux, J.; Montois, P.; Nassiet, V.; Baziard, Y.; Petit, J. A.; Dedryvère, R. *J. Adhes.* **2004**, *80*, 263.

23. Landete-Ruiz, M. D.; Martín-Martínez, J. M. *Int. J. Adhes. Adhes.* **2005**, *25*, 139.
24. Romero-Sánchez, M. D.; Pastor-Blas, M. M.; Martín-Martínez, J. M. *Int. J. Adhes. Adhes.* **2005**, *25*, 19.
25. Romero-Sánchez, M. D.; Pastor-Blas, M. M.; Martín-Martínez, J. M.; Walzakb, M. J. *Int. J. Adhes. Adhes.* **2005**, *25*, 358.
26. Kruse, A.; Krüger, G.; Baalman, A.; Hennemann, O.-D. *J. Adhes. Sci. Technol.* **1995**, *9*, 1611.
27. Friedrich, J.; Unger, W.; Lippitz, A.; Koprinarov, I.; Ghode, A.; Geng, S. H.; Kühn, G. *Compos. Interfaces* **2003**, *10*, 139.
28. Encinas, N.; Díaz-Benito, B.; Abenojar, J.; Martínez, M. A. *Surf. Coat. Technol.* **2010**, *205*, 396.
29. Encinasa, N.; Dillinghamb, R. G.; Oakleyb, B. R.; Abenojara, J.; Martíneza M. A.; Pantoja, M. *J. Adhes.* **2012**, *88*, 321.
30. Abenojar, J.; Martínez, M. A.; Encinas, N.; Velasco, F. *Int. J. Adhes. Adhes.* **2013**, *44*, 1.
31. Encinas, N.; Abenojar, J.; Martínez, M. A. *Int. J. Adhes. Adhes.*, **2012**, *33*, 1.
32. Comyn, J.; Mascia, L.; Xiao, G.; Parker, B. M. *Int. J. Adhes. Adhes.* **1996**, *16*, 97.
33. Laurens, P.; Sadras, B.; Decobert, F.; Arefi-Khonsari, F.; Amouroux, J. *Int. J. Adhes. Adhes.* **1998**, *18*, 19.
34. Iqbal, H. M. S.; Bhowmik, S.; Benedictus, R. *Int. J. Adhes. Adhes.* **2010**, *30*, 418.
35. Anagreh, N.; Dorn, L.; Bilke-Krause, C. *Int. J. Adhes. Adhes.* **2008**, *28*, 16.
36. Kim, Y. J.; Jin, S. B.; Kim, S. I.; Han, J. G. *J. Adhes. Sci. Technol.* **2011**, *25*, 993.
37. Seidel, C.; Damm, C.; Muenstedt, H. *J. Adhes. Sci. Technol.* **2007**, *21*, 423.
38. Dorn, L.; Anagreh, N. *Kleben&dichten Adhäsion* **2000**, *44*, 30.
39. Rosenbauer, K. A.; Wilting, H.; Schramm, G. *GIT Fachz. Lab.* **1989**, *33*, 1113.