

# Influence of CO<sub>2</sub> Laser Radiation on the Surface Properties of Poly(ether ether ketone)

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Received 6 August 1996; accepted 17 October 1996

**ABSTRACT:** The influence of CO<sub>2</sub> laser radiation on the surface properties of poly(ether ether ketone) (PEEK) is shown. The influence on the surface chemistry is nearly negligible, but the roughness increases and the crystallinity in the surface region decreases with increasing laser intensity. The crystallinity of the surface region was determined by a newly developed procedure using photoacoustic infrared spectroscopy.

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## INTRODUCTION

Poly(ether ether ketone) (PEEK) is a high-temperature-resistant thermoplastic material which is used in an increasing number of technical applications,<sup>1</sup> e.g., wire insulations for nuclear power stations, automotive parts, coatings for heat exchangers, medical technique, or tubing for pure media. As PEEK is a thermoplastic polymer, it can be cut or welded with the aid of laser radiation, especially using a CO<sub>2</sub> laser, which is the most common kind of infrared laser. Another possible application of CO<sub>2</sub> laser radiation is the removal of contaminants from the PEEK surface. In all of these applications, one has to take possible changes of the surface chemistry and morphology into account, as the outstanding properties of PEEK strongly depend on them. For example, the heat of the laser can effect a change in the degree of crystallinity in the surface region. As the mechanical properties are strongly dependent on the degree of crystallinity, this is an important parameter for practical applications. The degree of crystallinity is typically determined by DSC tech-

niques, which is an appropriate method for homogeneous samples. However, one cannot expect that laser-treated samples are homogeneous, so DSC has limited usefulness for the determination of the crystallinity of such samples. Therefore, an alternative method was developed for this purpose, in which photoacoustic FTIR techniques were developed, using a calibration with homogeneous samples by DSC. Another point of concern is the change of the surface chemistry by the laser radiation, which may be desirable for some applications, e.g., adhesive bonding, but should be avoided for applications where the inertness of the material is important, e.g., reaction vessels or tubings. Changes of the surface chemistry were examined by contact angle measurement and XPS spectroscopy. In contrast to the extensive chemical changes from an excimer laser treatment, chemical changes of the polymer structure from the CO<sub>2</sub> laser treatment are expected to be minor, as the CO<sub>2</sub> laser radiation mainly heats the surface<sup>2</sup> of the high-temperature-resistant PEEK.

## EXPERIMENTAL

### Materials

All the experiments were carried out with a 200- $\mu$ m-thick film of poly(ether ether ketone), Vitrex 450G<sup>®</sup> from ICI.

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### Laser Treatment

The high-frequency CO<sub>2</sub> laser Rofin-Sinar RS 2500 ( $\lambda = 10.6 \mu\text{m}$ ) was used for all experiments in the continuous wave mode. The laser power at the sample was 1150 W, the intensity of the treatment was varied by varying the feed rate of the sample, i.e., at either 116, 203, 242, or 252 m/min. The laser treatment was done in air, argon, or carbon dioxide atmosphere and at an angle of incidence with respect to the surface normal of 0°.

### XPS Spectroscopy

XPS spectra were obtained using an ESCALAB 220i XL (Fisons Instruments) with a monochromatic AlK <sub>$\alpha$</sub>  X-ray source. The pass energy was 70 eV for the survey spectra and 20 eV for high-resolution spectra. The binding energy of the C1s component for the aromatic carbon was set to 284.5 eV as an internal standard. To determine the possible presence of hydroxyl groups in the presence of the ether groups of the polymer, the surfaces were treated with the vapor of trifluoroacetic anhydride for 30 min.<sup>3,4</sup> Spectra were recorded before the treatment and immediately after.

### DSC

DSC measurements were carried out with a Ta instruments DSC 2920. Heating rate was 50 K/min and the temperature range 30–400°C.

### FTIR Spectroscopy

The FTIR spectra were recorded with a Nicolet 740 spectrometer equipped with a MTEC 200 photoacoustic cell. Carbon black was used as reference material and at least 150 scans were recorded with a resolution of 8 cm<sup>-1</sup> for both the reference and the sample spectra. The mirror velocity was set to 0.16 cm/s, which corresponds to an information depth of 13.0  $\mu\text{m}$  for a wavenumber of 516 cm<sup>-1</sup> and 10.0  $\mu\text{m}$  for a wavenumber of 865 cm<sup>-1</sup>, respectively. The information depth was calculated according to the Rosenzweig-Gersho theory,<sup>5,6</sup> using a thermal diffusivity of 0.087 mm<sup>2</sup>/s, which was measured by the laser flash method.

### Microscopy

To check changes of the polymer morphology by the laser radiation, 10- $\mu\text{m}$ -thick cross-sections of

the PEEK films were cut by a microtome. The cross-sections were observed in a light microscope at magnifications of either 200 : 1 or 400 : 1 with polarized light.

### Contact Angle Measurement

Sessile drop measurements using a 26% solution of NaCl in water ( $\gamma = 78.3 \text{ mN/m}$ ), water ( $\gamma = 72.8 \text{ mN/m}$ ), glycerine ( $\gamma = 63.4 \text{ mN/m}$ ), formamide ( $\gamma = 58.2 \text{ mN/m}$ ), diiodomethane ( $\gamma = 50.8 \text{ mN/m}$ ) and ethylene glycole ( $\gamma = 47.7 \text{ mN/m}$ ) as test liquids for contact angle measurement were done using the Krüss G40 equipment. The critical surface tension was determined by the method of Zisman.<sup>7</sup>

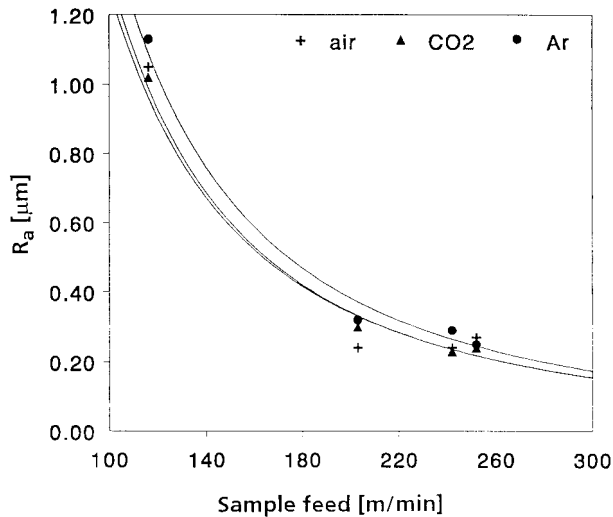
### Surface Roughness

The surface roughness was determined using the equipment from UBM company with a mechanical and an optical sensor. The  $R_a$  roughness was calculated using the instrument software.

## RESULTS AND DISCUSSION

### Surface Chemistry

One of the easiest methods to check changes of the chemical composition of a surface is the measurement of the surface tension. For the untreated material a critical surface tension of  $40.4 \pm 1.0 \text{ mN/m}$  was found. After the treatment by the laser radiation, the critical surface tension decreased to  $\sim 37.5 \pm 1.2 \text{ mN/m}$ . The change is just outside the difference of the standard deviations. The decrease is independent of the treatment time (sample feed 116, 203, 242, or 252 m/min) and atmosphere (air, CO<sub>2</sub>, or Ar), within the standard deviation. As not only the surface composition, but also the surface roughness has an influence on the wettability of a surface, the roughness needs to be measured. The roughness  $R_a$  of the untreated polymer is 0.13  $\mu\text{m}$ . Figure 1 shows the influence of the laser treatment on the surface roughness as a function of the sample feed for different atmospheres. The roughness decreases with increasing sample feed, which corresponds to a decreasing treatment time, by a power function. No significant influence of the atmosphere could be detected. As the roughness, but not the surface tension, depends strongly on the treatment time, the change in surface tension cannot be caused by a change of the roughness. Therefore



**Figure 1** Dependence of the surface roughness  $R_a$  of laser-treated PEEK for different treatment atmospheres from the sample feed.

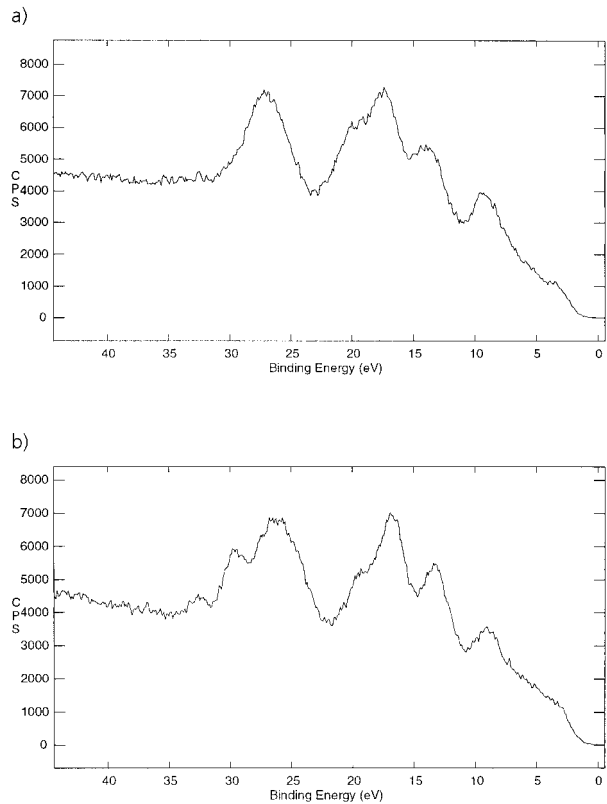
a small change of the surface composition is possible.

To analyze the surface composition, XPS spectra of samples treated in air, CO<sub>2</sub>, or Ar at a sample feed rate of 203 m/min were obtained. Table I shows the elementary composition of these samples together with the theoretical composition and that of the untreated sample.

As expected, only minor changes in the composition are caused by the laser treatment, including the high-resolution C1s and O1s spectra. All the spectra agree with the literature spectra<sup>8</sup> of untreated PEEK. Only the higher oxygen content of the sample treated in air is striking, but this has no influence on the high-resolution spectra. A difference was found in the valence band (VB) spectra only. Figure 2(a) shows the VB spectrum of an untreated sample, which agrees with the literature spectrum. Figure 2(b) shows the VB spectrum of the sample treated in air, in which there are two new components of the O2s-peak. These components are also present in the spectra of the

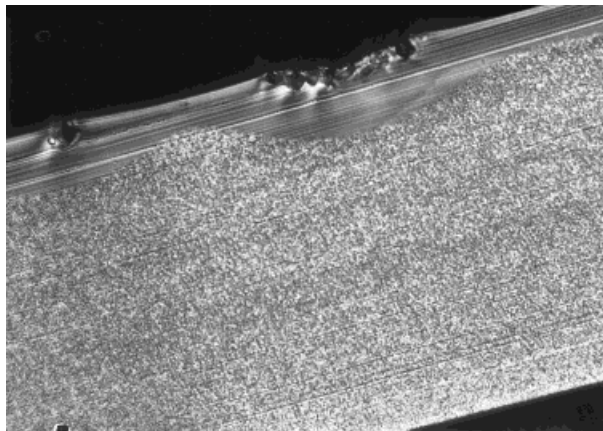
**Table I** Elementary Composition of the PEEK Samples after Laser Treatment in Different Atmospheres

Element	Theory	Untreated	Air	CO <sub>2</sub>	Ar
C	86.4	86.5	84.5	86.9	86.0
O	13.6	13.1	15.5	13.1	14.0
F	—	0.4	—	—	—
C/O	6.35	6.60	5.45	6.63	6.14



**Figure 2** Valence band spectra of PEEK. (a) untreated sample; (b) treated in air by CO<sub>2</sub> laser radiation with a sample feed of 203 m/min and a power of 1150 W.

samples treated in CO<sub>2</sub> or Ar, but the intensity is much smaller. As the structure of the VB spectra is not well understood and no significant changes in the O1s and C1s spectra are detectable, the relationship of the changes to chemical structures is not possible as yet. The presence of a small amount of hydroxyl groups on the surface of the sample treated in air would be in agreement with the unchanged C1s and O1s spectra. To verify the presence of hydroxyl groups, the samples were stored in the vapor of trifluoroacetic anhydride for 30 min and analyzed again. It was found that the fluorine content, which characterizes the number of hydroxyl groups on the surface, of the samples treated in CO<sub>2</sub> (3.2%) or in Ar (3.4%) is not much higher than that of the untreated sample (2.9%). This shows that on these samples hydroxyl groups are formed only to a minor degree. Against this a fluorine content of 7.3% was found on the sample treated in air. Therefore, the additional oxygen on this kind of samples is at least partly bound in the form of hydroxyl groups. Most likely the change of the VB spectrum is also caused by the hydroxyl groups.



**Figure 3** Cross-section of a PEEK sample treated by a  $\text{CO}_2$  laser (1150 W, sample feed 116 m/min), magnification 400 : 1, total thickness of the sample 200  $\mu\text{m}$ .

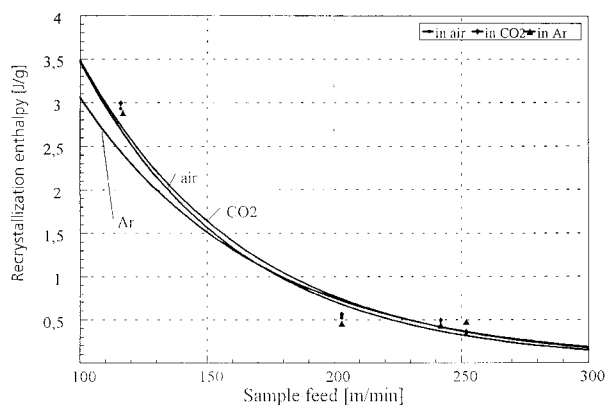
### Morphology of the Surface Region

Since the samples are affected thermally during laser treatment, one can expect a change of crystallinity in the surface region. That this is the case can be seen in Figure 3, which shows the cross-section of a sample treated in  $\text{CO}_2$  with a sample feed rate of 116 m/min. A sharp boundary between the affected and nonaffected parts of the sample can be seen. The thickness of the affected layer is  $25 \pm 5 \mu\text{m}$  and does not depend on the atmosphere in which the treatment is carried out. At the laser tracks a decomposition of the material can be seen. It seems that the affected material is amorphous, in contradiction to the crystalline base material.

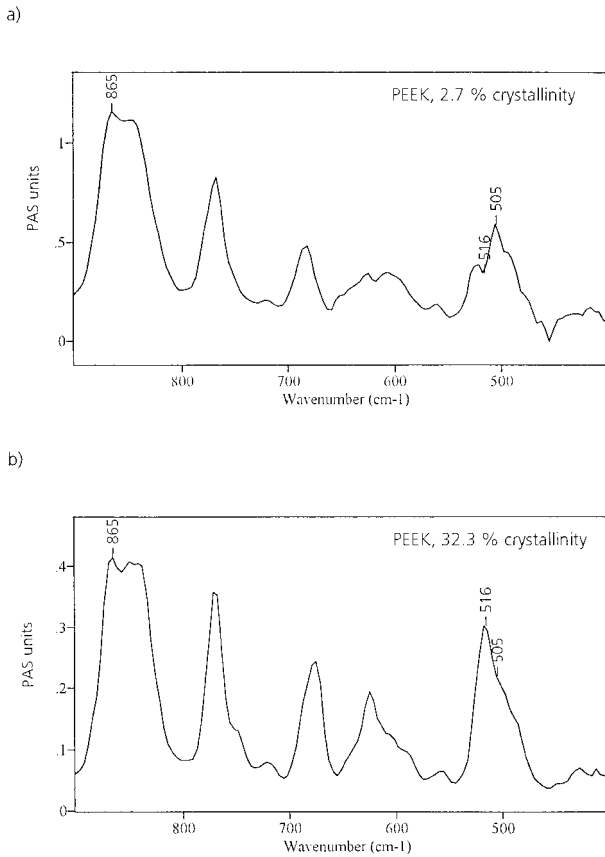
The fact that the affected material actually has a lower crystallinity can be seen in the DSC diagrams. At  $190^\circ\text{C}$  a recrystallization peak appears for all the samples examined. Figure 4 shows the recrystallization enthalpy as a function of the sample feed rate for the different treatment atmospheres. Again no influence of the atmosphere can be found and the recrystallization enthalpy decreases strongly with increasing sample feed rate. The result shows that the content of amorphous material increases with increasing treatment time, but the degree of crystallinity of the affected layer cannot be determined. A new procedure was developed for this, using photoacoustic FTIR (PAS).

First of all, the PEEK samples of different crystallinity were prepared by annealing at different rates and times. The degree of crystallinity of these homogeneous samples was determined by DSC using a heat of fusion of 162 J/g for crystalline PEEK.<sup>9</sup> The degree of crystallinity of the an-

nealed samples varied from 2.7 to 32.3%. The value for the original material is 25.3%. PAS spectra of the different samples were recorded and it was found that the peaks around  $516 \text{ cm}^{-1}$  change systematically with the degree of crystallinity. The band of the C-H out-of-plane vibration of the aromatic ring at  $865 \text{ cm}^{-1}$  was chosen as reference band. This band showed no changes with changing crystallinity; the band is intense and close to the relevant one. As an example, the important part of the spectra of the sample with the lowest (2.7%) and the highest (32.3%) degrees of crystallinity are shown in Figures 5(a) and 5(b), respectively. Up to now PAS infrared spectroscopy has not been used to study the morphology of PEEK, but multiple internal reflexion. The ratios  $1305/1280 \text{ cm}^{-1}$  and  $970/952 \text{ cm}^{-1}$  were used by Chalmers, Gaskin, and Mackenzie<sup>10</sup> to determine the degree of crystallinity, but were not found to be appropriate for the evaluation of the PAS spectra. The use of Raman spectroscopy has been published by Everall, Lumsdon, and Chalmers,<sup>11</sup> who analyzed the relationship of the bands at 1608 and  $1597 \text{ cm}^{-1}$ , and Louden,<sup>12</sup> who used the ratio of the bands at 830 and  $810 \text{ cm}^{-1}$ . Small changes of these bands are visible in the PAS spectra, too, but are not resolved well enough for quantitative analysis. Figure 6 shows the relation of the peak intensities of the peaks at  $865 \text{ cm}^{-1}$  and  $516 \text{ cm}^{-1}$  as a function of crystallinity. The peak at  $516 \text{ cm}^{-1}$  shifts with varying crystallinity, so the intensity of the maximum was analyzed. With the aid of Figure 6 the crystallinity of the surface region of pure PEEK as well as that of filled PEEK with an unknown content of filler (e.g., carbon fiber-reinforced PEEK) can be determined. The application to the laser-treated samples is shown in

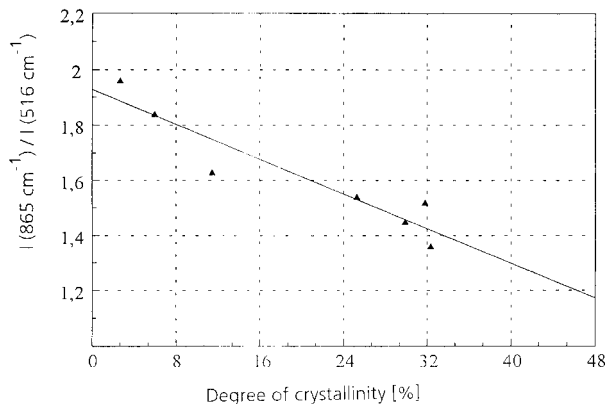


**Figure 4** Dependence of the recrystallization enthalpy of PEEK treated in different atmospheres determined by DSC.

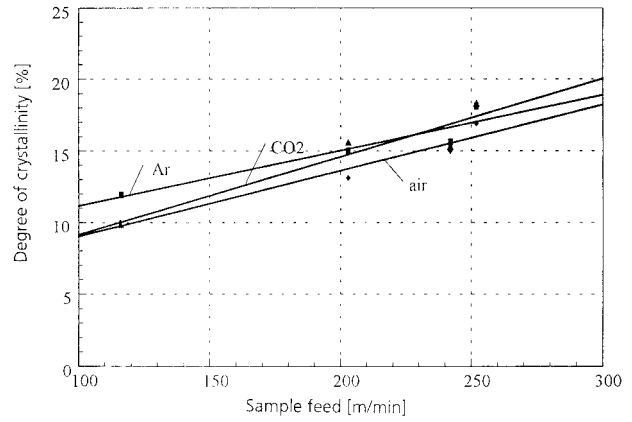


**Figure 5** PAS-FTIR spectra of PEEK samples with a low (a) and a high (b) degree of crystallinity.

Figure 7. As expected, the crystallinity is low in the upper 10–13 μm (this is the information depth under the chosen conditions, see Experimental) at a low sample feed rate and increases with increasing sample feed rate. It is always



**Figure 6** Relation of the intensity of the IR peaks at 865 and 516 cm<sup>-1</sup> in dependence on the degree of crystallinity, determined with homogeneous PEEK samples.



**Figure 7** Dependence of the degree of crystallinity from the sample feed in the upper 15 μm of PEEK samples treated in different atmospheres.

much below the value of the untreated PEEK (25.3%); therefore, one can suppose a loss of the mechanical strength in the upper surface regions of PEEK samples processed with the aid of CO<sub>2</sub> laser radiation.

**CONCLUSIONS**

It is shown that the chemical composition of the PEEK surface is not significantly influenced by CO<sub>2</sub> laser radiation. If the treatment is carried out in air, a small oxygen uptake is found, which is most likely in the form of hydroxyl groups. In contrast to the treatment of an epoxy resin by CO<sub>2</sub> laser radiation,<sup>13</sup> no other significant difference could be detected between the samples treated in air, carbon dioxide, or argon. No significant change of the wettability of the treated PEEK surfaces was found. Both results show that the inertness of the PEEK surface is influenced only to a minor degree by the radiation. Therefore the application of CO<sub>2</sub> laser radiation for the welding, cutting, or surface cleaning of PEEK can be recommended for cases where the surface should not be changed, such as for medical applications or for vessels for chemical reactions. To be on the safe side, the treatment should not be carried out in air. As the surface roughness increases with increasing treatment intensity, the intensity should be as low as possible. If the mechanical properties are relevant for the specific application, one has to take the decreasing crystallinity in the surface region into account. The degree of crystallinity decreases with increasing treatment intensity; therefore, the intensity should be as low as possible by this point of view, too. Recrystalli-

zation was found by DSC measurement of the treated samples, which means that the loss of crystallinity is reversible. For this reason, annealing of the laser-treated samples can be recommended to get back a homogeneous material. The measurement of the degree of crystallinity in the surface region was carried out by photoacoustic infrared spectroscopy. This newly developed procedure is applicable for the examination of the crystallinity of carbon fiber-reinforced PEEK, too. This is not possible by DSC, as the polymer content in the small DSC sample is usually not known.

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