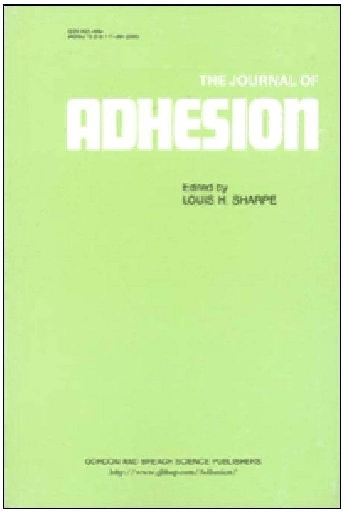
This article was downloaded by:
On: *22 January 2011*
Access details: *Access Details: Free Access*
Publisher *Taylor & Francis*
Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



The Journal of Adhesion

Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713453635

Surface modification of polyether ether ketone (peek) films for flexible printed circuit boards

C. Weiss[a]; H. Muenstedt[a]
[a] Institute of Polymer Materials, Department of Materials Science, University Erlangen-Nuernberg, Erlangen, Germany

Online publication date: 08 September 2010

To cite this Article Weiss, C. and Muenstedt, H.(2002) 'Surface modification of polyether ether ketone (peek) films for flexible printed circuit boards', The Journal of Adhesion, 78: 6, 507 — 519

To link to this Article: DOI: 10.1080/00218460213733

URL: http://dx.doi.org/10.1080/00218460213733

PLEASE SCROLL DOWN FOR ARTICLE

Full terms and conditions of use: http://www.informaworld.com/terms-and-conditions-of-access.pdf

This article may be used for research, teaching and private study purposes. Any substantial or systematic reproduction, re-distribution, re-selling, loan or sub-licensing, systematic supply or distribution in any form to anyone is expressly forbidden.

The publisher does not give any warranty express or implied or make any representation that the contents will be complete or accurate or up to date. The accuracy of any instructions, formulae and drug doses should be independently verified with primary sources. The publisher shall not be liable for any loss, actions, claims, proceedings, demand or costs or damages whatsoever or howsoever caused arising directly or indirectly in connection with or arising out of the use of this material.

The Journal of Adhesion, 78: 507–519, 2002
Copyright © 2002 Taylor & Francis
0021-8464/02 $12.00 +.00
DOI: 10.1080/00218460290010278

SURFACE MODIFICATION OF POLYETHER ETHER KETONE (PEEK) FILMS FOR FLEXIBLE PRINTED CIRCUIT BOARDS

C. Weiss
H. Muenstedt
Institute of Polymer Materials, Department of Materials Science,
University Erlangen-Nuernberg, Erlangen, Germany

The surface of polyether ether ketone (PEEK) films was modified using plasma treatment, corona, or surface etching to improve their adhesion with regard to glued copper foils and copper layers generated by physical vapor deposition.

After the pretreatments, surface chemical analysis was performed by X-ray photoelectron spectroscopy (XPS). The wetting behavior was qualitatively investigated by contact angle measurements. Surface topography was monitored by laser scanning microscopy (LSM). After coating, the adhesion strength of the copper layer was measured by a peel force test. Plasma treatment, corona discharge, or etching lead to a significant increase in adhesion. This increase is caused by a change in surface topography as well as by the incorporation of polar groups into the surface.

Keywords: Polyether ether ketone; PEEK; Metallization; Adhesive bonding; Physical vapor deposition; PVD; Plasma; Etching; Corona

INTRODUCTION

Polyether ether ketone (PEEK) is a high-temperature-resistant, semicrystalline, thermoplastic polymer. It is characterized by a high melting point (340°C), a high oxidative and thermal stability, and excellent mechanical properties. Moreover, it is intrinsically

Received 5 September 2001; in final form 19 December 2001.

We would like to thank J. Friedrich, C. Beisert, and C. Seidel for their assistance in many aspects of this work. This work was supported by the Deutsche Forschungsgemeinschaft (Sonderforschungsbereich 356).

Presented at the 24th Annual Meeting of The Adhesion Society, Inc., held at Williamsburg, Virginia, USA, 25–28 February 2001.

Address correspondence to H. Muenstedt, Institute of Polymer Materials, Department of Materials Science, University Erlangen-Nuernberg, Martensstrasse 7, D-91058 Erlangen, Germany. E-mail: polymer@ww.uni-erlangen.de

fire-resistant [1]. Its thermal properties make PEEK suitable for applications which require high heat resistance, such as automotive parts or solderable electronic components. In addition, its resistance to a wide range of chemicals is outstanding [2]. However, as a result of the chemical stability the adhesive properties of surfaces are poor. Therefore, fundamental research as well as application-oriented work was performed to improve the adhesion properties of PEEK.

As an example, the development of high-temperature-resistant substrates for flexible printed circuit boards is addressed. Up to now, most flexible printed circuit boards are based on polyimide (PI) [3, 4]. Compared with PEEK, the water absorption of PI is very high and the chemical resistance to alkalis is very poor. Furthermore, in contrast to PEEK, the widely used thermosetting PI cannot be processed by film extrusion from the melt.

Therefore, films made from PEEK would have great potential as a basic material for flexible printed circuit boards if the adherence of copper could be markedly improved. One way to achieve this goal is surface modification by different pretreatment procedures.

EXPERIMENTAL

Materials

The study was performed on polyether ether ketone films from PEEK 380 G (manufacturer: Victrex plc, UK) with a thickness of 50 μm. The adhesive used was a two-component epoxy resin system. It was cured at 120°C for 1 h at a pressure of 0.15 N/cm^2. Prior to the different surface pretreatments all samples were degreased by cleaning with acetone.

Surface Treatment and Metallization

The PEEK films were exposed to different pretreatments (oxygen plasma, corona, and surface etching). The pretreated surfaces were coated with copper by adhesive bonding with a copper foil or by physical vapor deposition (PVD).

Adhesive bonding was performed using a rolled copper foil (thickness 18 μm) with a definite surface topography (see Figure 1). The plasma treatments of the PEEK films and the metallization by PVD was realized using a cathodic sputtering unit (Cemecon, model CC800). The sputtering gases were high purity argon or argon-oxygen mixtures. Before admitting the gas the sputtering chamber was evacuated to 0.5×10^{-4} Pa. During the plasma treatment and the sputtering process a pressure of 1.8×10^{-5} Pa and a microwave power

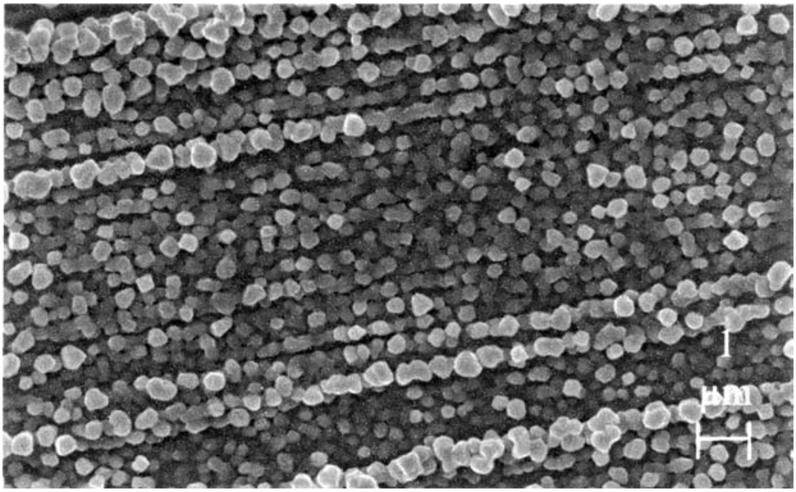


FIGURE 1 Surface topography of the rolled copper foil (SEM).

of 600 W were maintained. The plasma treatment was realized with a constant gas feed rate of 50 standard cubic centimeters per minute (sccm), the sputtering process with 250 sccm. By sputtering, a coating thickness of 3 μm was achieved. In order to measure the adhesion strength of the metallization by a peel force test, the coating thickness was increased up to 18 μm by an additional electrodeposition.

The corona treatment was performed using a commercial corona facility (Fetronic Feinmechanik/Elektronik GmbH, model CT 4/2″). The surface treatment was carried out over a period of 2 min at a level of 10 kV.

A chromic-sulphuric acid mixture was used to pretreat the PEEK surfaces by etching. The films were immersed at room temperature for a period of 60 s. The surfaces were then rinsed thoroughly with deionized water and dried in air.

Analytical Techniques

The adhesion strength of the coatings and the failure mode of the specimens were examined by a peel force test in accordance with DIN 60249. The peel tests were carried out using a tensile testing machine (Frank, model 81110 TM) equipped with a 1000 N force transducer.

Changes of the surface induced by the pretreatments were investigated as a function of the different pretreatment parameters. Before and after pretreatment the wetting behavior of the PEEK surface was determined. For this purpose a goniometer (Rame-Hart, Inc., model 100-00-230) with an optical protractor was used to determine advancing contact angles. The measurement was performed using the sessile drop technique with a volume of 2 μl (liquid: distilled water). Ten measurements per sample were made. Values given in this paper are averaged values of these measurements. The chemical analysis of the surface was performed using the Al K_α radiation of an X-ray photoelectron spectrometer (Physical Electronics, model PHI 5600ci). XPS analysis allows one to determine, on the one hand, the nature of the elements present on the surface and, on the other hand, the chemical environment of each element. Survey and high-resolution spectra were taken and the binding energies were referenced to the hydrocarbon peak at 284.5 eV [7]. The topography of the surfaces before and after treatment was characterized by compiling a non-contact laser-optical scan of the surface roughness using laser scanning microscopy (UBM, model Microfocus Expert). In each case a $2 \times 2\ \text{mm}^2$ surface was analyzed. Quantification was achieved by determining the arithmetical mean roughness value, R_a, in accordance with DIN 4768.

RESULTS AND DISCUSSION

Metallization by Adhesive Bonding

Figure 2 shows results of the peel force of a copper foil before and after different surface treatments. A significant increase in the peel force

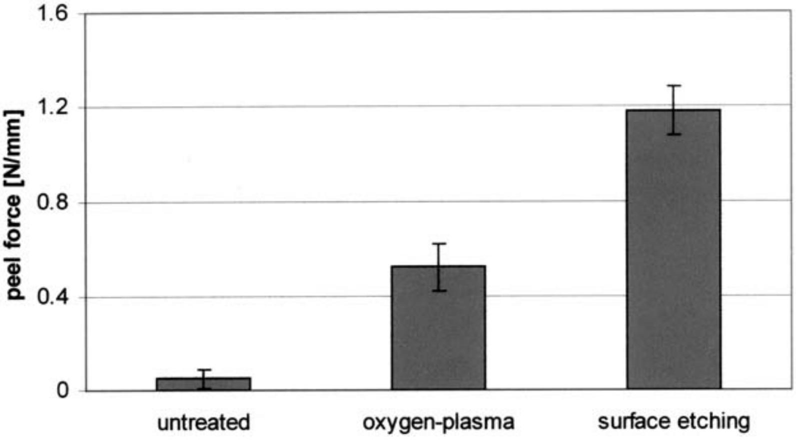


FIGURE 2 Peel force of the glued copper foil after various treatments (Substrate: PEEK film).

was observed after plasma treatment (oxygen-plasma) and surface etching (chromic sulphuric acid) as well. The failure mode changes from visually observed interfacial failure at the interface between the adhesive and the polymer for the untreated sample to an interfacial failure between adhesive and copper after treatment. The peel force of 0.6 N/mm which is demanded for metallized PI was just reached after the oxygen-plasma treatment but was significantly exceeded after surface etching.

On investigating the surface topography by laser scanning microscopy, a significant change in surface roughness was found (see Figure 3). After plasma treatment the polymer surface was smoothed. Therefore, the surface roughness decreased from $R_a = 0.13\ \mu m$ to $R_a = 0.10\ \mu m$. However, after etching the surface roughness increased

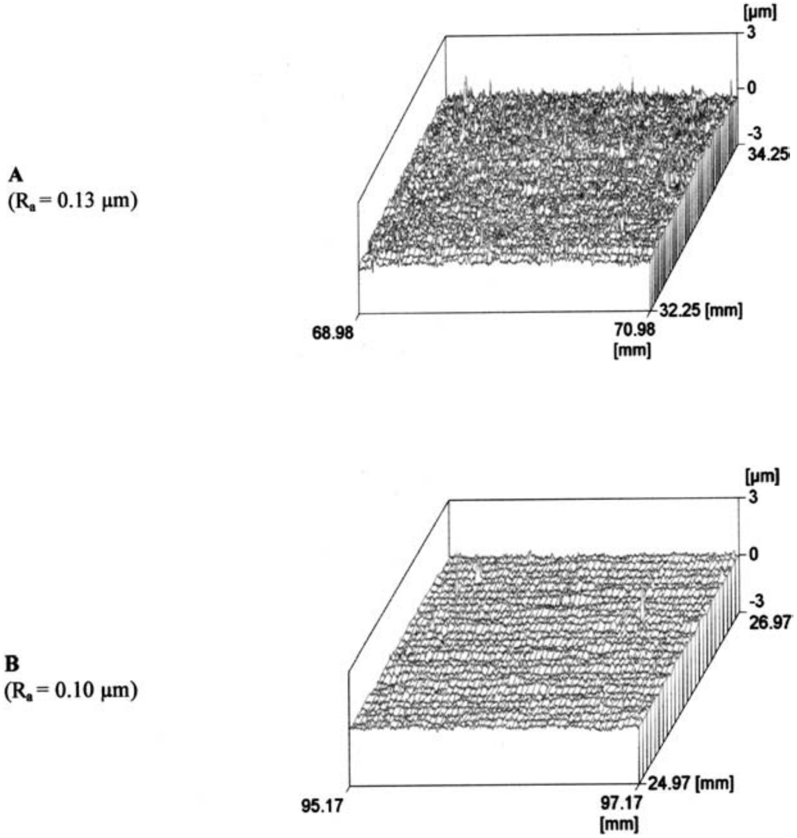


FIGURE 3 Surface topography of PEEK (laser scanning microscopy): untreated (A), oxygen-plasma (B), and etching with chromic sulphuric acid (C).

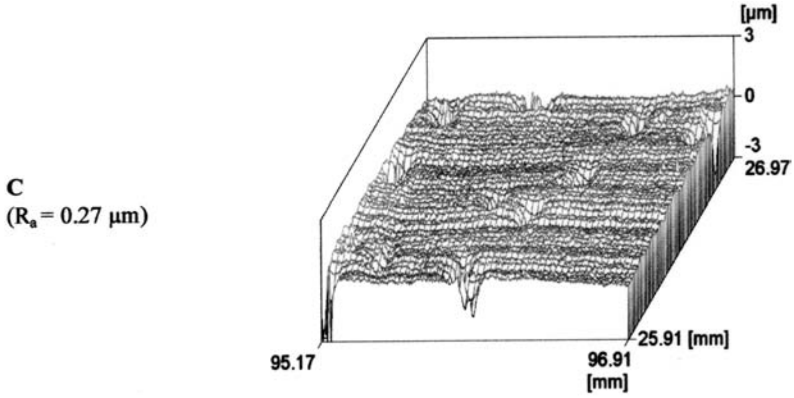


FIGURE 3 (*continued*).

obviously from $R_a = 0.13$ µm to $R_a = 0.27$ µm. This could be due to a partial removal of the amorphous areas of the polymer surface.

After etching or plasma treatment the wettability of the PEEK surface was improved (see Table 1). In comparison with the untreated surface, the contact angle decreased after surface etching by around 16% and after the plasma treatment by around 66%. This increase in water wettability is an indication of changes in surface chemistry caused by the pretreatment.

In the low-resolution XPS spectra (see Figure 4) differences between the untreated, plasma treated, and etched surfaces are obvious. From the measured carbon and oxygen concentration of the untreated PEEK surface, an O/C ratio of 0.16 follows, which is in good accordance with the stoichiometric value of the PEEK repeat unit. Surface etching raised the O/C ratio by 62% to 0.26; the plasma treatment increased the O/C ratio by 130% to 0.37.

This increase is caused by an incorporation of oxygen into the surface. Oxidized groups carrying a distinct polarity are formed during the pretreatment. Figure 5 shows the high-resolution C1s spectra of untreated PEEK. The spectrum of the untreated surface exhibits

TABLE 1 Influence of Various Treatments on Contact Angle, O/C Ratio, and Roughness

	Untreated	Etched	O_2-plasma
Contact angle [°]	84.4 ± 1.2	71.3 ± 1	28.2 ± 2.8
O/C ratio	0.16	0.26	0.37
Roughness R_a [µm]	0.13	0.27	0.10

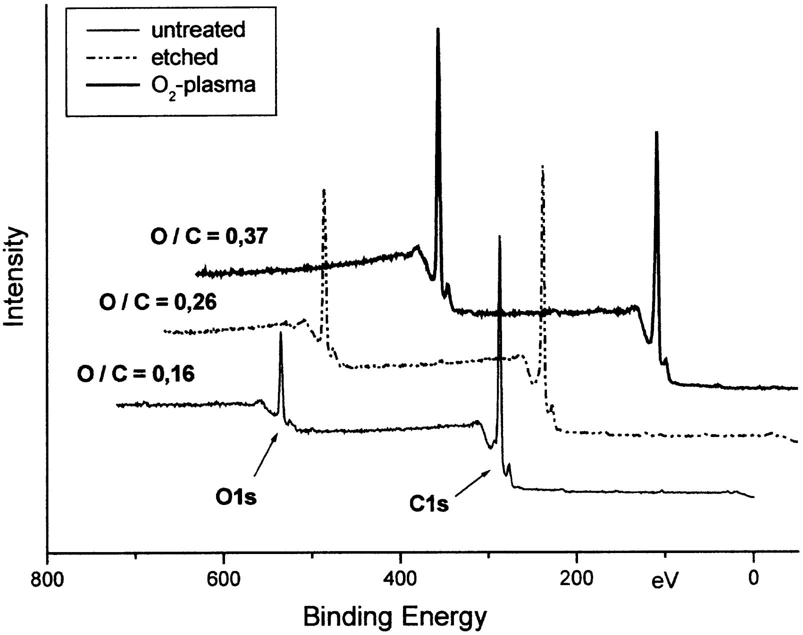


FIGURE 4 Low-resolution XPS spectra of PEEK after different pretreatments (spectra of etched and plasma-treated surfaces are shifted for clarity).

a high-intensity peak at 285.0 eV, which represents the aromatic carbons not bonded to oxygen atoms. The shoulder occuring at a higher binding energy of this peak is attributed to ether linkages at 286.0 eV and carbonyl bonds at 287.0 eV. The low-intensity peak at higher binding energy (291.0 eV) is a shake-up satellite due to a π-π^* transition. These binding energy values are in accordance with those reported in the literature [1, 5, 6].

For the etched sample, the high-resolution C1s spectra between 284.5 and 288.0 eV, (see Figure 6) and the plasma-treated sample between 284.5 eV and 290.0 eV (see Figure 7) show an increase of intensity. In the first case this could be due to an incorporation of alcohols or ethers [7–9]. In the case of plasma treatment this increase correlates with an incorporation of alcohols and ethers, as well as ketones and carboxyls [10–14].

Both pretreatments lead to an improvement of adhesion properties as Figure 2 demonstrates. Plasma treatment, as well as etching with chromic sulphuric acid, effects an incorporation of oxygen groups, which leads to an increase of secondary bonds (*e.g.*, Van der Waals forces) between the polymer surface and the adhesive. The surface

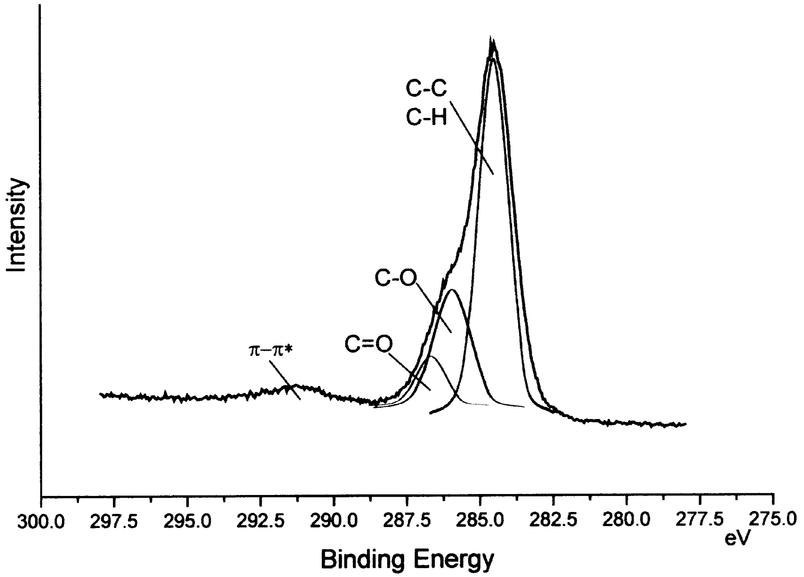


FIGURE 5 High-resolution XPS spectra (C_{1s}) of untreated PEEK.

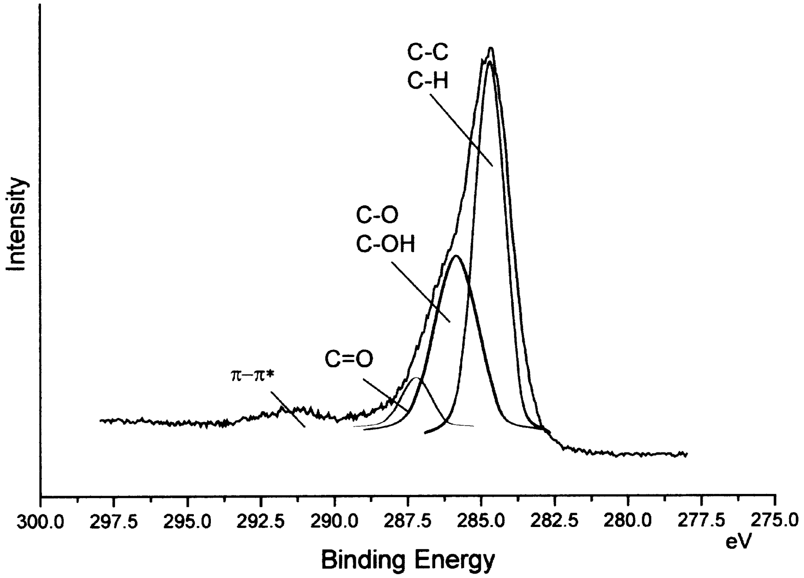


FIGURE 6 High-resolution XPS spectra (C_{1s}) of PEEK, etched with chromic-sulphuric acid over 60 s.

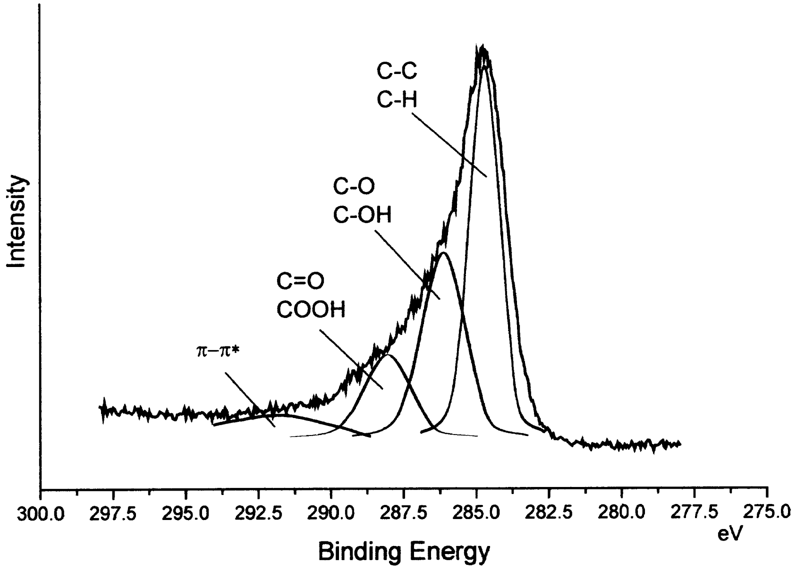


FIGURE 7 High-resolution XPS spectra (C_{1s}) of plasma-treated PEEK (oxygen plasma, 2 min).

topography after plasma treatment is quite different compared with the untreated sample. The surface after plasma treatment is smoother. However, etching with chromic sulphuric acid leads to an increase of surface roughness. Therefore, mechanical interlocking between the polymer and the adhesive becomes stronger.

Metallization by PVD

As an alternative to gluing copper foil to a PEEK film, the direct metallization by PVD was investigated. Figure 8 shows the results of a peel test. The peel force of the copper layer on an untreated PEEK surface was immeasurably small. The copper metallization already flaked off during the sample preparation. Corona treatment as well as argon plasma improved the adhesion properties significantly above the required level of 0.6 N/mm. After corona treatment a peel force of about 0.8 N/mm was measured. The effect of argon plasma treatment is even stronger. After the plasma treatment, the adhesion strength between the metal layer and PEEK is so high that a measurement of the peel force is not possible because a cohesive failure within the PEEK film occurs.

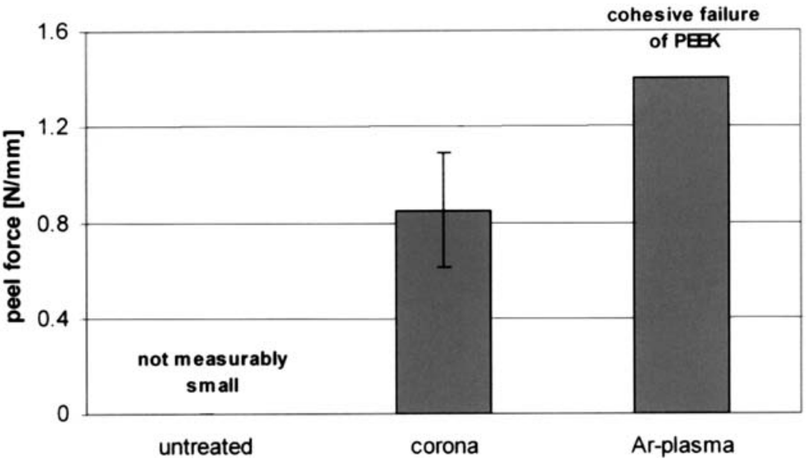


FIGURE 8 Peel force of copper layers obtained by PVD after various treatments (substrate: PEEK film).

After the pretreatment of the PEEK film, surface analysis was performed using XPS and contact angle measurements. Surface topography was analyzed by laser scanning microscopy. The results are summarized in Table 2.

After the corona treatment a change in surface topography was not observed. However, compared with the untreated surface the contact angle decreased by almost 30% and the O/C ratio increased by about 38% (see Figure 9). These results indicate an incorporation of oxygen groups into the PEEK surface. This change in chemical composition of the surface gives rise to the formation of different bonds between the substrate and the copper coating, which can result in dipole-dipole interactions or covalent bonds as the origin of an increase in the adhesion strength.

However, after argon plasma treatment an additional amount of oxygen in the surface was not detected, as Figure 9 and Table 2

TABLE 2 Influence of Various Treatments on Contact Angle, O/C Ratio, and Roughness

	Untreated	Corona	Ar-plasma
Contact angle [°]	84.4 ± 1.2	58.8 ± 2.8	47.5 ± 3.0
O/C ratio	0.16	0.22	0.15
Roughness R_a [μm]	0.13	0.13	0.10

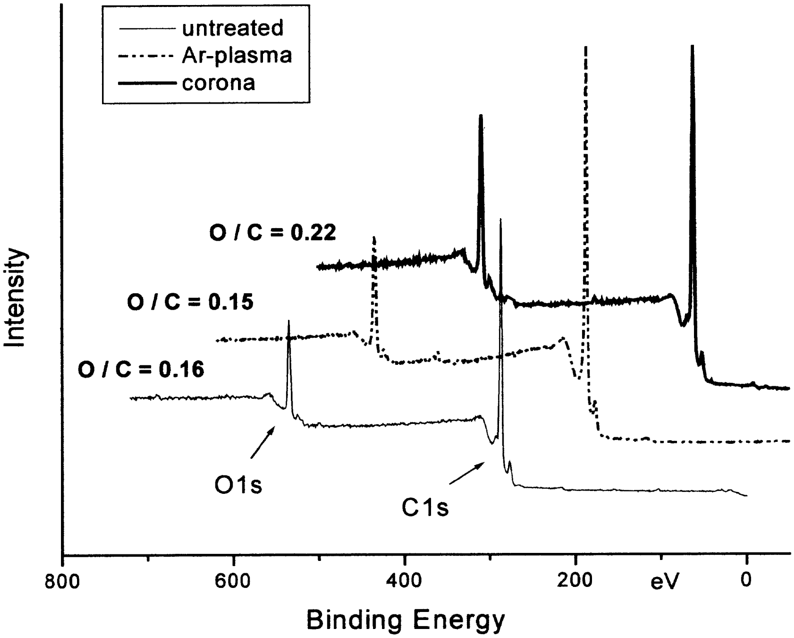


FIGURE 9 Low-resolution XPS spectra of PEEK after different pretreatments (spectra of corona and plasma-treated surfaces are shifted for clarity).

demonstrate. The O/C ratio did not change within the accuracy of the measurement. Changes in surface topography are comparable with the effects caused by oxygen plasma. After argon plasma treatment the surface was smoothed; therefore, the surface roughness decreased from $R_a = 0.13$ μm to $R_a = 0.10$ μm. The contact angle decreased by almost 44% to 47.5°. This has to be explained by surface effects not due to the incorporation of elements, such as oxygen or nitrogen. The high-resolution XPS spectra of carbon (see Figure 10) gives a hint as to the mechanism underlying the argon plasma treatment. The high-resolution C1s spectrum of the untreated surface shows a shake-up satellite peak at 291.9 eV. This peak can be related to the presence of $\pi \rightarrow \pi^*$ transitions arising from electrons in the aromatic ring [14, 15]. Compared with the untreated PEEK surface, the intensity of the $\pi \rightarrow \pi^*$ shake-up is significantly reduced after the argon plasma treatment. This could be due to a ring-opening reaction by cleavage of the aromatic structure. A similar reaction has been reported after surface treatment of polystyrene by argon plasma [10]. Because of this reaction the presence of reactive functional groups (radicals) is possible. These functionalities can lead to the formation of different bonds

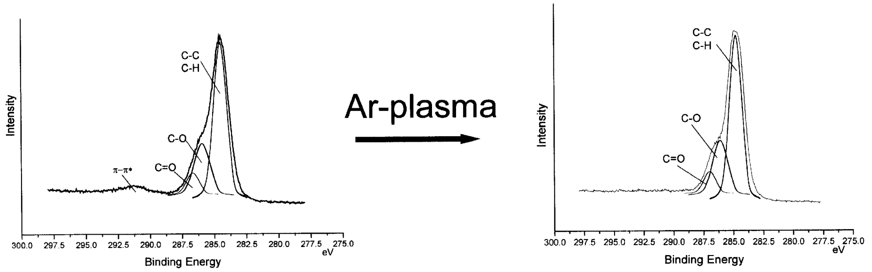


FIGURE 10 High-resolution XPS spectra (C_{1s}) of PEEK before (left) and after Ar-plasma treatment (right).

between the copper atoms and the PEEK surface (ionic bonds, covalent bonds) and therefore to an increase of the peel force.

CONCLUSIONS

Due to the high chemical resistance of PEEK, a peel strength of a copper layer sufficient for application cannot be achieved without surface treatment.

By different pretreatments (plasma treatment, corona discharge, and surface etching) surface energy and wettability of PEEK can be significantly enhanced. Therefore, these methods lead to an improvement in adhesion properties, which are good enough for matching the requirements of the particular industry.

All pretreatments result in a chemical functionalization of the PEEK surface. Etching and corona discharge, as well as oxygen plasma treatment, lead to incorporation of oxygen groups, whereas argon plasma only generates radicals on the surface. These changes in the chemical composition of the surface are the reason for formation of different bonds (*i.e.*, secondary bonds, covalent bonds, etc.) between the polymer molecules and the copper atoms.

Topographical analysis reveals differences in the surface changes brought about by the surface treatments applied. Compared with the untreated sample, corona does not change the surface roughness significantly, whereas oxygen plasma and argon plasma treatment lead to a decrease in surface roughness. This removal of polymer material from the surface has the effect of cleaning, known as plasma etching. However, etching with chromic sulphuric acid causes an increase of surface roughness which may be due to the weaker chemical resistance of the amorphous regions of the PEEK. Therefore, mechanical interlocking between polymer and adhesive becomes an effective factor for the increase in peel strength in addition to chemically-induced changes in polarity.

REFERENCES

[1] D. J. Pawson, A. P. Ameen, A. P. Short, P. Denison, & F. R. Jones, *Surf. Interface Anal.*, **18**, 13–22 (1992).

[2] T. E. Attwood, P. C. Dawson, J. L. Freeman, L. R. J. Hoy, J. B. Rose, & P. A. Staniland, *Polymer*, **22**, 1096–1103 (1981).

[3] K. Gilleo, *Handbook of flexible circuits.* New York: Van Nostrand Reinhold (1992).

[4] C. Weiß & H. Münstedt, *Proceedings of the 4th International Congress Molded Interconnect Devices*, Erlangen-Germany (2000), pp. 273–283.

[5] L. J. Matienzo & F. D. Egitto, *Polym. Degrad. and Stab.*, **35**, 181–192 (1992).

[6] G. K. A. Kodokian & A. J. Kinloch, *J. Mater. Sci. Lett.*, **7**, 625–627 (1988).

[7] W. J. Brennan, W. J. Feast, H. S. Munro, & S. A. Walker, *Polymer*, **32**, 1527–1530 (1991).

[8] Perkin Elmer Corporation, *Handbook of X-ray photoelectron spectroscopy*, Eden Prairie, MN: Company Edition (1997).

[9] F. Garbassi, M. Morra, & E. Occhiello, *Polymer surfaces.* New York: John Wiley & Sons (1994).

[10] L. J. Gerenser, *J. Adhes. Sci. Technol.*, **7**(10), 1019–1040 (1993).

[11] C. Jama, O. Dessaux, P. Goudmand, L. Gengembre, & J. Grimblot, *Surf. Interface Anal.*, **18**, 751–756 (1992).

[12] A. Baalmann, K. D. Vissing, E. Born, & A. Gross, *J. Adhesion*, **46**, 57–66 (1994).

[13] J. Comyn, L. Mascia, & G. Xiao, *Int. J. Adhes. Adhes.*, **16**, 97–104 (1996).

[14] S. W. Ha, R. Hauert, K. H. Ernst, & E. Wintermantel, *Surf. Coat. Technol.*, **96**, 293–299 (1997).

[15] D. T. Clark & A. Dilks, *J. Polym. Sci., Part A: Polym. Chem.*, **15**, 15–30 (1977).