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*High Performance Polymers* 2014 26: 188 originally published online 22 October 2013
DOI: 10.1177/0954008313506724

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*Original Article*

High Performance Polymers

High Performance Polymers
2014, Vol. 26(2) 188–196
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DOI: 10.1177/0954008313506724
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# Evidence of chemical compatibilization reaction between poly(ether ether ketone) and irradiation-modified poly(tetrafluoroethylene)

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## Abstract

Poly(tetrafluoroethylene) (PTFE) micropowder is used as a lubricant in thermoplastic high-performance polymers, for example, in poly(ether ether ketone) (PEEK) to improve their tribological properties regarding friction and wear significantly. The achievable effect for improving such properties by using PTFE is not only determined by the added amount of PTFE micropowder in the PEEK-PTFE compound but rather by the possibility to couple and compatibilize the PTFE with the matrix material chemically that has a direct influence on the distribution of the PTFE particles in the polymer matrix and causes improved tribological and mechanical properties. The proof of a chemical reaction between PTFE and PEEK is difficult because the high-molecular weight PEEK is insoluble in all common solvents. The evidence of chemical coupling reaction between PEEK and irradiation-modified PTFE is shown by model studies using reactive OH-terminated PEEK oligomers. The use of diphenyl sulfone as a high-boiling reaction medium was necessary for the precondition to melt both reactants. In this way, qualitative differences have been achieved and confirmed using Fourier transform infrared spectroscopy. Thus, a safer and indirect detection of the chemical coupling (cc) between PEEK and PTFE (PEEK–PTFE–cc) was achieved.

## Keywords

PTFE, PEEK–PTFE–cc compounds, compatibilization reaction, chemical coupling

## Introduction

The modification of high-molecular weight poly(tetrafluoroethylene) (PTFE) by irradiation with electron beams is a process that has been investigated for many years at the Leibniz-Institut für Polymerforschung Dresden, Dresden, Germany. In this way, a PTFE micropowder is obtained by polymer degradation. In addition, reactive groups on the surface of PTFE particles are formed by radiation in the presence of air/oxygen. These groups allow the PTFE micropowder to react chemically with suitable thermoplastics by chemical coupling (cc).

The coupled polymer chains are stably anchored onto the PTFE particle surface by covalent bonds and compatibilize the PTFE in the respective matrix. This results in high stability during processing with regard to the PTFE distribution and low-friction coefficients as well as significantly higher wear resistance during tribological applications and hence provides longer service life of the components. Regardless of the excellent chemical resistance, PTFE is very sensitive to high-energy irradiation, such as electron beams, $\gamma$-rays, or X-rays. The high-energy radiation cleaves C–C and C–F bonds of the polymer chain, whereby primarily a degradation of the polymer chain takes place. Moreover, macro radicals are formed, which have a very long life time partially, due to the rigid structure of PTFE (Figure 1). The terminal or pendent radicals have a lifetime of several years at room temperature. In the presence of oxygen perfluoroalkyl peroxy radicals are formed, from which perfluoroalkane acid fluoride (–COF) arises by PTFE chain shortening and again perfluoroalkyl radicals. Acid fluorides can hydrolyze in the presence of water/moisture to acid groups (–COOH). The irradiation of PTFE has the following effects:

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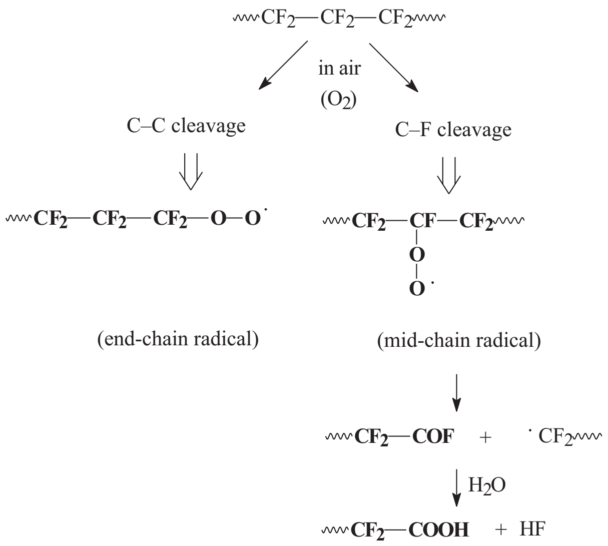


**Figure 1.** Degradation mechanism of poly(tetrafluoroethylene) during irradiation in air.[1,2]

- the reduction of the molecular weight by chain scission,
- the formation of persistent peroxy radicals ($–CF_xOO^{\cdot}$),
- the functionalization of the PTFE with carbonyl fluoride (–COF) and carboxylic acid (–COOH) groups after hydrolysis as shown in Figure 1.

Previously, the evidence of a cc of PTFE with polymers, for example, polyamides was shown directly with polyamide 6 (PA6) using Fourier transform infrared (FTIR) spectroscopy, where the coupling is effected by the reaction of –COF and –COOH groups with amide groups of the PA6 during reactive extrusion by a transamidation reactions (Figure 2). The aim was the combination of material properties of PA6 with excellent sliding properties of PTFE. The proof was shown by a special IR amide I absorption band at 1707–1709 cm$^{-1}$ for $–CF_2–CO–NH–PA6–$ groups when the excess PA was extracted.[3–5] This result was the basis and the beginning of the development of the new generation of chemically coupled and compatibilized polymer–PTFE tribomaterials.

The proof of the coupling of PTFE with poly(ether ether ketone) (PEEK) is more difficult because the high-molecular weight PEEK is insoluble in all common solvents. Only by means of hot methane sulfonic acid an extraction of PEEK can be performed. However, it is not saved that the extraction is carried out completely, and it could not be distinguished between coupled and free PEEK in IR spectroscopy. FTIR spectra might also show bands of a partially nonbonded PEEK. A proof of the cc needs two requirements:

1. The matrix polymer has to be extracted easily and completely and
2. It has to be shown that *no* coupling takes place under the same conditions with nonfunctionalized PTFE, for example, during the extrusion of the matrix polymer, so that no IR absorption bands of the matrix polymers are found anymore in the extracted PTFE (as negative evidence).

In order to meet the requirement (1), PEEK analogue oligomers with a higher content of phenolic end groups were synthesized, which are completely soluble in chloroform ($CHCl_3$) due to their small chain lengths and molecular weights, respectively.

For requirement (2), a PTFE must be used, which contains no or nearly no functional groups but otherwise possesses similar properties as an irradiation-modified PTFE (as the above-mentioned negative evidence). That means, the PTFE must also have significantly lower molecular weights (around $5 \times 10^5$ g mol$^{-1}$) than virgin PTFE (typically $10^7$ g mol$^{-1}$) to enable the processing by extrusion. It cannot be excluded the assumption that PEEK components are incorporated only physically into the additive PTFE. Therefore, it cannot be completely removed from such melt-processed mixtures by extraction. PTFE particles are in any case large enough to enclose parts or molecules of PEEK polymers into their interior and thereby PEEK residues are inaccessible for solvents. It must also be kept in mind that the chemical bonding between high-molecular weight polymer chains with small amounts of reactive end groups of PTFE is probably not particularly large and, therefore, a number of potential reaction sites cannot be saturated. To reduce such uncertainties, it was attempted to develop other techniques for the coupling of the PEEK polymer to the PTFE micropowder. It is also necessary to secure a greater probability of a reaction between the polymers and to ensure the visibility of new compounds. Therefore, we have been decided that well-defined OH-terminated PEEK oligomers will be used for the coupling reaction with radiation-activated PTFE instead of high-molecular weight polymers. We chose well-defined OH-terminated oligomers rather than the high-molecular weight PEEK polymer for a cc to irradiation-activated PTFE. The real coupling mechanism will be investigated next time intensively.

## Experimental

### Materials for preparing OH-PEEK oligomers

4,4′-Difluorobenzophenone (DFB; Sigma-Aldrich Chemie GmbH, Munich, Germany) was recrystallized twice from toluene and vacuum dried prior to use. 2,2′-Bis (4-hydroxyphenyl) propane (bisphenol A (BPA); Avocado Research Chemicals Limited, London, United Kingdom) was recrystallized twice from ethanol/water (1/1 v/v) and vacuum dried before use. Toluene (Fisher Scientific GmbH, Schwerte, Germany) was dried with sodium and *N*-methyl-2-pyrrolidone

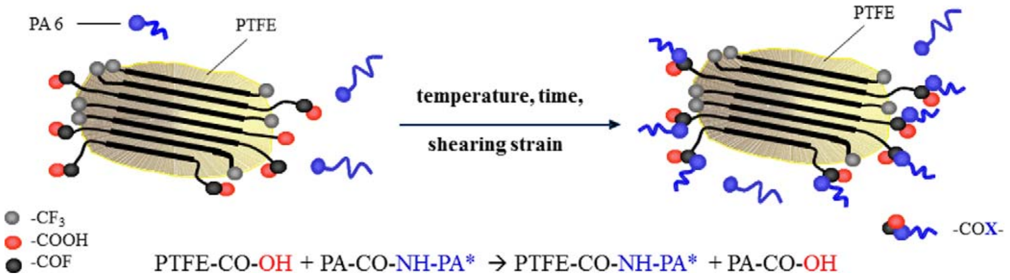


**Figure 2.** Mechanism of the coupling reaction between poly(tetrafluoroethylene) and polymers using polyamide 6 as example.

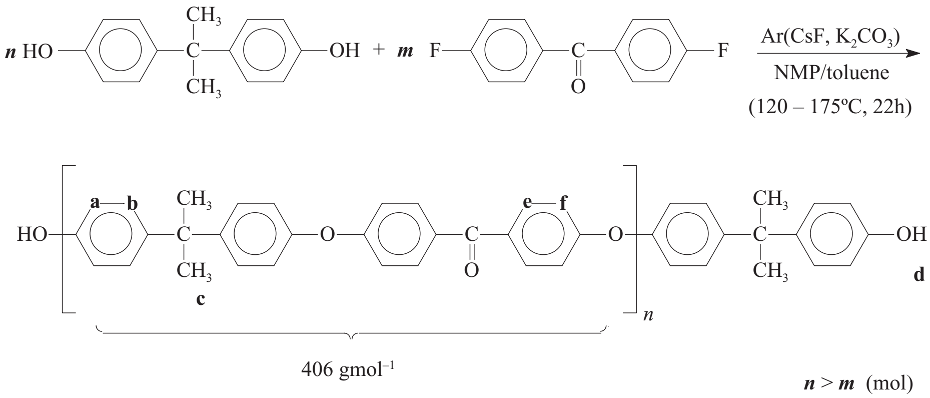


**Figure 3.** Synthesis of OH-PEEK oligomers.
PEEK: poly(ether ether ketone).

**Table 1.** Synthesized OH-terminated PEEK oligomers.

| OH-PEEK oligomer | Molar ratio DFB/BPA | DP[a] | $M_n$[b] (g mol$^{-1}$) |
|---|---|---|---|
| 1 | 1/1.1 | 10 | 4300 |
| 2 | 1/1.05 | 20 | 8300 |
| 3 | 1/1.02 | 50 | 20,500 |

PEEK: poly(ether ether ketone); DFB: 4,4′-difluorobenzophenone; BPA: 2,2′-bis(4-hydroxyphenyl); DP: degree of polymerization; NMR: nuclear magnetic resonance; $M_n$: number-average molecular weight; $CDCl_3$: deuterated chloroform; $^1H$ NMR: proton nuclear magnetic resonance.
[a] DP using both $M_n$ of NMR and repeating unit (406 g mol$^{-1}$).
[b] $^1H$ NMR spectroscopy carried out in $CDCl_3$.

(NMP, Sigma-Aldrich Chemie GmbH, Munich, Germany) with calcium hydride, and both solvents were distilled before use. Potassium carbonate ($K_2CO_3$, Fluka) was dried in vacuum at 100°C before use. Cesium fluoride (CsF, Aldrich) was dried 12 h at 150°C in vacuum. PEEK oligomers were synthesized by reaction of DFB with BPA in mixture of NMP with toluene (4/1 v/v) according to the method followed by Meier-Haack et al.[6] using $K_2CO_3$ and CsF at 175°C each for 22 h (Figure 3).

Obtained products were dried in vacuum at 150°C to remove residual solvents (to constant weight).

OH-PEEK: Proton nuclear magnetic resonance ($^1H$ NMR) spectroscopy (atom numbering according to Figure 3: $^1H$ NMR (500 MHz, deuterated $CHCl_3$ ($CDCl_3$), $\delta$, ppm): 1.71 s(c 6H), 6.76 dt(d H), 7.02 qt(a 2H, f 2H), 7.10 dt (d′ H), 7.26 dt (b 2H), 7.78 dt (e 2H).

The properties of the resulting OH-terminated PEEK oligomers are summarized in Table 1.

## *PTFE materials*

### *Commercial PTFE micropowder.*

- Zonyl® MP1100 (emulsion polymer, produced and irradiated by DuPont) has a high concentration of functional groups, for example, carboxyl groups.
- Zonyl® MP1600 (emulsion polymer, produced by a special direct polymerization technique by DuPont Fluoroproducts, Wilmington, USA) has nearly no functional groups (Table 2).

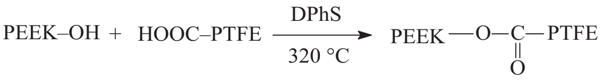
### *Modified PTFE regenerate.*

- PTFE-A: PTFE regenerate from the cutting processing of PTFE semifinished parts (suspension polymer and milled chipping) was irradiated by γ-rays, and then finely ground using a rotor speed mill (120 μm). This PTFE was irradiated in an oxygen atmosphere resulting in a particularly high concentration of functional groups (–COF and –COOH).
- PTFE-B: The same PTFE regenerate was wetted before irradiation. The obtained degraded PTFE has

**Table 2.** The modified-PTFE powders used for the investigation of the coupling reaction with OH-PEEK oligomers.

| | | | | Functional groups ((C=O)/($CF_2$) × $10^6$; from FTIR) | | | |
|---|---|---|---|---|---|---|---|
| No | PTFE samples | $M_w$ (g $mol^{-1}$) | ESR (spin $mg^{-1}$) | –COF | $–COOH_{free}$ | $–COOH_{associated.}$ | Total |
| 1 | PTFE-P Zonyl® MP1100 | $2.5 \times 10^5$ | 765 | 603 | 177 | 498 | 1278 |
| 2 | PTFE-P Zonyl® MP1600 | – | – | – | – | – | – |
| 3 | PTFE-A (500 kGy/$O_2$/CaO)[a] | $1.7 \times 10^5$ | 821 | 765 | 103 | 56 | 924 |
| 4 | PTFE-B (500 kGy/–/$CaCO_3$/$H_2O$) | $3.8 \times 10^5$ | 53 | 16 | 0 | 0 | 16 |

PEEK: poly(ether ether ketone); PTFE: poly(tetrafluoroethylene); $M_w$: molecular weight; ESR: electron spin resonance; FTIR: Fourier transform infrared spectroscopy; $O_2$: oxygen; CaO: calcium oxide; $CaCO_3$: calcium carbonate; $H_2O$: water.
[a] Low-bulk density.



$$\text{PEEK–OH} + \text{HOOC–PTFE} \xrightarrow[320\ °C]{\text{DPhS}} \text{PEEK}-\text{O}-\underset{\overset{\|}{\text{O}}}{\text{C}}-\text{PTFE}$$

**Figure 4.** Chemical reaction between COOH-PTFE and OH-PEEK oligomers.
PEEK: poly(ether ether ketone); PTFE: poly(tetrafluoroethylene).

> almost no functional groups and no free radicals. The mechanism is unknown but the formation of peroxide radicals and further functional groups is prevented by the added water.

Thus, comparable PTFE products were available, with or without functional groups (Table 2).

## *Model reactions*

*Aim.* Evidence for the coupling of PTFE with OH-PEEK oligomers is through the functional groups (indirectly by extraction of the excess/noncoupled OH-PEEK oligomer after the coupling reaction) by IR spectroscopy

Evidence for the absence of the cc reaction with the absence of functional groups in PTFE supports the evidence of coupling by the statement that OH-PEEK oligomer is generally fully extractable.

*Approach.*

1. Preparation of soluble OH-PEEK oligomers.
2. Coupling of PTFE with the OH-PEEK oligomers
   - using a microcompounder (5 $cm^3$, DSM, Netherlands), (15 wt% PTFE, 3 min, 270°C)
   - in solution (diphenyl sulfone (DPhS) media, protective atmosphere of argon, sodium hydroxide drying tube) at 320°C,
3. Extraction of noncoupled OH-PEEK oligomer from PTFE

The coupling mechanism between OH-PEEK oligomers and modified/activated PTFE is not explained completely. This mechanism will be investigated and published next time (Figure 4).

The coupling between OH-PEEK oligomers and PTFE regenerates was performed using different methods, to rule out inclusions of the matrix polymer in the PTFE formed by shearing during the extrusion process in the microcompounder, which would simulate a coupling reaction as a false statement. In this procedure, a medium is used, which does not permit the formation of "stable" physical mixtures with nonextractable PEEK contents but permits chemical reactions between the components. As a solvent for both polymer materials DPhS was chosen whose boiling point is 379°C and thus exceeds the melting point of PTFE (327°C). The interaction of the PEEK-OH with the DPhS was also tested. Already at a temperature of 220°C both substances form a solution-like state. After cooling the mixture was tested for the solubility with CHCl3 and *N*,*N*-dimethylacetamide (DMAc). In both solvents, the substances are completely soluble and can be well extracted from other blends.

According to Figure 5, 12 wt% of OH-PEEK oligomer was mixed with 36 wt% of PTFE at 330°C with stirring and under argon atmosphere in DPhS (first and second step). Afterward, the solution was stirred for further 1.5 h at 325–330°C. The hot-molded mixture was poured into methanol, stirred, and washed several times. Then, the product was boiled in methanol for additional 0.5 h and washed in methanol for further 12 h. The separated solid was dried under vacuum at 60°C. The light brown product is cooled during grinding, divided, and then extracted with CHCl3 for 4 days each at 61°C or at 220°C with DMAc using the Soxhlet apparatus (third step). The samples of reactants, products, and extracts were analyzed using FTIR spectroscopy. These experiments are summarized in Table 3.

# Characterization

## *Determination of the molecular weights of the OH-PEEK oligomers*

NMR spectroscopy was carried out on a DRX 500 spectrometer (Bruker, Germany) operating at 500.13 MHz for $^1H$ using $CDCl_3$ as solvent. The spectra were referenced to the solvent signal $\delta(^1H) = 7.26$ ppm.

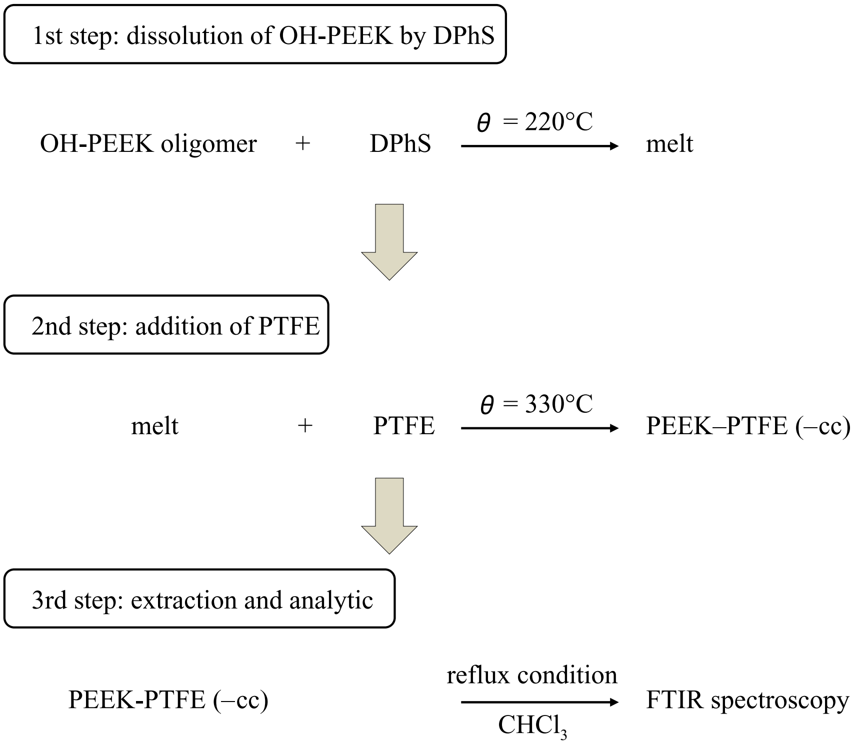


**Figure 5.** Description of the approach for performing of model reactions.

**Table 3.** Realized model reactions (1–4).

| | | PEEK–PTFE–cc compounds | |
|---|---|---|---|
| No[a] | Educts | Solvent for synthesis | Solvent for extraction |
| – | OH-PEEK oligomer | DPhS | DPhS |
| 1 | OH-PEEK + Zonyl® MP1100 500 kGy[b] | –[c] | $CHCl_3$ |
| 2 | OH-PEEK + Zonyl® MP1600[d] | –[c] | $CHCl_3$ |
| 3 | OH-PEEK + PTFE-A 500 kGy | DPhS | $CHCl_3$ |
| 4 | OH-PEEK + PTFE-B 500 kGy | DPhS | $CHCl_3$ |

PEEK: poly(ether ether ketone); PTFE: poly(tetrafluoroethylene); cc: chemical coupling; DPhS: diphenyl sulfone; $CHCl_3$: chloroform.
[a] According to the numbering in Table 2.
[b] Commercial product, irradiated emulsion polymer, produced by DuPont.
[c] Prepared with a microcompounder (15 wt% PTFE, 3 min, 270°C).
[d] Commercial product, nonirradiated emulsion polymer (prepared by controlled polymerization by DuPont).

### *Characterization of blends*

The IR spectra were recorded using FTIR spectrometer Tensor 27 (Bruker, Germany) in transmission mode (32 scans, 2 $cm^{-1}$ resolution, 4000–400 $cm^{-1}$). Powders were pressed into films at room temperature with the thickness ($d$). Molar ratios of –COF and –COOH were calculated according to equation (1) using a calibration factor (CF in millimeter) as described by Buckmaster et al.[7] The IR absorbance ($A$) was measured at 1883 $cm^{-1}$ (–COF), 1815/1809 $cm^{-1}$ (–$COOH_{free}$) and 1777 $cm^{-1}$ (–$COOH_{associated}$), respectively.

The electron spin resonance (ESR) spectra were recorded with an ESR spectrometer (MiniScope MS 200; MagnetTech GmbH, Germany) at room temperature. The modulation amplitude was 0.1 mT, and the microwave power was 1.0 mW.

Scanning electron microscopy was performed using a Leo 435 VP (Zeiss, Jena, Germany) with secondary electron detection. The preparation of the samples was carried out as cryo fracture in liquid nitrogen (−170°C).

## Results and discussion

Reference spectra of OH-PEEK oligomer and Zonyl® MP1100 were recorded (Figure 6), which are necessary

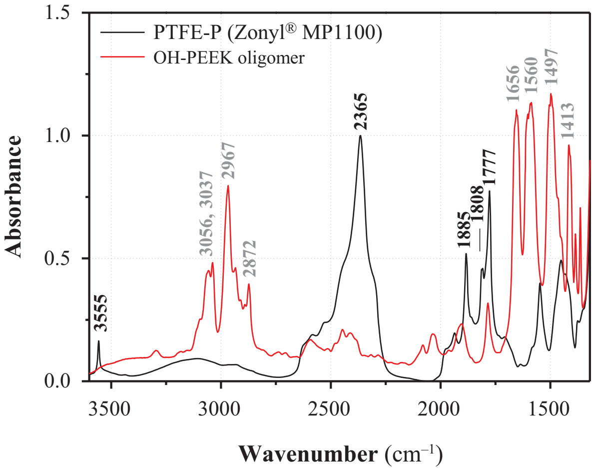


**Figure 6.** ATR spectra of high molecular weight virgin PTFE (Zonyl® MP1100) and OH-terminated PEEK-oligomer (compared with Table 4).
ATR: attenuated total reflectance; PEEK: poly(ether ether ketone); PTFE: poly(tetrafluoroethylene).

for the evaluation of the PEEK/PTFE products. The reference spectrum of PEEK could be measured only as attenuated total reflectance spectrum since it cannot be pressed to a film sample for transmittance spectrum.

The FTIR bands belonging to the OH-PEEK oligomers are marked in red (compared with Table 4).

The OH-PEEK oligomer 2 was mixed with Zonyl® MP1100 and Zonyl® MP1600, respectively, and these mixtures were compounded for 3 min at 270°C in the microcompounder. After grinding the PEEK–PTFE–cc, products were extracted with $CHCl_3$ at 61°C. This procedure was performed also with nonirradiated PTFE (Zonyl® MP1600), which theoretically should contain nearly no functional groups. Nevertheless, only very small residues of PEEK-oligomer were identified in the FTIR spectrum (Figure 7). The cause is likely that in Zonyl® MP1600 a very low concentration of COOH groups exists, which can attend in the coupling reaction with the OH-PEEK oligomer.

The Zonyl® MP1100 shows a distinctive coupling reaction with the OH-PEEK oligomer. Zonyl® MP1600 shows a minor, still observable coupling reaction to the OH-PEEK oligomer.

Different methods of coupling of OH-PEEK oligomers with PTFE were tested by laboratory experiments, and the type of the coupling was indirectly determined. It is possible to say if a modified PTFE with a certain number of functional groups is melted and extruded with another polymer or oligomer to form a compound, both physical mixed and chemically coupled products of the two components could be formed. The presence of chemical bonds between polymers was confirmed by the *quantitative* difference of extracted products of OH-PEEK oligomer and PTFE with many functional groups or PTFE with no functional groups (Figure 7).

Only chemical bonds between activated PTFE and OH-PEEK oligomer could be formed in the case, if both compounds can react with each other in DPhS. This medium reduces significantly the possibility of a physical inclusion of the PEEK in the PTFE at high reaction temperatures.

Two alternative tests have been performed for comparison with equal reaction conditions and different PTFE components:

- irradiated PTFE (No 3) possesses many functional groups and
- nonirradiated PTFE (No 4) has almost no functional groups.

Similarly, to Zonyl® MP1600, no chemical coupling should be detected with PTFE No 4.

The results of these experiments are shown in Figure 8 and the special intensified parts in Figures 9 and 10. The presence of OH-PEEK oligomer in the extracted PTFE product No 3 is clearly observed: methyl bands at 3000 $cm^{-1}$ and ring vibrations at 1600 $cm^{-1}$ after extraction are still very pronounced (Figures 9 and 10).

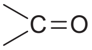
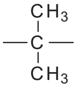
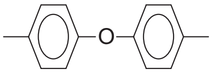
The extracted PTFE product of No 4 has no detectable methyl bands 3000 $cm^{-1}$ and/or ring vibrations around 1600 $cm^{-1}$ as well as other absorption bands, which originate from OH-PEEK oligomer meaning no coupling reaction is detectable.

The blue spectrum in Figures 9 and 10 represents the proof of coupling reaction in the extracted PEEK–PTFE–A–cc (No 3).The presence of a chemical bonding between the PTFE and the PEEK oligomer is clearly confirmed by the *qualitative* differences between the extracts of PEEK-PTFE, containing either PTFE with many functional groups or without functional groups. In the case of missing functional groups, there is no evidence for a chemical linkage as can be seen in Figures 9 and 10. The direct evidence of the covalent bond between OH-PEEK oligomer and activated PTFE is not possible because the concentration is too low for an analytical proof.

This is a safe indirect evidence of the chemical coupling reaction between OH-PEEK oligomer and chemically activated PTFE. The investigations will be continued. PTFE is not dimensionally stable upon cooling from the melt. Due to this shrinkage, cracks usually result that disrupt binding to the matrix and the resulting compound has reduced mechanical properties. This phenomenon is clearly reduced by the chemical compatibilization between the PEEK and the PTFE because PTFE is bonded to the matrix. Figure 11 clearly shows an example of commercial PEEK (VESTAKEEP® 3300G, Evonik Industries, Deutschland) with 20 wt% PTFE (PTFE-A).

The chemical compatibilization of commercial PEEK with PTFE also revealed improved mechanical and tribological characteristics in comparison to the commercial PEEK. The impact strength of PEEK–PTFE–cc materials increases from 3.5 to 26.0 kJ $m^{-2}$. The coefficient of wear on steel 100Cr6 (block-on-ring test, $F_N$ = 200 N) decreases from $1.0 \times 10^{-5}$ to $9.6 \times 10^{-7}$ $mm^3$ (or N $m^{-1}$).

**Table 4.** Assignment of the IR vibration bands of high-molecular weight virgin PTFE (Zonyl® MP1100) and OH-terminated PEEK-oligomer (compared with Figure 1).

| IR band ($cm^{-1}$) | Chemical structure | Designation | References |
|---|---|---|---|
| 3555 | $–COOH_{free}$ | –OH stretching vibrations of acid group | 1 |
| 3056, 3037 | $=C–H$ | aromatic | 8 |
| 2967 | $–CH_3$ | Stretching vibration | 8 |
| 2872 | $–CH_3$ | Stretching vibration | 8 |
| 2365 | $–CF_2–$ | Backbone, overtone | 1 |
| 1885 | $–COF$ | Carbonyl vibration | 1 |
| 1808 | $–COOH_{free}$ | Carbonyl vibration | 1 |
| 1777 | $–COOH_{associated}$ | Carbonyl vibration | 1 |
| 1715 |  | Stretching vibration | 8 |
| 1656 | $–C=C–$ | Aromatic ring vabration | 8 |
| 1560 | $–C=C–$ | Aromatic ring vibration | 8 |
| 1497 | $–C=C–$ | Aromatic ring vibration | 8 |
| 1413 | $–CH_3$ | Deformation vibration | 8 |
| 1350 |  $—\overset{CH_3}{\underset{CH_3}{C}}—$ | $CH_3$ deformation vibration | 8 |
| 1250 |  | C–O stretching vibration | 8 |

PEEK: poly(ether ether ketone); PTFE: poly(tetrafluoroethylene); IR: infrared.

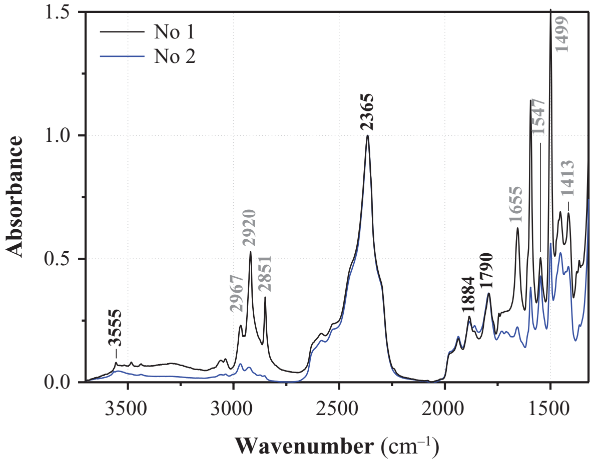


**Figure 7.** IR spectra of reaction products using the microcompounder with 15 wt% PTFE (No 1: PEEK–PTFE–P–cc (Zonyl® MP1100) and No 2: PEEK–PTFE–P–cc (Zonyl® MP1600), see Table 3). IR: infrared; PEEK: poly(ether ether ketone); PTFE: poly(tetrafluoroethylene).

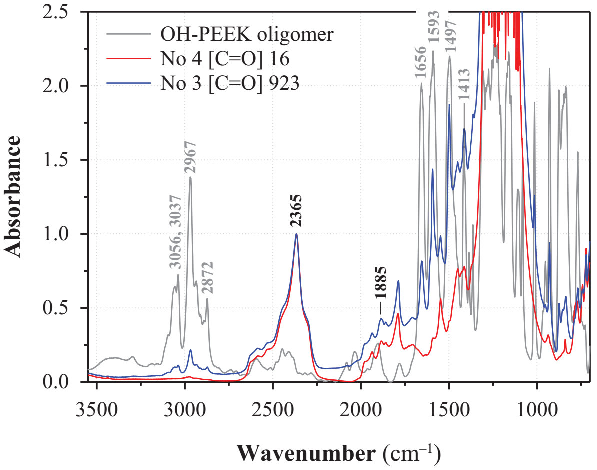


**Figure 8.** IR spectra of the extracted product of the reactive coupling between PEEK and PTFE (the samples extracted with CHCl3 are compared to the PEEK oligomer). IR: infrared; PEEK: poly(ether ether ketone); PTFE: poly(tetrafluoroethylene).

Based on these results, it can be concluded that by the compatibilization of PTFE-A (20 wt% in VESTAKEEP 3300G) achieved increased impact strength and improved antiwear performance.[9–11]

## Conclusions

Two different methods for the coupling of special PEEK oligomers with PTFE were tested, and the products were analyzed using FTIR spectroscopy. It can be asserted that if a sufficiently activated PTFE with functional groups immediately merged with another functionalized polymer or oligomer by compounding, a cc with a compatibilization of the immiscible products could be observed. This compatibilization improves the physical interactions in the material system. The presence of chemical bonds between the coupling partners is confirmed analytically. Quantitative differences between the extracts of PTFE with many functional groups (Zonyl®

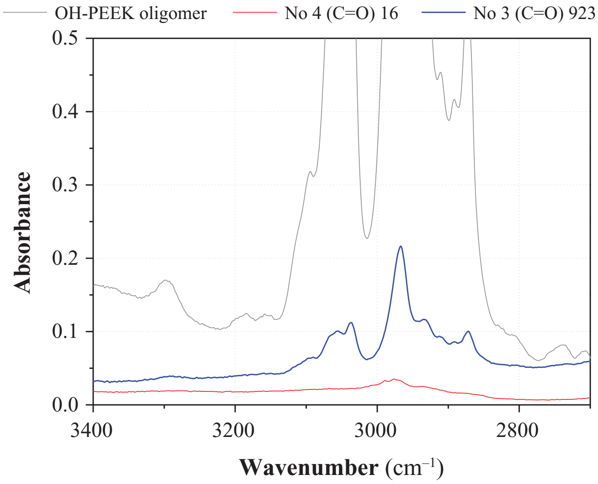


**Figure 9.** IR spectra of the extracted product of No 3 and No 4 (magnified section: 3400–2700 cm$^{1}$) compared with OH-PEEK oligomer (aliphatic and =CH aromatic vibrations).
IR: infrared; PEEK: poly(ether ether ketone).

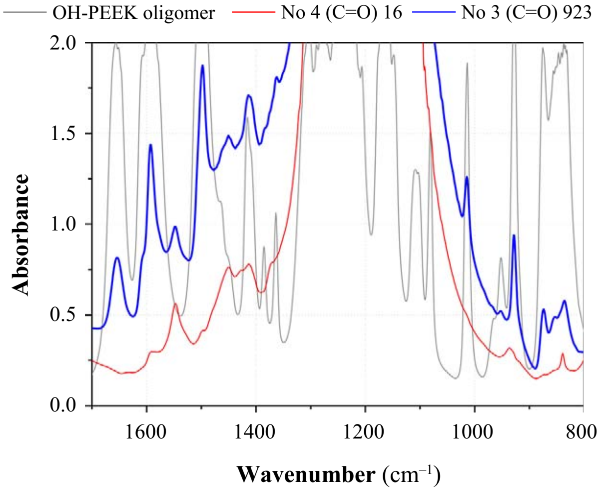


**Figure 10.** IR spectra of the extracted product of No 3 and No 4 (magnified section: 1700–800 cm$^{-1}$) compared to OH-PEEK oligomer (C=C aromatic and ring vibrations).
IR: infrared; PEEK: poly(ether ether ketone).

MP1100) or without functional groups (Zonyl® MP1600) are a clear evidence. The presence of only chemical linkage between the polymers is confirmed by qualitative differences between the extracted PTFE products from PEEK–PTFE–cc with an activated PTFE with many functional groups, where bonds occur, and PEEK–PTFE with PTFE without functional groups, in which no bonds could be formed.

Such qualitative differences have been achieved by our experiments and confirmed by FTIR spectroscopy as a safe and indirect detection of the cc between activated PEEK and PTFE to PEEK–PTFE–cc.

Only chemical bonds, formed between polymers, compatibilize the materials in a blend system and

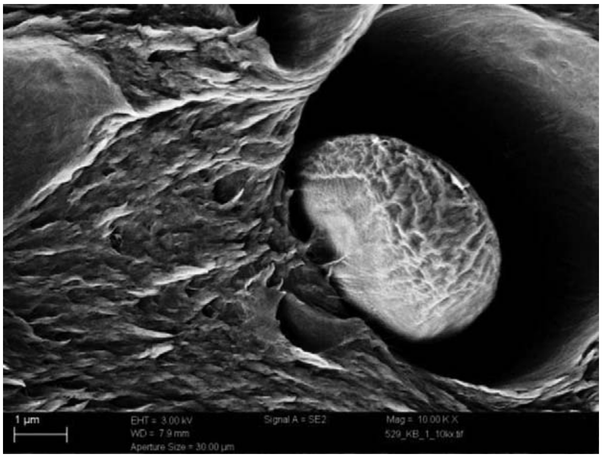


**Figure 11.** SEM micrographs of cryofractured surfaces of PEEK–PTFE–cc using irradiated PTFE-A (20 wt%).
SEM: scanning electron microscopy; PEEK: poly(ether ether ketone); PTFE: poly(tetrafluoroethylene); cc: chemical coupling.

improve the stability during processing and the mechanical as well as tribological properties in PEEK–PTFE–cc materials. In addition, shearing during processing of polymers has a significant contribution to the effective cc reaction.

## Acknowledgments

The authors would like to thank Dr H. Komber for the nuclear magnetic resonance measurements and interpretation, Mrs G. Adam and Dr M. Malanin for the Fourier transform infrared characterization of the poly(tetrafluoroethylene) samples, and Dr C. Vogel for helpful discussions.

## Funding

The present work was financially supported by the Bundesministerium fuer Bildung und Forschung (BMBF) Innovationsinitiativen Neue Länder (grant number 03FO2172).

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