Macromol. Symp. ***126,*** *267–281 (1997)*

IMPROVEMENT OF ADHESIVE BONDING OF THERMOPLASTIC POLYMERS BY DIFFERENT SURFACE TREATMENTS

Thomas Zeiler*, Petra Pfeffer, Marcus Kürner, Helmut Münstedt

Institute of Polymer Materials, Department of Material Science, University of Erlangen-Nürnberg
D-91058 Erlangen, Martensstr. 7, Germany

Abstract: Injection moulded samples of six species of thermoplastic polymers were exposed to different surface treatments and successively glued together to form single lap shear joints. Lap shear strength and failure mode of these specimens were examined. The surfaces obtained after treatment were characterized by electron spectroscopy for chemical analysis, contact angle measurements and atomic force microscopy.

INTRODUCTION

Polymers are applied in fields where interactions of their surfaces with other materials play an important role. Special surface properties with regard to chemical composition, hydrophilicity, roughness and cristallinity are required for the success of these applications. Polymeric materials often do not possess all the requested properties. However, their advantages with respect to chemical and physical behaviour, processability, and price are so obvious that surface modifications which transform these materials into high valuable finished products become more and more important in the plastics industry. In recent years much effort has been undertaken to develop surface treatments in order to alter chemical and physical properties of polymer surfaces without significant changes of the bulk properties. Common techniques are etching, corona discharge, flame or low pressure plasma treatments. Excimer laser irradiation is a method which is nearly

CCC 1022-1360/98/$ 10.00

unknown up to now in the field of improving the bonding behaviour of thermoplastic materials because of its comparatively recent availability. Treatments like corona, plasma, and laser have advantages in relation to the former widely used chemical etching, because there are fewer problems with respect to environmental pollution and industrial safety (Refs. 1-2).

Aim of this investigation is to make a comparison between the new method of excimer laser treatment and the well-known and established plasma treatment with regard to their effectiveness to improve adhesive bonding. In order to be able to draw conclusions which are not influenced by secondary effects like sample manufacturing or geometry of the joints all experiments and characterizations have been performed in the same manner with identical materials.

In literature plasma treatment is mostly investigated for materials like PE and PP. Only a small number of papers describes investigations which deal with plasma treatments of other polymeric materials which are difficult to glue. A good review which summarizes plasma treatment activities is given by Liston et al. (Ref. 3). In the case of laser treatment half a dozen papers (Refs. 4-9) address the question if laser treatment can be used to improve adhesive bonding. To obtain a deeper understanding of surface treatments and their relevance for the group of high performance polymers measurements were performed on some high temperature resistant polymers. Beside the practical problem how to improve the bonding strength of glued polymers the answers to questions about the physical and chemical state of the treated surfaces and the bonding mechanism are addressed in this paper.

EXPERIMENTAL

Laser treatments were performed by a pulsed XeCl laser (Siemens XP 2020) with a wavelength of 308 nm and a typical pulse duration of 20 ns. Ten pulses with frequency a of 1 Hz were applied. For plasma applications a parallel plate reactor (Himont PS 2055, volume 1.52 m^3) with an excitation frequency of 13.56 MHz under oxygen at a pressure of 60 Pa was used.

Water contact angles were measured by the sessile drop method. The ESCA spectra were obtained by a Perkin Elmer PHI 5600CI using an Al K-α electrode without a monochromator. The angle between the surface and the x-ray-radiation was 45° in all cases. The surface topography was examined by atomic force microscopy (Nanoscope II).

The materials examined were the semicrystalline polymers Polyetherketoneetherketoneketone (PEKEKK, Ultrapek A 2000 of BASF AG), Polyetheretherketone (PEEK, Victrex 450G of Victrex Ltd.), Polyphenylenesulfide (PPS, Fortron 6061B4 of Hoechst AG), Polybutyleneterephthalate (PBT Ultradur B 4500 of BASF AG) and the amorphous polymers Polyetherimide (PEI, Ultem 1000 of General Electric Ltd.) and Polyethersulfone (PES, Ultrason E 3010 of BASF AG). Injection moulded tensile rods according to DIN 53455 No.3 were used. The bonding of the single lap shear joints was carried out using an epoxy resin (UHU endfest 3000, UHU Company). The hardening of the two component adhesive took place in an oven at 100°C for one hour. Measurements of the shear strength of the single lap shear joints with an overlap of 7 mm were performed at room temperature and a speed of 5mm/min.

RESULTS

Lap shear strength and failure mode

A significant increase of lap shear strength of the semicrystalline polymers can be observed after low pressure plasma and excimer laser treatment, as well. The increase of lap shear strength above a factor of 4 is often limited by a change of failure from the adhesive mode of the boundary layer to the cohesive mode of the bulk material, which limits, of course, any further increase of lap shear

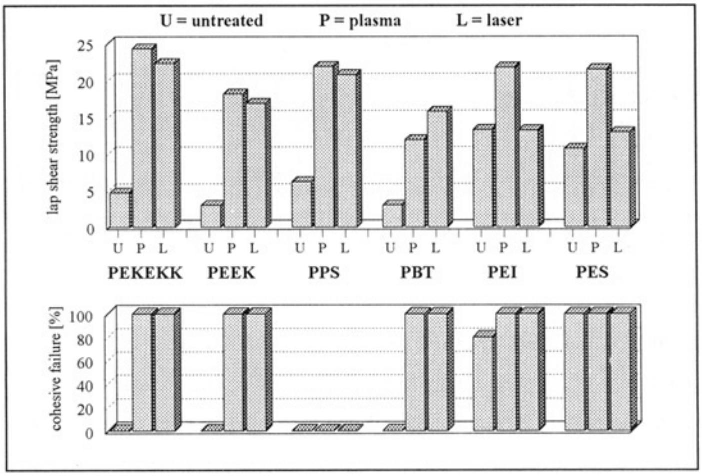

Fig. 1: Lap shear strength and failure mode of plasma and laser treated polymers (optimized parameters)

strength (Fig. 1). The appearance of the cohesive failure mode is caused by stress concentrations at the ends of the overlap. The value of these stresses is about a factor of 4 higher than the average stress (Refs. 10-12). In the case of the amorphous polymers PEI and PES cohesive failure is the dominating mode even without pretreatment. Therefore, a significant increase of lap shear strength can only be expected after a successive treatment, if there is a corresponding change in the bulk properties of the polymer. Using oxygen plasma the lap shear strengths of PEI and PES increase from 10 MPa to about 20 MPa without a change in failure mode. This finding may have its origin in a mechanical strengthening of the surface layer. Gerenser (Ref. 13) made similar observations investigating PE and PET. Excimer laser treated surfaces show nearly the same behaviour as untreated surfaces.

The discussion of the influence of treatment parameters on adhesion is difficult, because material failure complicates the interpretation. In the case of PPS which does not exhibit cohesive failure a discussion is easier. Fig. 2 and Fig. 3 show that in the case of PPS a growing plasma power and an increasing plasma treatment time lead to better adhesion. For most of the other examined polymers an increase of lap shear strength is observed until cohesive failure occurs. A similar behaviour can be observed for PPS samples irradiated with different laser energies (Fig. 4). It can clearly be seen from all the figures that the dependences are not linear but that the lap shear strength approaches a plateau value with increasing energy and treatment time.

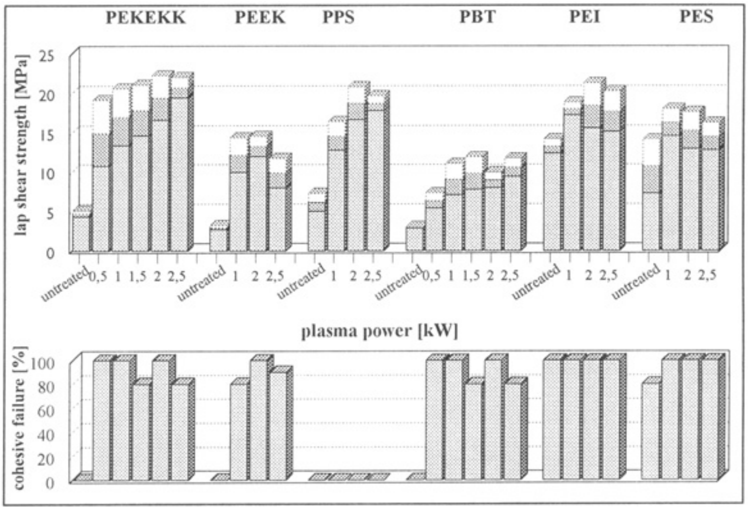

Fig. 2: Lap shear strength of plasma treated (3 min) polymers as function of plasma power

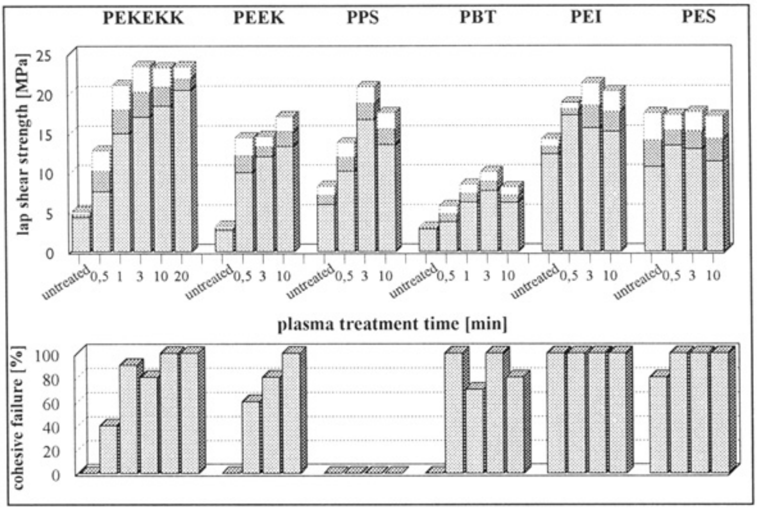

Fig. 3: Lap shear strength of plasma treated (2000 W) polymers as a function of plasma treatment time

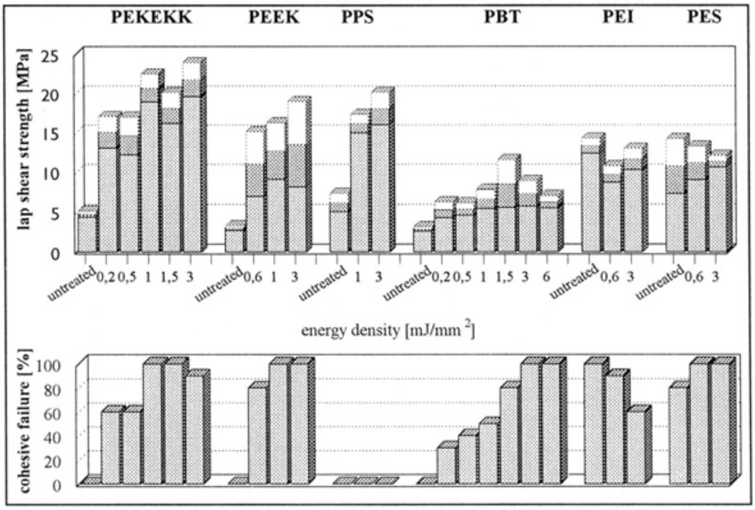

Fig. 4: Lap shear strength of laser treated (10 pulses, 1 Hz) polymers as a function of energy density

Stability

Another important property with respect to applications is the stability of the surface treatments. Therefore, treated samples were exposed to normal laboratory conditions, then glued and tested. Because the failure mode does not change with increasing ageing time (Fig. 5), no significant change of lap shear strength can be expected if cohesive failure dominates. In the case of PPS where no cohesive failure occurs the lap shear strength of plasma treated samples leads to a decrease of lap shear strength from 17 MPa to 8 MPa during 30 days. In contrast, laser treated

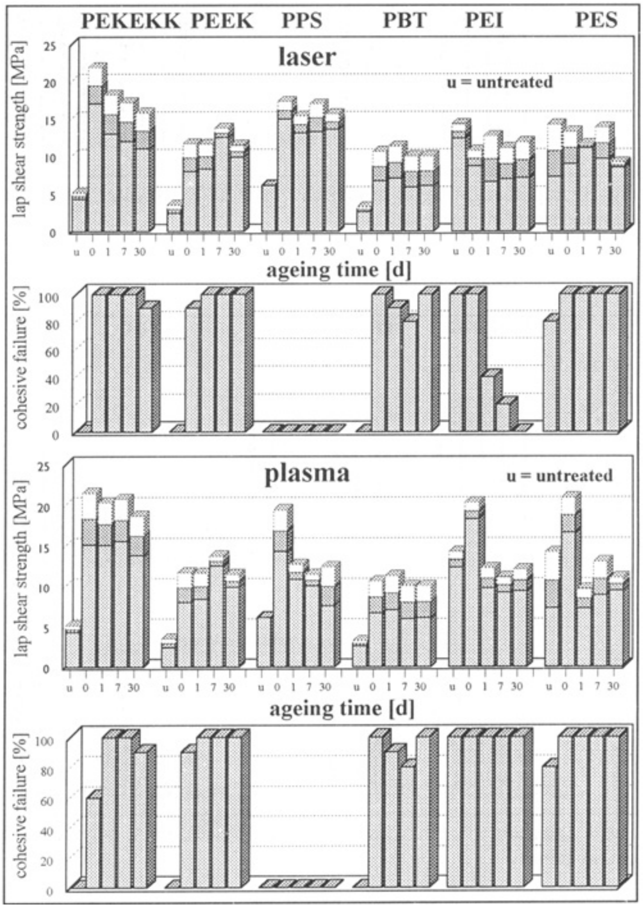

Fig. 5: Lap shear strength and failure mode of laser (1 mJ/mm^2, 1 Hz, 10 pulses) and plasma (2000 W, 3 min) treated polymers as a function of ageing time

PPS surfaces show no influence of ageing time on lap shear strength.

In general for all semicrystalline polymers the values of lap shear strengths obtained after 30 days of ageing before bonding are still significantly higher than those of untreated polymers.

The two amorphous polymers show a different behaviour. For the plasma treated materials a sharp decrease of the lap shear strength compared to values of treated materials after one day of ageing is found. The lap shear strength of laser treated PES is not changed if the surfaces were aged before bonding. In contrast, PEI shows a decrease of adhesion corresponding to a change in failure behaviour from cohesive to adhesive failure in the boundary layer.

Wetting behaviour

The wetting properties of the laser and plasma treated polymers are quite different. After an oxygen plasma treatment of three minutes the water contact angles decrease significantly from about 80° to values between 10° and 30° (Table 1). In the case of laser treatment the contact angle remains nearly unchanged for PBT and PES. All other polymers show contact angles which lie significantly above those of untreated specimens.

Table 1: Comparison of the wetting behaviour after laser (1mJ/mm^2, 10 pulses, 1Hz) and plasma (2000 W, 3 min) treatment

contact angle °						
material	PEKEKK	PEEK	PPS	PBT	PEI	PES
untreated	78	79	78	79	73	80
laser	112	129	166	73	122	88
laser + cleaning with ethanol	48	58	79	47	49	61
laser + 1 month ageing	114	130	139	77	122	90
laser, cleaning + 1 month ageing	63	78	77	74	65	70
plasma	12	12	27	20	19	12
plasma + 1 month ageing	38	36	40	28	45	28

After removing a dark carbon like layer from the surface of the treated polymers by using ethanol as a solvent contact angles below those of untreated surfaces can be detected. An exception is observed for PPS which shows an unchanged angle after cleaning indicating that polar groups have not been created by the laser.

Ageing of the plasma treated surfaces leads to an increase of contact angles and therefore the wetting behaviour becomes poorer. Laser treated surfaces do not show any significant change of wetting behaviour within a month. If the surface layer is removed by using ethanol, ageing can be observed, however, in a similar way as after plasma treatment. The wetting behaviour of plasma treated surfaces is significantly better than that of untreated polymers even after 30 days of ageing. After 30 days of ageing most of the laser treated and cleaned samples show higher contact angles than direct after treatment, but they are still lower than those of the untreated specimens.

From Fig. 6 which shows the contact angle as a function of ageing time for different plasma treated polymers it is obvious that the ageing is dominated by two processes of different time dependence: A fast increase of contact angles within one day and a slow increase within the time period between one day and one month. The second process between one day and one month is particularly pronounced in the case of the amorphous products PEI and PES.

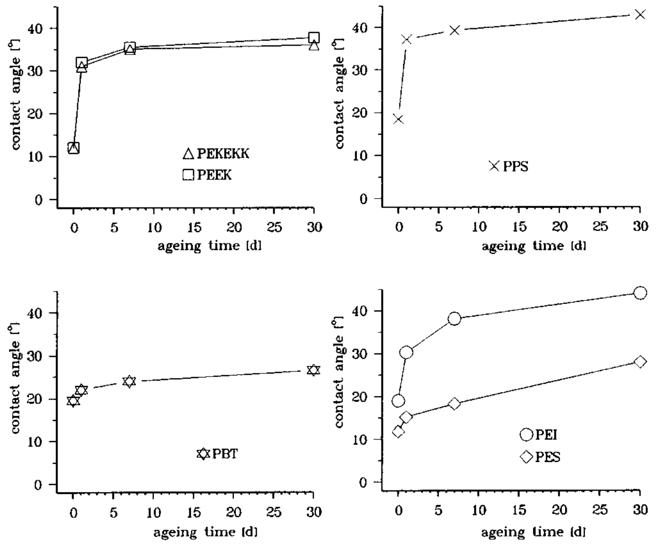

Fig. 6: Contact angle of plasma treated (2000 W,3 min) polymers as a function of ageing at room temperature

In order to get more insight into the mechanism of ageing, contact angles as a function of the ageing temperature were measured. Fig. 7 shows that higher temperatures during ageing accelerate the growth of the contact angles. Within one hour at temperatures above the glass transition temperature (215°C for PEI and 225°C for PES) the contact angles of amorphous polymers increase up to the values of the untreated surfaces. The semicrystalline specimens also show a sharp increase of contact angles during ageing under higher temperatures, but the crystallinity seems to retard the ageing.

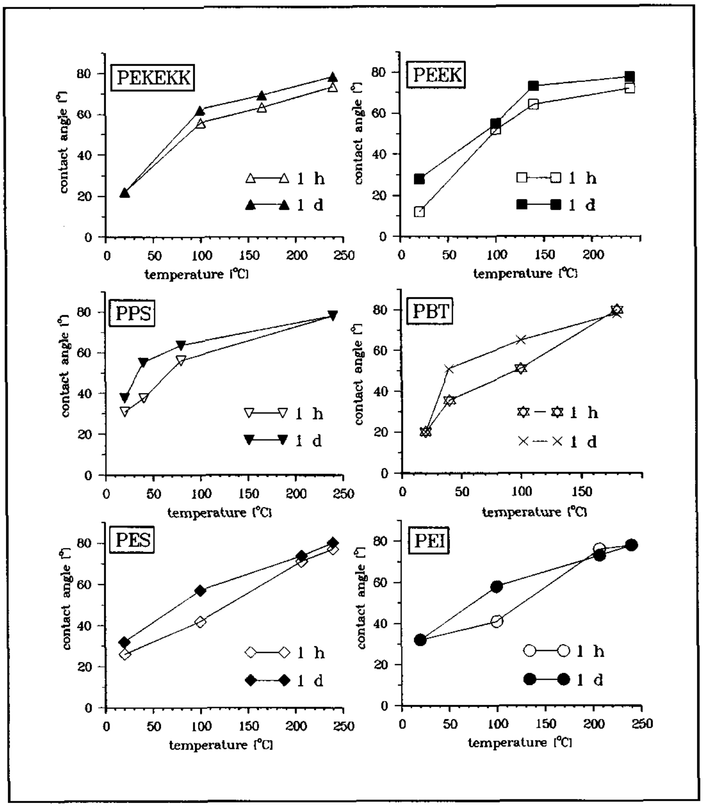

Fig. 7: Contact angles of plasma treated (2000 W, 3 min) polymers as a function of the ageing temperature for ageing times of 1 h and 1 d, respectively

The C1s-spectra of all plasma treated polymers qualitatively show the same result. The insertion of oxygen into the surface increases the O/C ratio (Table. 2) and broadens the C1-spectra (Fig. 8) in the range of higher binding energies. The broadening of the C1s-spectra is caused by oxygen containing polar groups like alcohol, carbonyl, carboxyl, carbonate, and peroxide.

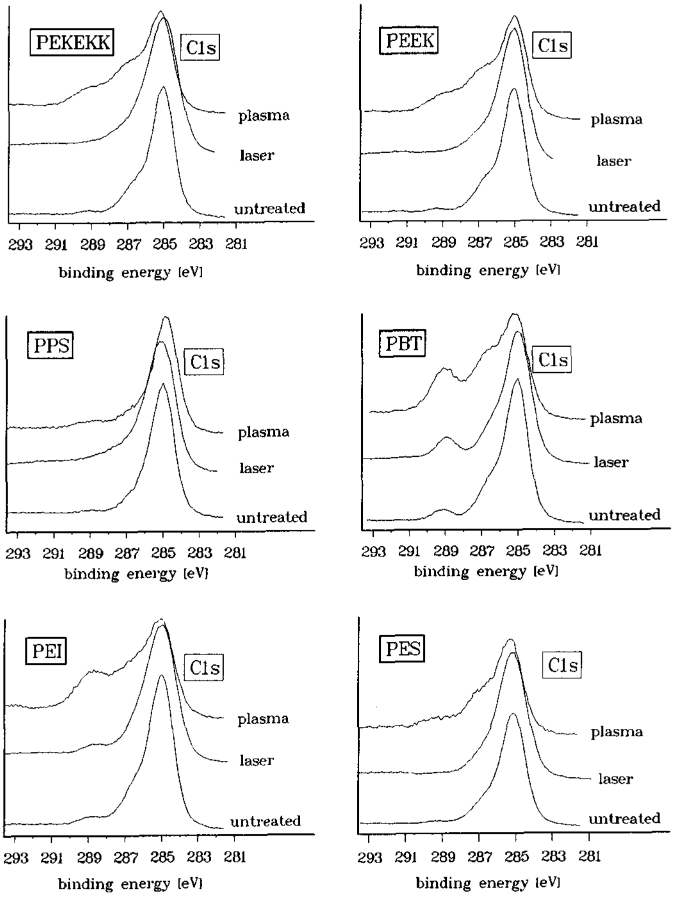

Fig. 8: C1s-spectra of laser (1 mJ/mm^2, 10 pulses, 1 Hz, cleaned with ethanol) and plasma (2000 W, 3 min) treated polymers

Table 2: O/C ratios of laser (1 mJ/mm^2, 10 pulses, 1 Hz) and plasma (2000 W, 3 min) treated polymers

material	PEKEKK	PEEK	PPS	PBT	PEI	PES
untreated	0.15	0.16	0.15	0.25	0.14	0.23
laser	0.04	0.03	0.04	0.14	0.05	0.06
laser + cleaning with ethanol	0.16	0.13	0.09	0.30	0.18	0.21
plasma	0.56	0.53	0.38	0.62	0.57	0.60
plasma + 1month ageing	0.42	0.42	0.30	0.46	0.33	0.45

Laser treated surfaces give a much smaller O/C ratio than untreated polymers (Table 2). Their C1s-spectra show one peak, only, which belongs to C-C and C-H bonds. After removing the carbon like layer functional groups can also be detected (see e.g. PBT in Fig. 8), which are normally hidden under the layer of ablated material.

In the case of plasma treated polymers it becomes obvious from table 2 that after 30 days the oxygen content of the surface is smaller. Ageing leads to a decrease of oxygen indicating the disappearence of polar groups from the surface.

The S2p spectrum of PPS in Fig. 9 demonstrates that the plasma treatment leads to an oxidation of sulfur to sulfone groups, which have a binding energy of 169 eV (Ref. 14). This result throws some light on the finding that laser and plasma treatments enhance the lap shear strength of PPS (Fig. 2-4) without changing the O/C ratios as much as for the other polymers (Table 2).

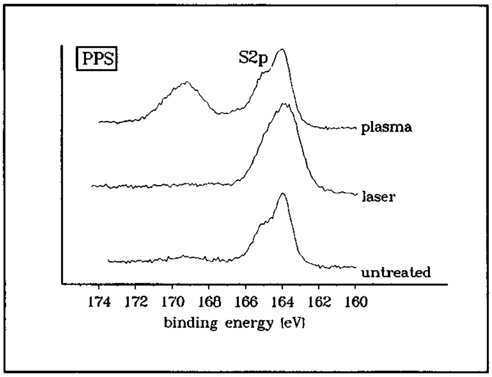

Fig. 9: S2p spectra of laser (1mJ/mm^2, 10 pulses, 1 Hz, cleaned with ethanol) and plasma (2000 W, 3 min) treated PPS

Topography

Investigations of untreated polymer specimens by the atomic force microscope show a smooth surface interrupted by grooves caused by the injection mould (Fig. 10). After laser irradiation one obtains a similar picture without any structure. Comparable results have been obtained from scanning electron micrographs. After cleaning the surface with ethanol, however, a rough surface with a lot of hillocks can be seen (Fig. 11). The peak to valley height varies from several hundred nanometers in the case of untreated polymers to some micrometers after laser treatment. In some cases a regular structure with waves perpendicular to the melt flow during injection moulding can

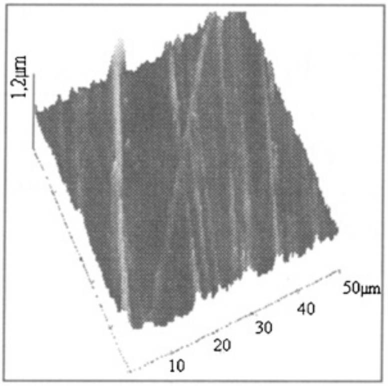

Fig. 10: Atomic force micrograph of untreated PEI

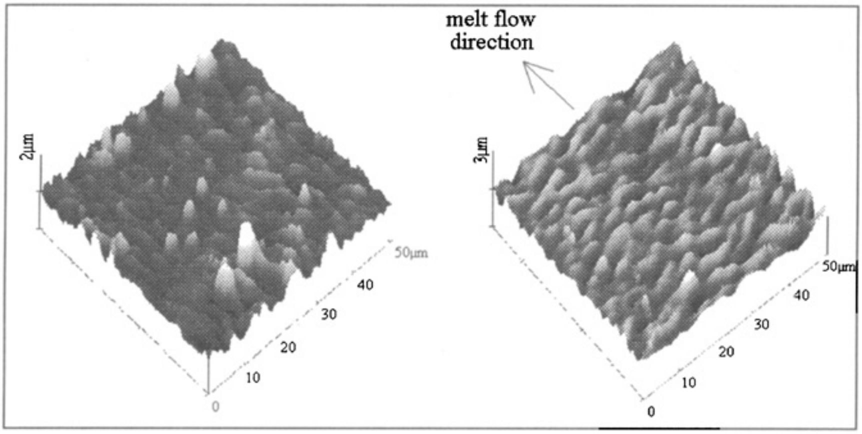

Fig. 11: Atomic force micrographs of laser treated (1mJ/mm^2, 10 pulses, 1 Hz) PEEK (left) and PEI (right) after cleaning

be detected (see PEI in Fig. 11). Bahners (Ref. 15) has found similar effects for injection moulded PET. Plasma treated surfaces (Fig. 12) show a rougher surface than untreated surfaces, but the irregular structure is less pronounced than after laser treatment (Fig. 11).

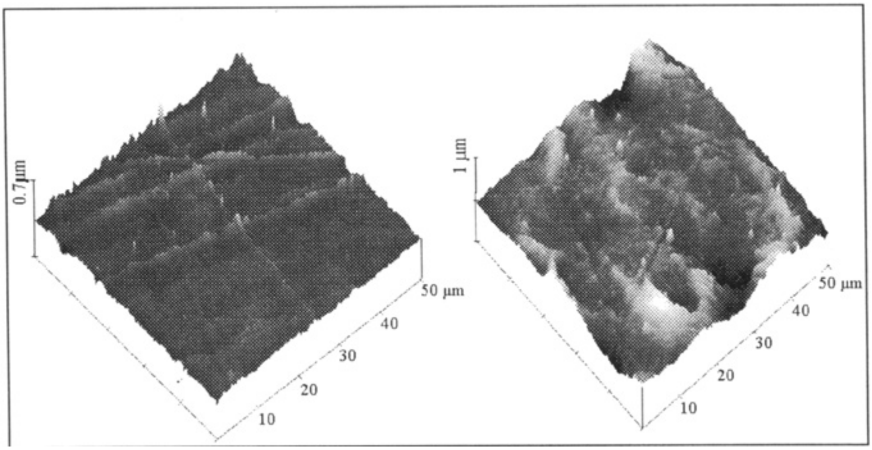

Fig. 12: Atomic force micrographs of plasma treated (2000 W, 3 min) PEI (left) and PEEK (right)

DISCUSSION

The improvement of adhesion by plasma treatment can be related to two changes of the material. The inserted oxygen reacts with the polymer and forms polar groups which have two effects. Firstly, they reduce the surface tension which results in a better wetting of the surface by the adhesive. Secondly, the bonding of the adhesive to the polymer molecules will be enhanced.
The second change, namely the increase in surface roughness has two effects, too. Firstly, the larger surface area offers more molecular sites for interactions between adherent and adhesive. Secondly, mechanical interlocking between adhesive and the sample surface becomes stronger.

Laser treated polymers show a similar improvement of adhesive bonding as plasma treated materials. The existence of chemical bonding between surface and adhesive in spite of the presence of a carbon layer can be explained by the absorption of the carbon by the adhesive. Then the surface is able to interact with the adhesive in a similar way as in the case of plasma treatment.
The more pronounced microroughness compared with the plasma treatment enhances the effects

of surface enlargement and mechanical interlocking.

The phenomena effecting ageing can be related to the driving force of the surface of the material to get its initial hydrophobic state restored. A mechanism which leads to poorer adhesion is the rotation of functional groups around the axis of the polymer molecule moving from the surface into the bulk. This leads to a reduction in surface energy and to a hydrophobic recovery. Another possibility to decrease surface energy is the diffusion of functionalized surface molecules into the bulk material. This can happen if the mobility of these molecules is great enough.

ESCA spectra and contact angle measurements support these models of hydrophobic recovery. Recent investigations by Occhiello et al. (Refs. 16-17) using the oxygen isotope, ^{18}O as plasma gas prove that ^{18}O functionalized molecules move into the bulk material.

Because mobility is necessary for diffusion and reorientation as well, the surface modification of polymers with a glass temperature distinctly higher than the ageing temperature is relatively stable with respect to ageing (Fig. 6). Temperatures near the glass transition accelerate hydrophobic recovery (Fig. 7).

CONCLUSION

Plasma treatment and UV-laser irradiation have shown to be able to improve lap shear strength of some engineering plastics by a value up to 4. Reasons for improved adhesion are mechanical and chemical surface modifications. Using an excimer laser, the microroughness of the polymer surface is more pronounced than after plasma treatment and therefore mechanical adhesion plays a greater role using this method. In the case of plasma treatment chemical modifications are dominant. Ageing of plasma treated polymers is caused by hydrophobic recovery. Laser treatment produces a carbon layer on the surface which is absorbed by the adhesive. Below this carbon layer polar groups similar to those after plasma treatment are found. Ageing leads to a decrease of polarity.

REFERENCES

(1) G. Liebel, *Dünne Schichten*, No. 1, 36 (1991)
(2) E.M. Liston, *NATO ASI Series E* **220**, 223 (1993)

(3) E.M. Liston, L. Martinu, M.R. Wertheimer in *"Plasma Surface Modification of Polymers"*, M. Strobel, C. Lyons, K.L. Mittal (Ed.), VSP Netherlands 1994, p. 3

(4) A. Buchman, H. Dodiuk, M. Rotal, J. Zahavi, *Int. J. Adhesion Adhesives* **11**, 144 (1991)

(5) J. Breuer, S. Metev, G. Sepold, O.D. Hennemann, H. Kollek, G. Krüger, *Appl. Surf. Sci.* **46**, 336 (1990)

(6) J. Breuer, S. Metev, *Laser & Optoelectronic* **28**, No.1, 48 (1996)

(7) R. Bütje, L. Dorn, S. Hohmann, W. Wahono, *Laser & Optoelectronic* **21**, No. 6, 62 (1989)

(8) K.A. Pike, *Chemtracts Makromol. Chem.* **2**, 42 (1991)

(9) D. J. Doyle, *IVALEO Laser Materials Processing*, Oct. 1992, Bellingham, 260 (1993)

(10) O. Hahn, B. Wender, *Forschungsberichte des Landes Nordrhein-Westfalen* Nr. 3187, Westdeutscher Verlag, Opladen 1984

(11) M. Goland, E. Reissner, *J. Appl. Mechanics 15*, A17 (1938)

(12) T. Zeiler, *Oberflächenmodifizierung von thermoplastischen Polymerwerkstoffen im Hinblick auf die Verbesserung ihrer Verklebbarkeit*, Thesis University of Erlangen-Nürnberg 1997

(13) L.J. Gerenser, *J. Adhesion Sci. Technol.* **4**, 303 (1987)

(14) D. Briggs, D.M. Brewis, M.B. Konieczko, *J. Material Sci.* **11**, 1270 (1976)

(15) T. Bahners, W. Kesting, E. Schollmeyer, *J. Appl. Surf. Sci.* **69**, 12 (1993)

(16) E. Occhiello, M. Morra, F. Garbassi, D. Johnson, D. Humphrey, *Appl. Surf. Sci.* **47**, 235 (1991)

(17) F. Garbassi, M. Morra, E. Occhiello, *"Polymer Surfaces - From Physics to Technology"*, Wiley, New York 1994