PII: S0032-3861(97)00304-2

Polymer Vol. 39 No. 3, pp. 573–582, 1998

0032-3861/97/$17.00+0.00

*FT*i.r. spectroscopy on electron irradiated polytetrafluoroethylene[†]

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(Received 24 March 1997)

The partial degradation of polytetrafluoroethylene caused by electron irradiation was investigated by infrared (i.r.) transmission, diffuse reflectance (DR) and photoacoustic (PAS) spectroscopy. We studied the influence of the radiation dose and the hydrolysis conditions on the structure. Irradiation produces COF groups with a band at 1884 cm^{-1} in the transmission spectra. Under ambient conditions these COF groups hydrolyse with the atmospheric humidity to free (1810 cm^{-1}) and associated (1776–1792 cm^{-1}) COOH groups. We could establish the presence and the nature of these groups in near surface regions and in the bulk phase. The formation of carboxylic groups in different states of association also depends on the hydrolysis conditions. Various forms of hydrogen bonding can be found for different associated COOH groups (1776 and 1792 cm^{-1}). Hence we could assign the band at 1776 cm^{-1} to the vibration of a dimer consisting of two hydrogen bonded carboxyl groups. The band at 1792 cm^{-1} comes from 'monomeric' acid groups associated with water via hydrogen bonds. After hydrolysis under extreme conditions using alcoholic sodium hydroxide changes in band intensities and a strong new band at 1784 cm^{-1} were observed. This fact indicates a change of association states on the surface. Subsequently ester groups were formed in a surface acylation reaction of COF groups with ethanol which give this new band. From the DR and PAS spectra it can be concluded that most COOH groups are localized in the near surface region. In every case a small part of the COF groups remains after hydrolysis. The COF band in the spectra of hydrolysed PTFE only disappears when the permeation conditions for water vapour at the PTFE surface were improved. This fact indicates that COF groups in irradiated PTFE are not only localized on the surface of the PTFE particles. The results establish the hypothesis that a part of the COF groups is inaccessibly arranged in the inner part of the irradiated PTFE particle, and spontaneous hydrolysis is preferred in near-surface regions. © 1997 Elsevier Science Ltd.

(Keywords: infrared spectroscopy; PTFE; electron irradiation)

INTRODUCTION

Polytetrafluoroethyene and electron irradiation

Polytetrafluoroethylene (PTFE, Teflon) has a unique position in the plastics industry due to its chemical inertness, heat resistance and low coefficient of friction. Although the very low surface energy of PTFE is beneficial to a large number of applications, it does raise problems in some areas of use. For instance, it is often difficult to incorporate PTFE homogeneously into other materials by blending and grinding. The high molecular weight PTFE is unsuitable for those applications. Therefore, it is necessary to create tetrafluoroethylene polymers, called PTFE micropowders, with molecular weights significantly lower than that of normal PTFE. The high molecular weight PTFE can be converted to micropowder by gamma or electron beam irradiation treatment. A partial degradation of PTFE by electron irradiation in air, described by Lunkwitz[1], leads mainly to the formation of acid fluoride groups (COF). This formation is particularly expected in near-surface regions. The COF groups hydrolyse to carboxylic acid groups (COOH) in the presence of atmospheric humidity. Such modified PTFE powder can interact with other materials by their COOH groups in an excellent manner. The emphasis of our work was to investigate the influence of the radiation dose and the hydrolysis conditions on the chemical structure of this powder by i.r. spectroscopy.

Infrared spectra of polytetrafluoroethylene

The vibrational behaviour of PTFE has been investigated by several authors[2–5]. Irradiated PTFE has similarly been investigated in numerous studies[6–9]. The partial degradation of PTFE by electron irradiation in air or oxygen leads to the formation of COF groups. The C=O stretching vibration of the COF band appears at 1884 cm^{-1}. After hydrolysis the formed COOH groups are only partly associated because of their relative slow concentration. The C=O band of the free acid groups as well as the associated acid groups are at 1810 and 1776 cm^{-1}[6–8]. The OH stretching vibrations of these COOH groups are at 3557 cm^{-1} (free groups) and 3100 cm^{-1} (associated groups), respectively. CF_3 side groups are formed during the degradation. We can identify these groups on the band at 981 cm^{-1}.

We have combined some different i.r. spectroscopic techniques for the investigation of this partial decomposition of PTFE: transmission spectroscopy with an i.r. microscope, diffuse reflectance spectroscopy (DR) and photoacoustic spectroscopy (PAS).

EXPERIMENTAL

Materials and electron irradiation

The PTFE used in this work was obtained from Hoechst

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[*] To whom correspondence should be addressed

[†] Dedicated to Professor Hans-Jörg Jacobasch on the occasion of his 60th birthday

AG (Hostaflon TF-1760). The irradiation experiments were performed with a universal electron beam accelerator (1 MeV, ELT 1.5, Institute of Nuclear Physics, Novosibirsk). The samples were irradiated in the presence of air on a step by step basis using a radiation dose of 100 kGy each time.

Infrared spectroscopy

All i.r. measurements were carried out on a Bruker (Karlsruhe) IFS 66 *FT*i.r. spectrometer with an i.r. microscope. We used the praying mantis cell from Harrick (Ossing, NY) for the diffuse reflectance and the cell from MTEC Photoacoustics (Ames, IA) for the photoacoustic measurements.

Small thin film samples ($d \sim 50\,\mu$m) were obtained by pressing the PTFE powder at room temperature. The transmission spectra of these films were recorded using the i.r. spectrometer (100 scans, 2 cm^{-1} resolution) and the i.r. microscope (spot size 50 μm, 100 scans, 2 cm^{-1} resolution). We used the polymer powder without further preparation for the PAS (1.6 kHz frequency, 500 scans, 8 cm^{-1} resolution, reference: carbon black standard) and for the DR we mixed the PTFE powder with KBr (200 scans, 2 cm^{-1} resolution). The model substances perfluorododecane (ABCR, Karlsruhe) and ethyl perfluorononanoate (PROSYNTH®, Riedel de Haen, Hannover) were prepared as thin liquid films between KBr discs. Infrared transmission spectra were recorded at 2 cm^{-1} resolution.

Temperature dependence i.r. measurements

Heating stage. Samples irradiated at 1 MGy were annealed at 200°C for 10 h. Then we performed the i.r. measurements using the heatable x–y sample stage of the i.r. microscope with an automatic temperature controller and a heating rate of 10K per minute.

Temperature cell. We used a modified SPECAC (Orpington, England) variable temperature cell with an automatic temperature controller and a heating rate of 10K per minute adjusted in the sample compartment of the spectrometer.

Hydrolysis of the PTFE powder

Spontaneous hydrolysis. Under ambient conditions (25°C) the powder was exposed in air for 2 weeks.

Controlled hydrolysis. The PTFE powder was refluxed in alcoholic sodium hydroxide (10% NaOH) solution (50% ethanol/50% water) for 2 h.

Storage of the PTFE powder in a saturated ethanol atmosphere

Samples irradiated at 1 MGy were pressed and annealed in a vacuum oven at 80°C for 2.5 h to remove adsorbed water. Then a stream of ethanol vapour was slowly passed into the evacuated system at 50°C. After reaching ambient pressure the samples were taken and measured immediately.

RESULTS AND DISCUSSIONS

We investigated the influence of radiation dose and hydrolysis conditions on the spectra of PTFE, in particular in the range of COF and COOH groups. To explain the spectral effects of the irradiated and hydrolysed samples we have also measured i.r. spectra at elevated temperatures, because it is well known that hydrogen bonding phenomena for example are extremely temperature dependent.

The concentration of the C=O groups rises due to increased degradation of PTFE at higher radiation doses (see *Figure 1*). The samples were stored under ambient conditions so that spontaneous hydrolysis of the COF groups was proceeding as expected. The intensities of the i.r. bands of the associated acid group (1776 cm^{-1} with a shoulder at 1792 cm^{-1}) and of the COF group (1884 cm^{-1}) rise in the corresponding transmission spectra. Our interpretation is that the band at 1776 cm^{-1} is the C=O stretching vibration of the carboxyl groups which is disturbed by hydrogen bonds between two acid groups (associated dimer, in agreement with Refs [6,8]). In contrast to Refs [3,7,8] we

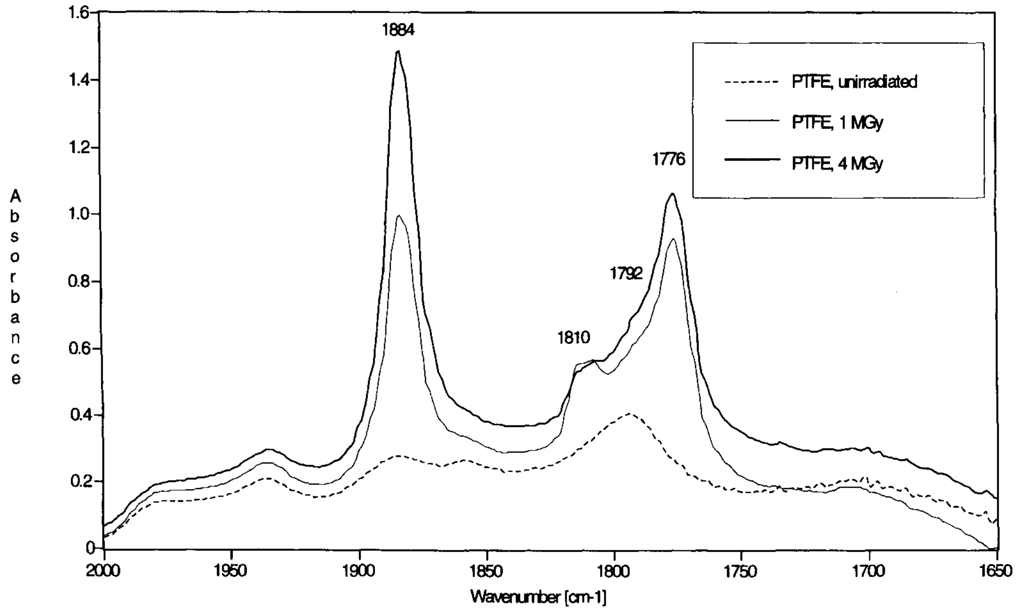


Figure 1 Infrared transmission spectra (films) of PTFE in the region 2000–1650 cm^{-1}, unirradiated and irradiated with doses of 1 and 4 MGy

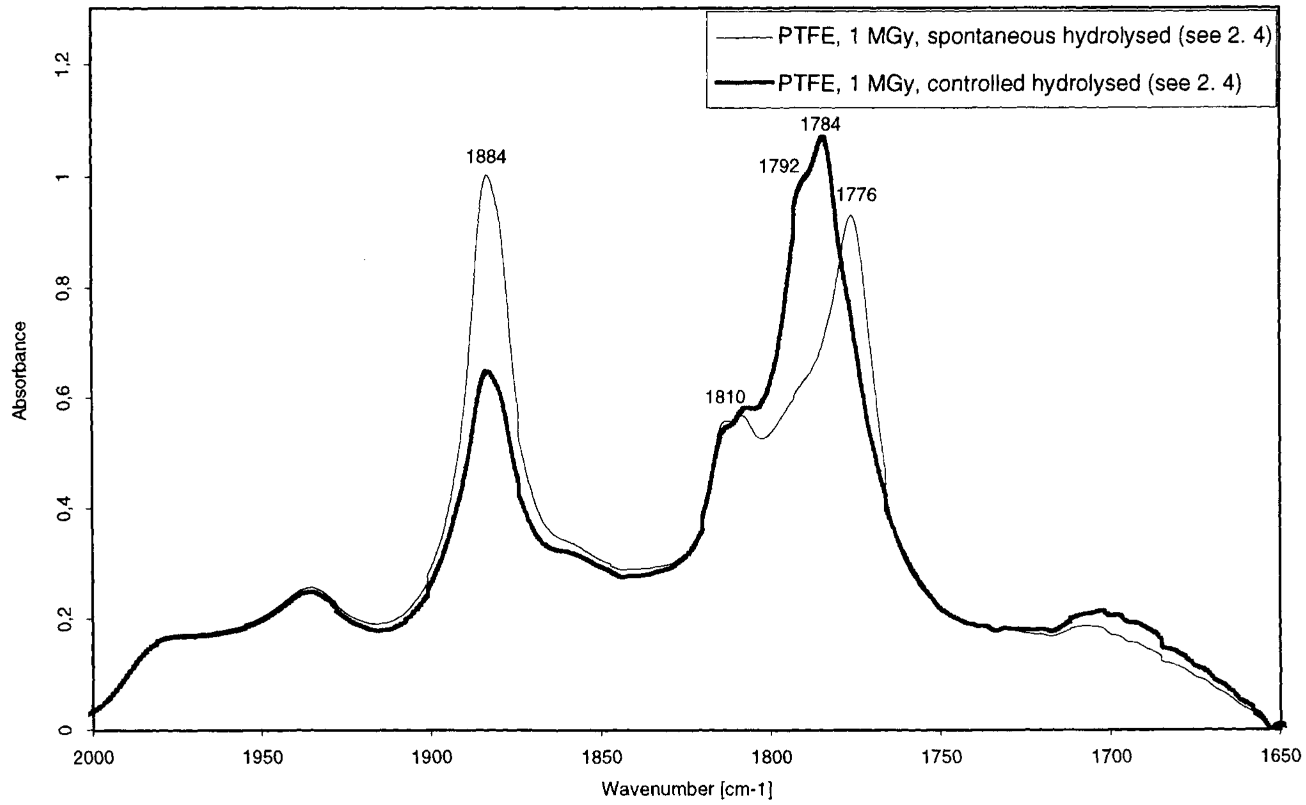


Figure 2 Infrared spectra (films) of PTFE, irradiated with a dose of 1 MGy, differently hydrolysed in the region 2000–1650 cm^{-1}

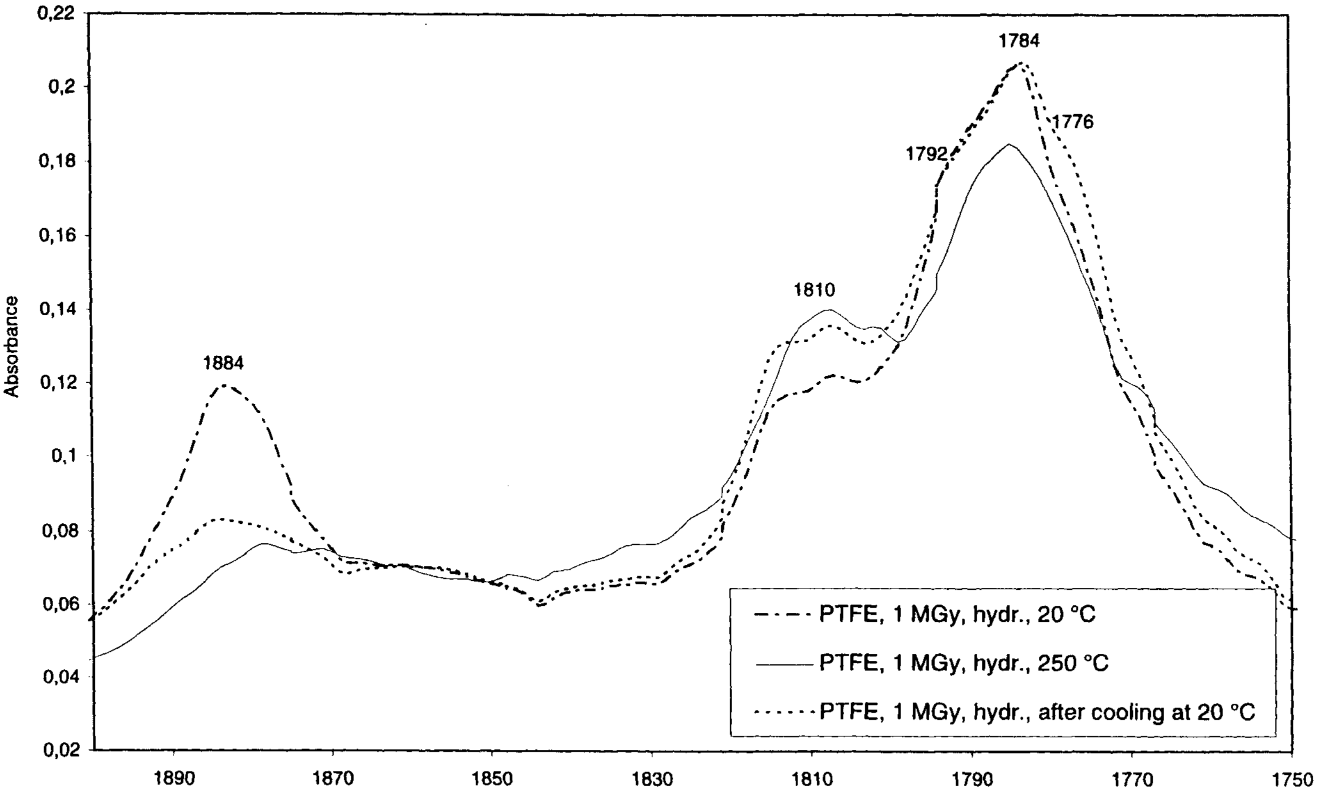


Figure 3 Infrared spectra (films) of PTFE in the region 1900–1750 cm^{-1}, irradiated with a dose of 1 MGy and controlled hydrolysed, than measured at 20 and 250°C, and after cooling again at 20°C

interpret that the band at 1792 cm^{-1} is a overlap of two bands. The smaller part is a combination band (638 + 1152 cm^{-1}) as in unirradiated PTFE and the bigger important part is a C=O band of the COOH groups influenced by hydrogen bonds between these COOH groups and water. These investigators assign this band exclusive to a C=CF$_2$ group terminal group[7,8] or to the combination band 638 + 1152 cm^{-1} [3]. We show in *Figures*

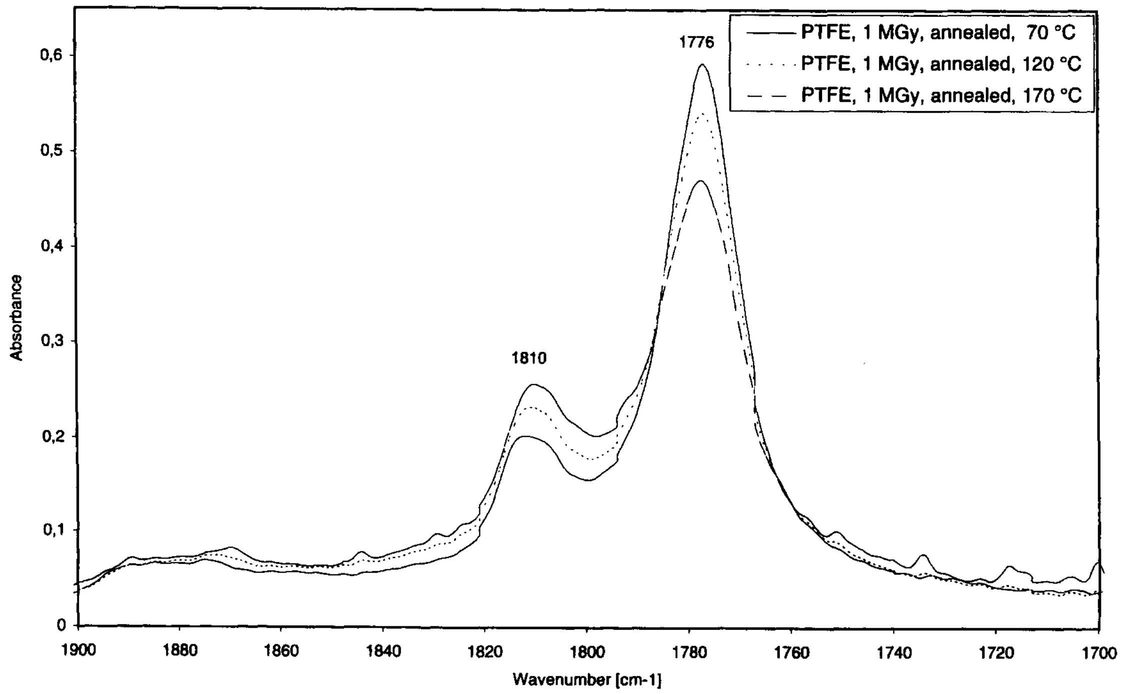


Figure 4 Infrared spectra (films, i.r. microscope with heatable sample stage) of PTFE at different temperatures after irradiation with a dose of 1 MGy and annealing in the region 1900–1700 cm^{-1}

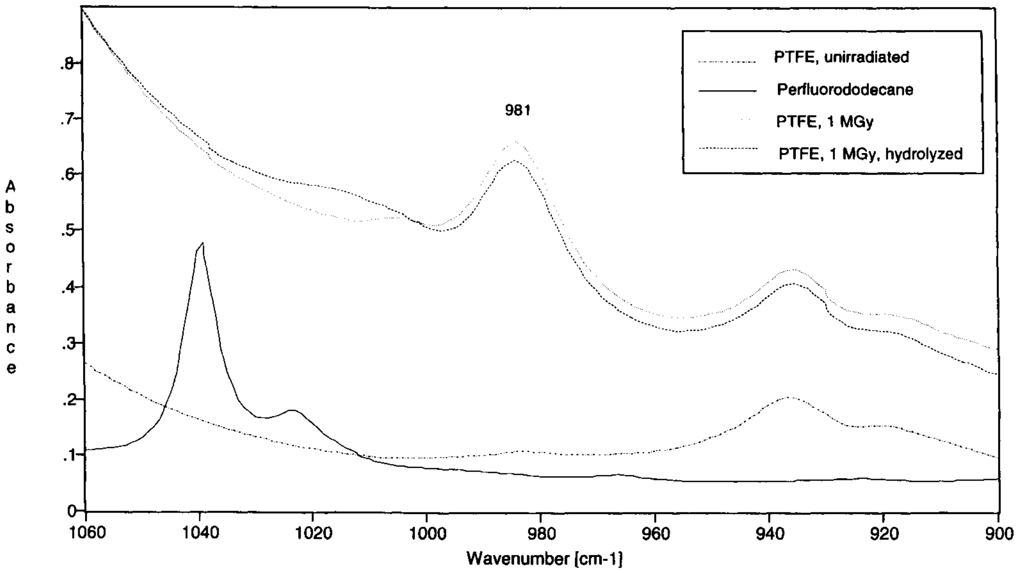


Figure 5 Infrared spectra (films) of PTFE and perfluorododecane in the region 1060–900 cm^{-1}

2 and 3 that our new assignment is more plausible. The concentration of the free acid groups indicated by the band at 1810 cm^{-1} is approximately unchanged, and this interpretation is also in agreement with previous works[6,8]. The concentration of the associated acid groups increases at a stronger rate because the degree of association is directly connected with the carbonyl concentration. Under these conditions a part of the COF groups has to be inaccessible in the inner part of the particles. These particles do not hydrolyse at atmospheric humidity. Measurements at different temperatures under the i.r. microscope confirm the assignment of the free and associated C=O stretching vibrations (see *Figure 4*). Before these measurements we had annealed the PTFE at 200°C for 10 h to eliminate all COF groups through accelerated hydrolysis. During our i.r. spectroscopic heating cycles the intensity of the band of the associated COOH groups at 1776 cm^{-1} decreases with increasing temperature. The reason for this is the destruction of the hydrogen bonds of the associated dimers. Simultaneously the intensities of the bands of the free acid groups at 1810 cm^{-1} increase. After cooling we have again the initial state.

Figure 5 shows that the band at 981 cm^{-1} is also a result of degradation of PTFE caused by irradiation. This band is not in the spectra of unirradiated PTFE and of the model compound perfluorododecane. Thus it is proposed that this band is not a CF_3 terminal group, but a CF_3 side group, in agreement with Ref. [7]. In the i.r. spectrum of poly(tetrafluoroethylene-co-hexafluoropropylene) this band represents also a CF_3 side group.

The influence of the different hydrolysis conditions on the COOH and COF groups is demonstrated in *Figure 2* more

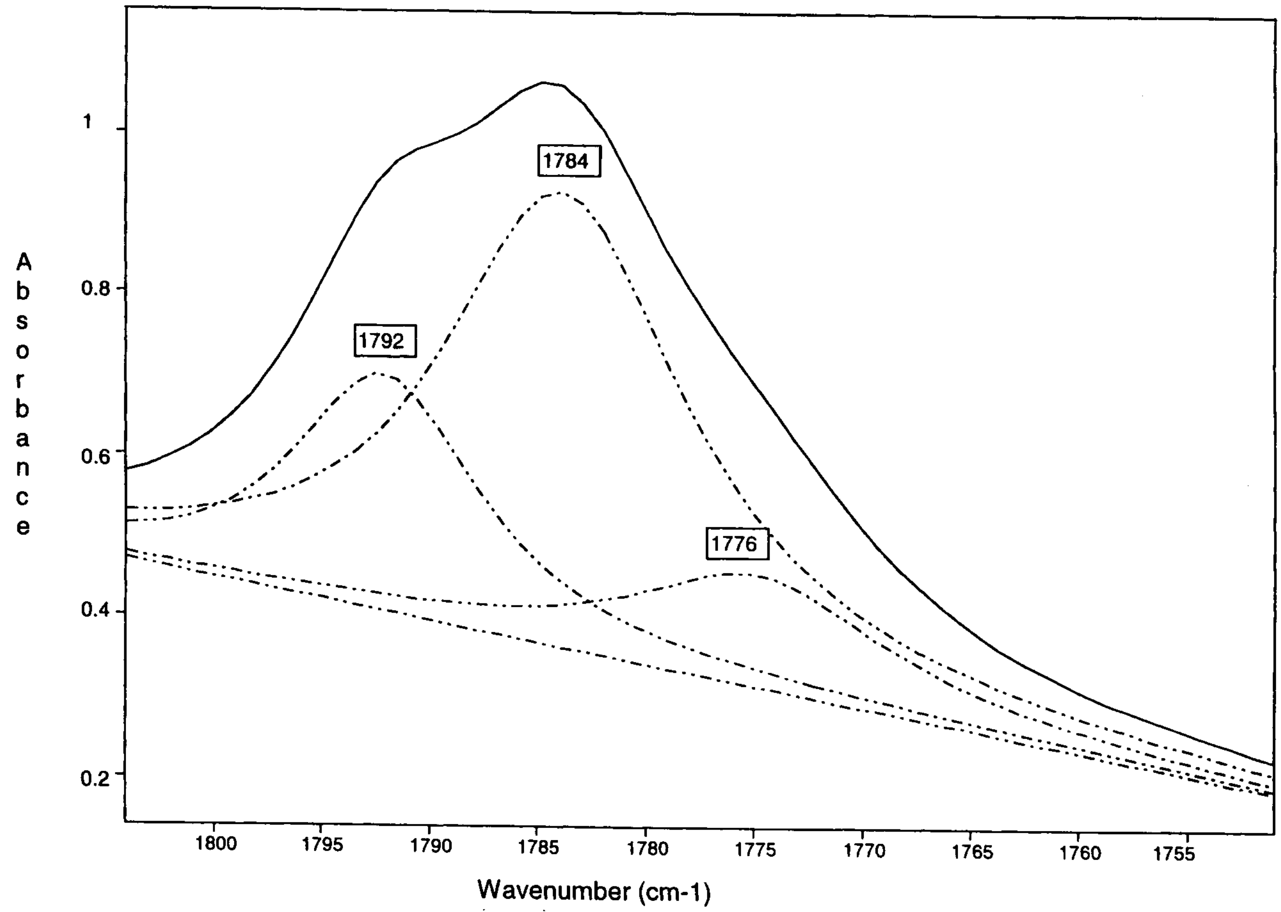


Figure 6 Infrared band separation in the region 1800–1750 cm^{-1} with the program CurveFit (Grams) of irradiated (with a dose of 1 MGy) and hydrolysed PTFE

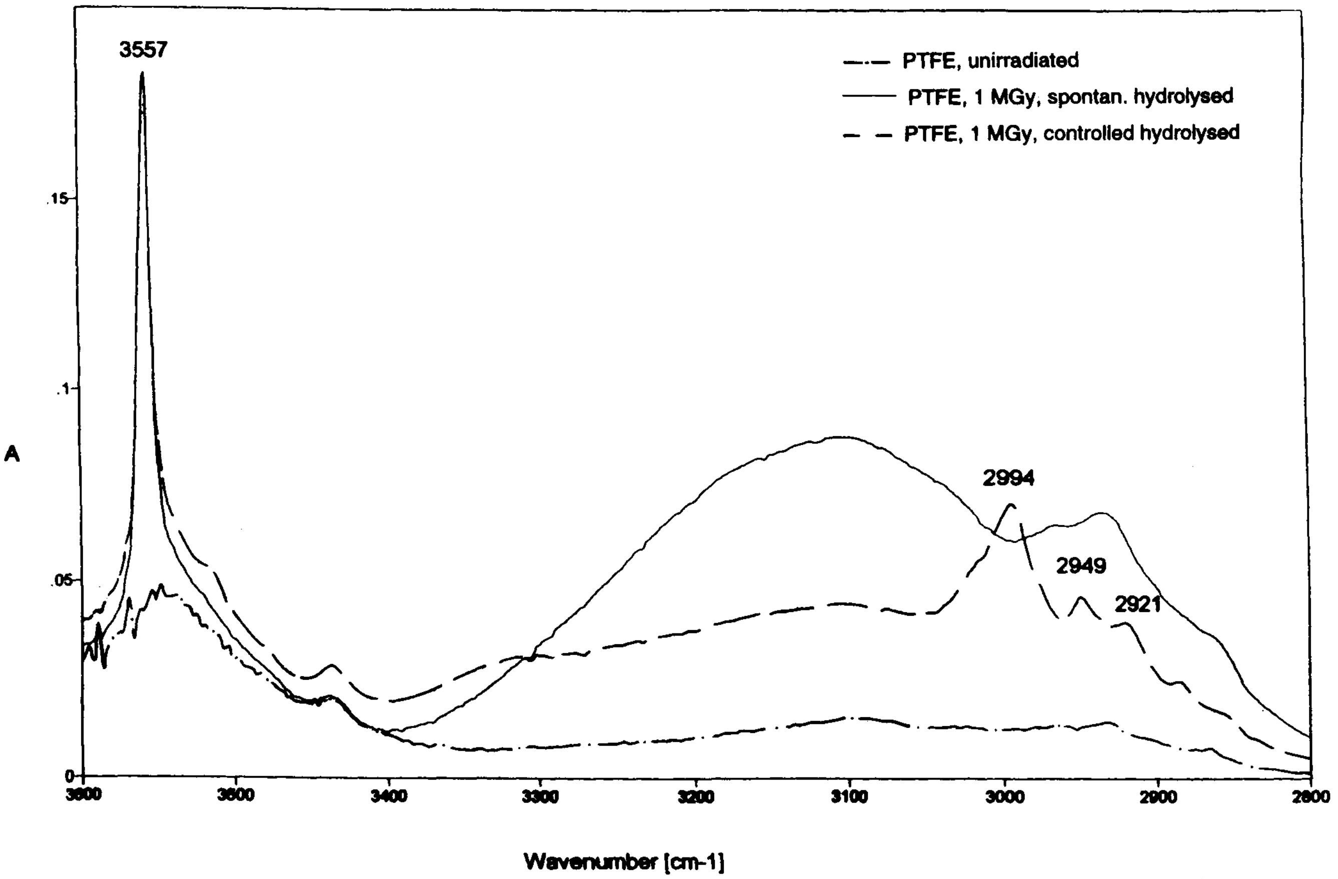
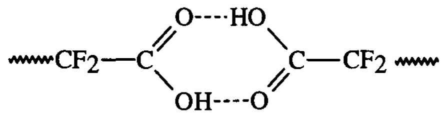
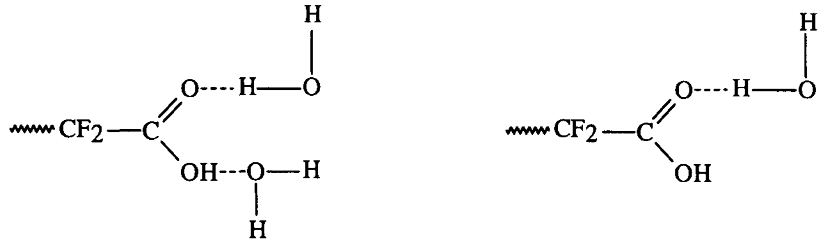


Figure 7 Infrared spectra (films) of PTFE, irradiated with a dose of 1 MGy, differently hydrolysed in the region 3600–2800 cm^{-1}

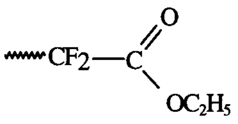
clearly. We propose the following structures:



1776 cm^{-1} (**a**)



1792 cm^{-1} (**b**)



1784 cm^{-1} (**c**)

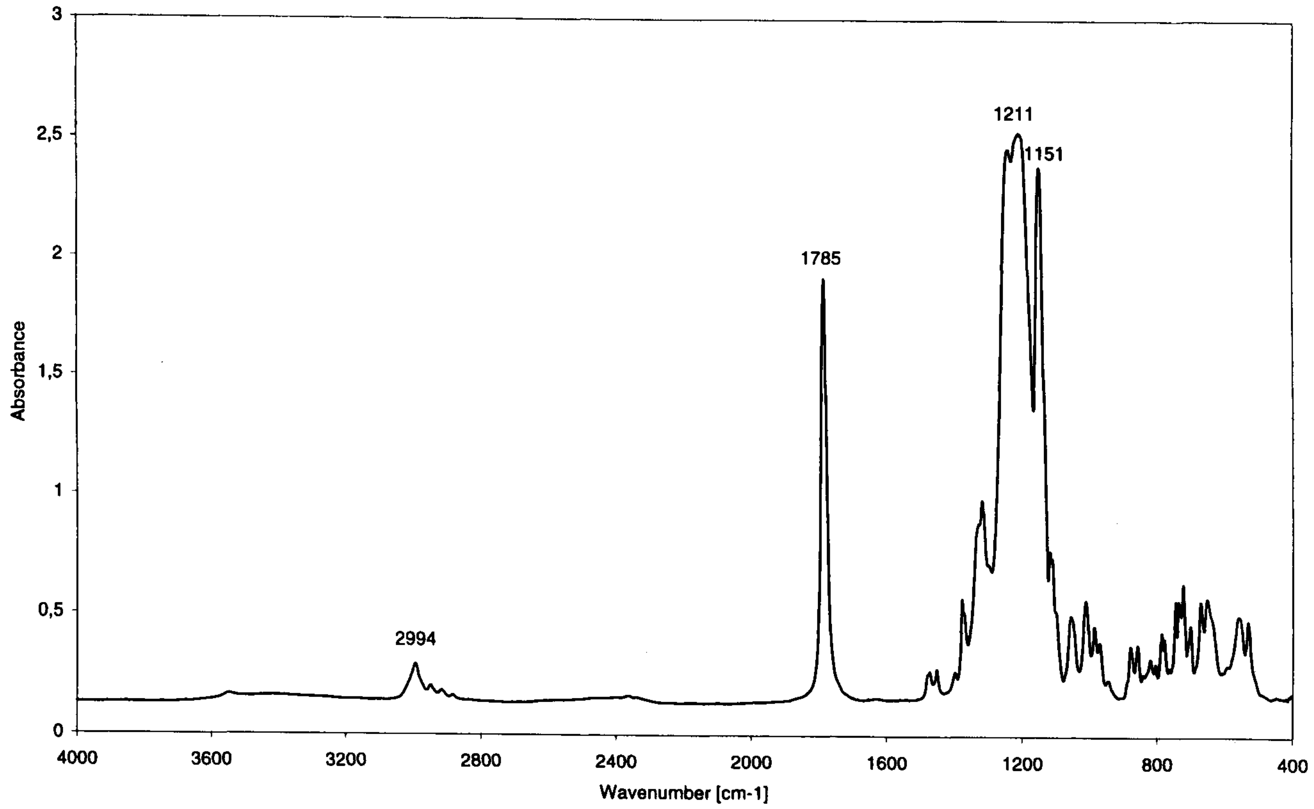


Figure 8 Infrared spectra of the low molecular weight model ester ethyle perfluorononanonate.

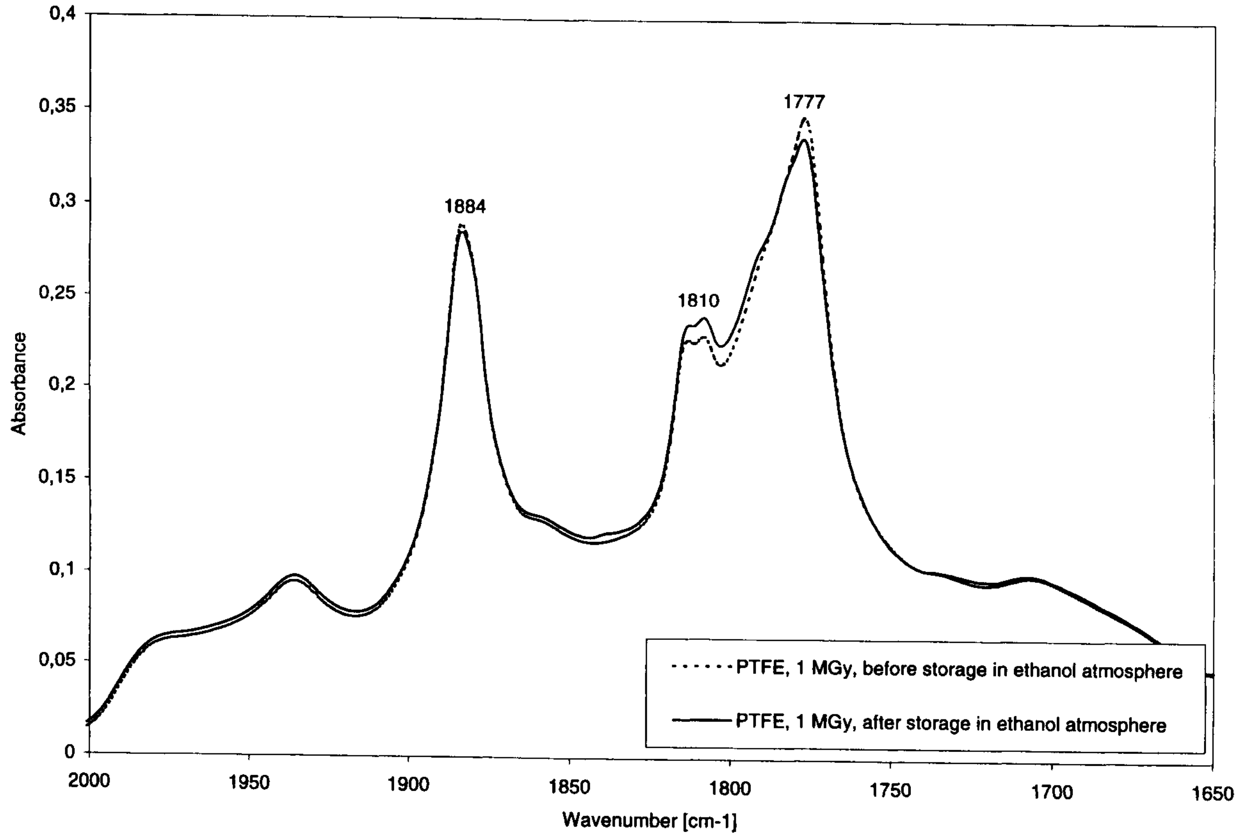


Figure 9 Infrared spectra (films) of PTFE irradiated with a dose of 1 MGy, in the region 2000–1650 cm^{-1}: (- - -) pressed powder annealed at 80°C for 2.5 h *in vacuo*; (————————) after subsequent storage in saturated ethanol atmosphere at 50°C

During controlled hydrolysis the intensity of the COF band at 1884 cm^{-1} decreases and the band of the associated COOH dimer at 1776 cm^{-1} (a) decreases strongly and a new band at 1784 cm^{-1} (c) appears. The band at 1792 cm^{-1} (b) remains at constant wavenumber with increasing intensity. The band separation, see in *Figure 6*, in this region clearly shows the existence of three different bands. This fact indicates that carbonyl fluoride groups and acid dimers (a) were consumed during this process. The new band (c) is a result of the reaction of the COF groups in the sodium hydroxide containing an ethanol–water mixture. Simultaneously the interaction between carboxyl groups and water was increased (b).

Bro and Sperati[6] observed a new band at 1686 cm^{-1} after titration of a COOH group containing fluorocarbon polymer in the same mixture which is characteristic of formed COON2 groups. We did not find similar absorptions in the spectra of our controlled hydrolysed samples. That means that sodium carboxylate was not formed under these conditions.

It is well known that alcohol can attack acyl halogenide groups in nucleophilic reactions. This way esters can be synthesized in water solutions with NaOH. So we conclude that during the controlled hydrolysis of the irradiated PTFE in the ethanol–water mixture a substantial amount of ester groups was formed, indicated by their carbonyl band at 1784 cm^{-1}. The corresponding CH stretching vibrations of the ester ethyl groups arise at 2994, 2949 and 2921 cm^{-1}, seen in *Figure 7*.

Figure 8 shows the spectrum of a corresponding low molecular weight model ester. The bands at 1785 cm^{-1} and near 2990 cm^{-1} are from the ester carbonyl group and ester ethyl group, respectively.

Esterification takes place only during refluxing of the irradiated PTFE in ethanol/water indicated to the band at 1785 cm^{-1}. This was not observed after storage in a saturated ethanol atmosphere. We found no band at 1785 cm^{-1} in the spectra, see *Figure 9*. Only adsorbed ethanol molecules were indicated by their CH stretching vibrations at 2991 cm^{-1}, see *Figure 10*. As expected, adsorbed water was removed from the surface during evacuation. This can be concluded from the decrease of the bands at 3701 and 3100 cm^{-1} and also from the decrease of the band at 1776 cm^{-1} (associated carboxyl groups) and the simultaneous increase of the band at 1810 cm^{-1} (free carboxyl groups) through breaking of the dimer bond.

Figure 2 again shows that a small part of the COF groups also remains under the controlled hydrolysis conditions. Because of this fact we increased the temperature of this hydrolysed PTFE in a variable temperature cell up to 250°C, see *Figure 3*. The result was the disappearance of the COF band at higher temperatures. The interpretation is that at temperatures above 100°C the water vapour essential better permeates the pores of the PTFE powder as liquid water. The COF groups hydrolyse entirely under this extreme condition. So it is seen in *Figure 3* that after cooling the COF band disappears. The intensity of the band of the associated COOH groups at 1776 cm^{-1} decreases at 250°C. Simultaneously the intensity of the band of the free acid groups rise. We observed an increase of the COOH groups at 1776 and 1810 cm^{-1} after cooling. The band at 1776 cm^{-1} indicates the reformation of the dimer on air. It proves that the hydrolysed COF groups at 250°C lead to COOH groups. These COOH groups have the same structure as the COOH groups formed by hydrolysis on atmospheric humidity. It is clearly to see that the band at 1792 cm^{-1} is unquestionably a reversible temperature dependence band. So it is improbable that this band assigns

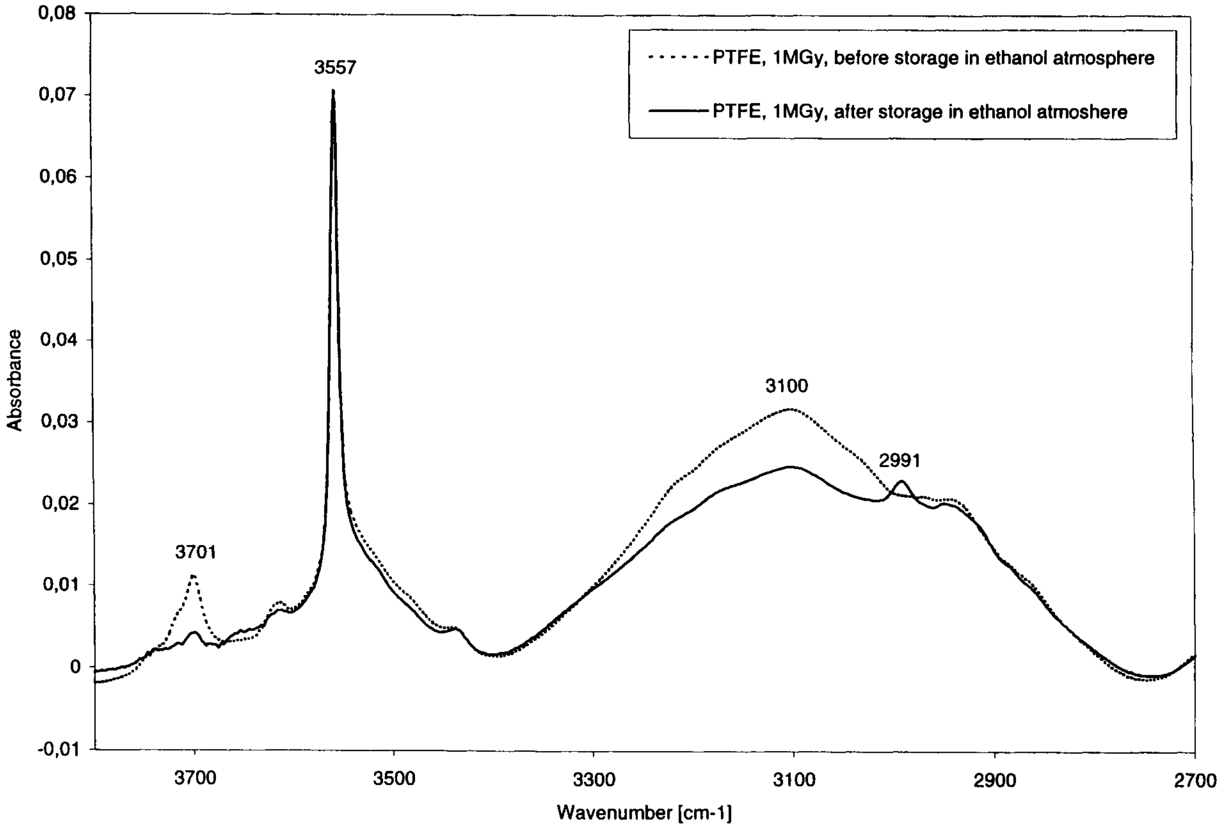


Figure 10 Infrared spectra (films) of PTFE irradiated with a dose of 1 MGy, in the region 3800–2700 cm^{-1}: (- - -) pressed powder annealed at 80°C for 2.5 h *in vacuo*; (——————) after the subsequent storage in saturated ethanol atmosphere at 50°C

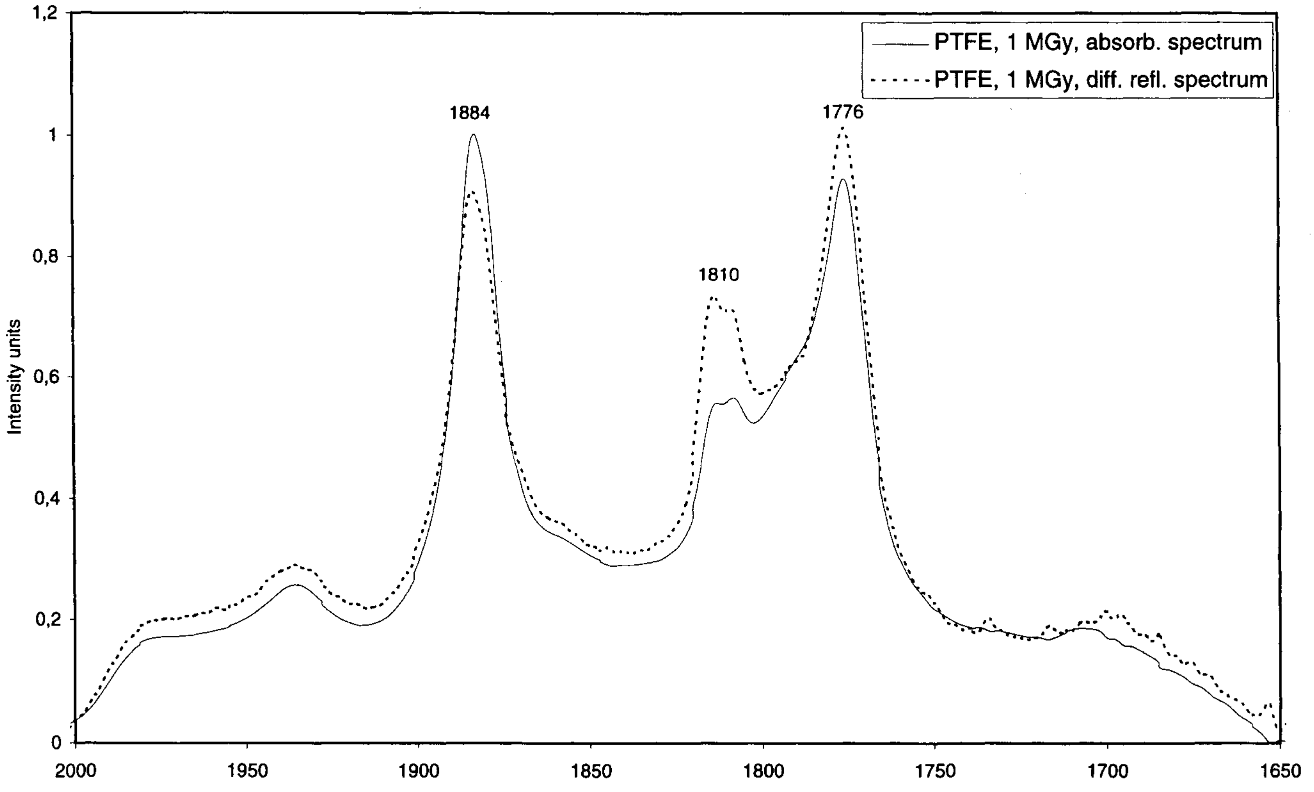


Figure 11 Comparison of the i.r. spectra of the bulk (transmission, film) and the surface (diffuse reflectance, powder) of PTFE in the region 2000–1650 cm^{-1}, irradiated with a dose of 1 MGy

exclusively, as stated in the current literature[3,7,8], because a vibration of a $C{=}CF_2$ double bond does not change under the influence of temperature and/or hydrolysis.

Our investigations using the i.r. transmission technique show that the COF groups were only completely degraded under extreme conditions. This fact indicates that the formation of the COF groups does not only occur on the surface of the PTFE particles. This is why we used the

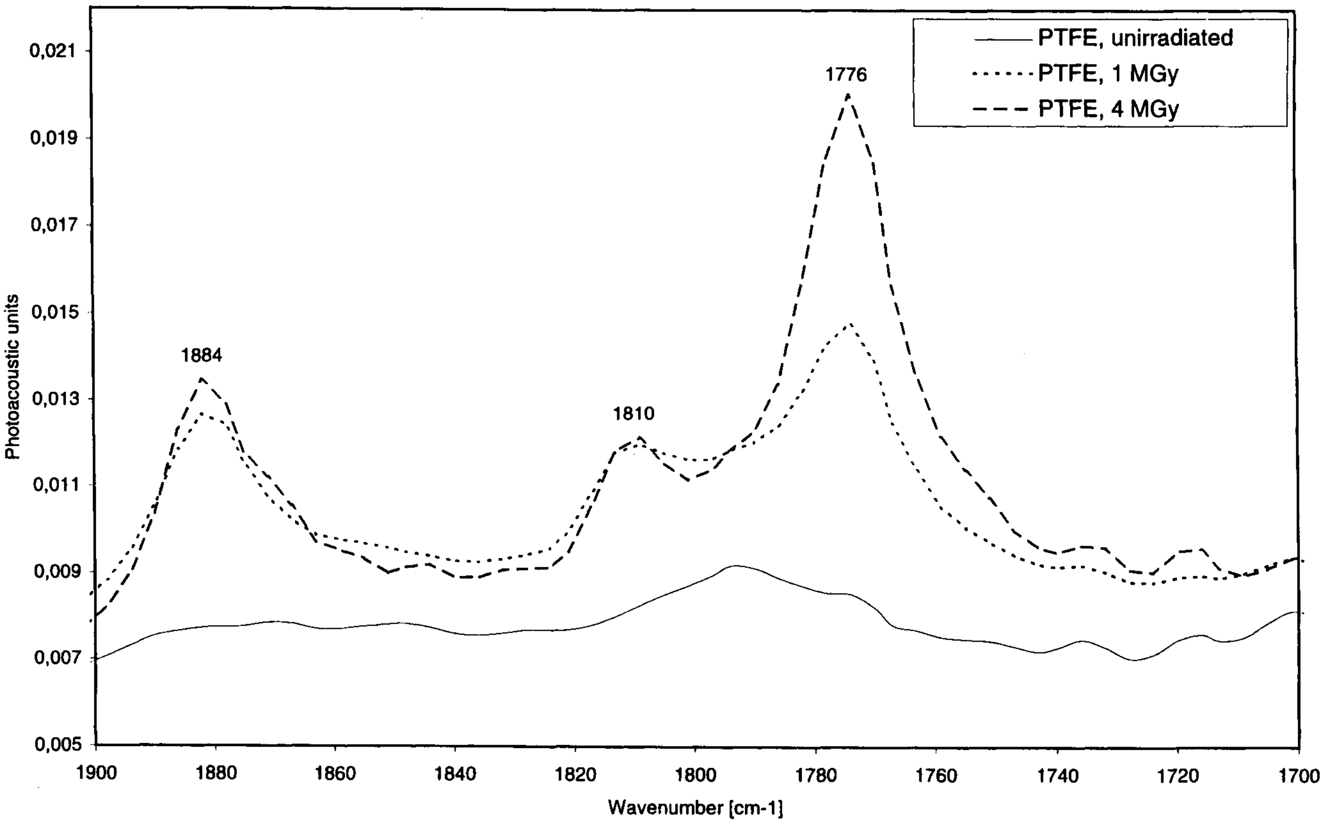


Figure 12 Photoacoustic (1.6 kHz) i.r. spectra (powder) of PTFE in the region 1900–1310 cm^{-1}, unirradiated and irradiated with doses of 1 and 4 MGy

diffuse reflectance spectroscopy to obtain more information about the distribution of the COF groups as well as the free and associated COOH groups between the surface regions and the inner part of particles. *Figure 11* shows the differences in the band ratios between the spectrum from transmission measurements of pressed films (characterization of the bulk phase) and the DR spectrum of the powder (characterization of the near surface region). In the DR spectrum the bands of free (1810 cm^{-1}) and associated (1776 cm^{-1}) acid groups are more intensive. This demonstrates a higher amount of both types of COOH groups in the surface region. On the other hand the amount of COF groups (1884 cm^{-1}) is smaller in the DR spectrum. The result establishes the hypothesis that a part of the COF groups is inaccessibly arranged in the inner part of the particle.

A further i.r. spectroscopic technique for the investigation of near surface regions is photoacoustic spectroscopy. We used this technique for the investigation of the influence of the radiation doses on the formation of new functional groups. The results are depicted in *Figure 12*. Here we can see that the intensity of the band of associated COOH groups strongly increases with the band of the COF groups, in contrast to the intensities shown in *Figure 1*. The intensity of the band of the free acid groups is approximately unchanged. This supports the results of DR spectroscopy that the concentration of the COF groups is diminished in near-surface regions. The conclusion is that the hydrolysis is preferred in near-surface regions.

CONCLUSIONS

We have investigated the influence of radiation dose and hydrolysis conditions on chemical structure of electron irradiated polytetrafluoroethylene by different methods of *FT*i.r. spectroscopy. The degradation of PTFE in air by irradiation leads to free and associated carboxylic acid and acid fluoride groups.

The concentration of these groups is different in near-surface regions and in the bulk phase. The hydrolysis of the COF groups is preferred in near-surface regions. We could establish this fact with various i.r. techniques, such as i.r. microscopy in transmission mode, diffuse reflectance spectroscopy and photoacoustic spectroscopy. These last two methods are more surface sensitive. The nature of the different associated carboxylic groups was determined with i.r. measurements after spontaneous and controlled hydrolysis and at different temperatures. These i.r. measurements show that the band at 1776 cm^{-1} is the band of an associated dimer, and the band at 1792 cm^{-1} is the band for hydrogen bonds between acid groups and water. After controlled hydrolysis a new band at 1784 cm^{-1} appears and the bands at 1776 and 1884 cm^{-1} decrease. This fact indicates that COF and associated COOH groups were influenced during refluxing in ethanol/water. The new band forms from the carbonyl groups of the formed esters. A small part of the COF groups also remains under this hydrolysis. Nevertheless, the COF band disappears after increasing the temperature up to 250°C due to the induced reaction of buried COF groups with water vapour. This fact indicates that the COF groups are not only present on the surface of the PTFE particles. Diffuse reflectance i.r. spectroscopy and photoacoustic i.r. spectroscopy demonstrate a greater amount of both COOH groups and a smaller concentration of the COF groups in the near-surface region. This result establishes the hypothesis that part of the COF groups is inaccessibly arranged in the inner part of the irradiated PTFE particle and that hydrolysis is preferred in near-surface regions.

ACKNOWLEDGEMENTS

The authors thank the Deutsche Forschungsgemeinschaft for financial support. They thank also W. Bürger (W.L. Gore and Associates GmbH) and V. Steinert (IPF, Dresden) for helpful discussions.

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