

# CHEMICALLY MODIFIED PTFE PARTICLES AS SOLID LUBRICANT ADDITIVE FOR THE FIXATION ON SUBSTRATE SURFACES

T. Hoffmann<sup>1\*</sup>, D. Lehmann<sup>1</sup>, M. Anders<sup>2</sup>, T. Schmidt<sup>2</sup>, T. Heinze<sup>3</sup>, M. Michael<sup>3</sup>

<sup>1</sup>Leibniz-Institut für Polymerforschung Dresden e.V., 01069 Dresden, Hohe Str. 06, Germany

<sup>2</sup>Institut für Technische Logistik und Arbeitssysteme, Fakultät Maschinenwesen, Technische Universität Dresden, Germany

<sup>3</sup>Institut für Fördertechnik und Kunststoffe, Fakultät Maschinenbau, Technische Universität Chemnitz, Germany

## ABSTRACT

During the irradiation of high molecular weight poly(tetrafluoroethylene) (PTFE) in presence of oxygen perfluoroalkyl(peroxy) radicals and functional groups are formed which allow chemical coupling reactions (cc = chemical compatibilized) with oils and plastics. Contrary to the well-known inert properties of perfluorinated organic compounds high-effective additives can be produced by radiation modification and subsequent chemical compatibilization of such substances with olefinically unsaturated groups of oils/lubricants. By the irradiation process high molecular weight PTFE degrades by C-C and C-F bond scission to lower molecular weight PTFE microparticles which possess perfluoroalkyl(peroxy) radicals. These radicals are used for the chemical compatibilization reaction with olefinically unsaturated groups base oils. The tribological properties and the dispersion stability of the resulting oil-PTFE-cc (cc = chemical compatibilized) dispersions are significantly enhanced in comparison to physical mixture of oil and PTFE micropowder. These oil-PTFE-cc-dispersions show primarily anti-wear (AW) properties. The use of reactive groups (e.g. phosphite groups) in the oil gives the dispersions extreme pressure (EP) properties additionally. This article demonstrates the usefulness of the oil-PTFE-cc-dispersions in rolling bearings using phosphite-modified PTFE products as additive in lubricants (FE-8 test). The investigations are completed by the examination of roller elements by SEM/EDX analysis. A model is shown to explain the effect of phosphite groups on oxidic/hydrolytic metal surfaces.

Keywords: PTFE, high performance lubricant, oil-PTFE-cc dispersion

\*Corresponding author: Thorsten Hoffmann ([jthoffmann@arcor.de](mailto:jthoffmann@arcor.de)), phone: +49 17697813310

## INTRODUCTION

Regardless of its excellent chemical resistance, poly(tetrafluoroethylene) (PTFE) is very sensitive to high-energy radiation, such as electron beam and  $\gamma$ - or X-ray irradiation. 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

functional groups and macro radicals are formed. Perfluoroalkyl(peroxy) radicals arose in the presence of air/oxygen have a lifetime of several years at room temperature due to the rigid structure of PTFE. The radiation modification of poly(tetrafluoroethylene) is an established method and has been extensively studied at the Leibniz-Institut für Polymerforschung Dresden [1,2].

In addition to the above mentioned perfluoroalkyl(peroxy) radicals reactive groups (-COF, -COOH) are formed on the surface of PTFE particles during irradiation in presence of air/oxygen by PTFE chain degradation. Radicals and functional groups enable the chemical reaction of PTFE micropowder with suitable oil groups as well as with thermoplastics realizing the chemical compatibilization [3–5].

The perfluoroalkyl(peroxy) radicals on the surface of PTFE particles react fast with olefinically unsaturated groups of oil molecules by radical addition reactions during the dispersion process. The concentration of radicals in the particles has to be  $> 5 \cdot 10^{17}$  spin  $\cdot$  g<sup>-1</sup> PTFE to achieve a chemical compatibilization reaction with oil molecules. After this primary compatibilization reaction secondary allylic radicals are formed at the compatibilized molecules as intermediates and may react with further oil molecules at a slower reaction rate or can be stabilized to final products e.g. by recombination.

The chemically compatibilized oil chains are anchored to the PTFE particle surface by covalent bonds. This leads to a stable dispersion, as a precondition for the lubrication effect of the PTFE particles in the friction gap. The model of the chemical compatibilization reaction between PTFE micropowder and olefinically unsaturated groups of oils to oil-PTFE-cc dispersions is illustrated in Figure 1 and described in the references [6–8]. These oil-PTFE-cc dispersions show primarily anti-wear (AW)

properties. The use of reactive groups in oil gives the dispersions extreme pressure (EP) properties additionally. In addition, it should be noted that the molecular weight of the primary particle of irradiated PTFE is much greater ( $> 250,000$  g $\cdot$ mol<sup>-1</sup>) than the molecular weight of the oil molecules ( $\sim 1,000$  g $\cdot$ mol<sup>-1</sup>). Typical representatives are ester-based oils (TMP-ester) and poly- $\alpha$ -olefin (PAO). Their chemical structure and molecular weight are shown in Figure 1.

During the dispersion process the fragmentation and distribution of agglomerated PTFE microparticles takes place firstly. This process is important for the accessibility of the perfluoroalkyl(peroxy) radicals located in the amorphous areas of the PTFE micropowder and thus the necessary prerequisite for the reaction with the double bonds of oil groups. The diameter of a single PTFE microparticle is 0.2  $\mu$ m however these microparticles tend toward agglomeration. Figure 2 shows a typical agglomerate that has a dimension of more than 10  $\mu$ m. It is therefore necessary to shear that agglomerated particles. For reactive dispersion, the rotor-stator principle (Ultra-Turrax<sup>®</sup>) was used as shearing method. The energy input necessary for fragmentation and distribution of the agglomerated PTFE particles is achieved with this process by shearing, impact and turbulence. The medium is drawn axially into the dispersing unit and pressed radially through the openings on the tool (see Figure 2). The very high shearing forces are generated by high speed and small distance between the rotor and stator [9].

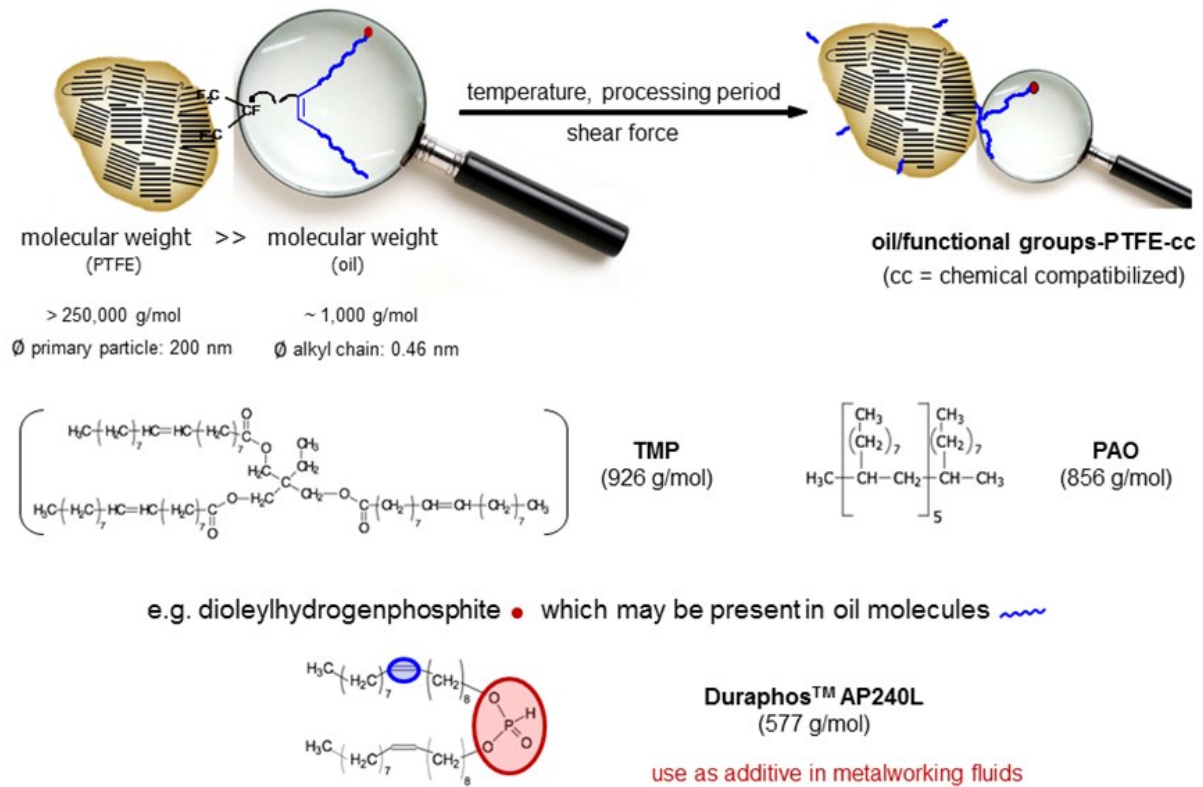


Figure 1. Preparation of oil-PTFE-cc dispersions by radical transfer reaction between perfluoroalkyl(peroxy) radicals and olefinically unsaturated oil groups which may have additionally functional groups.

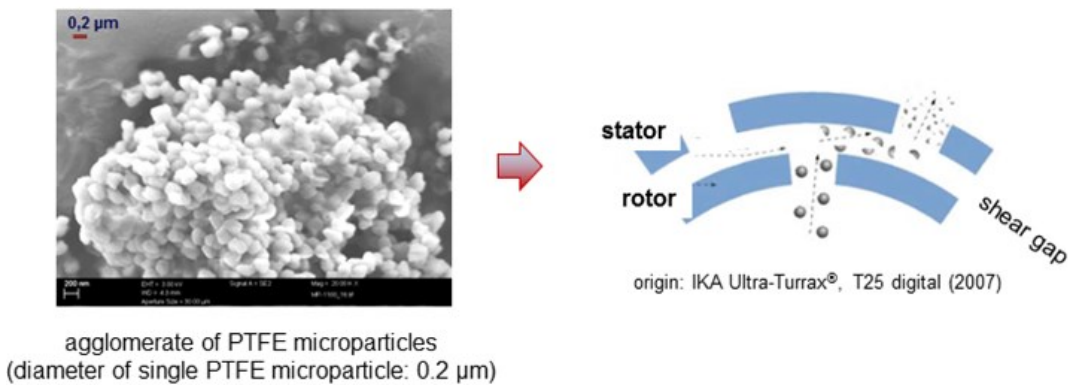


Figure 2. SEM micrograph of agglomerated PTFE microparticles (SE 2 detector, 20,000x enlargement) (left); effective fragmentation and distribution of agglomerated PTFE microparticles is prerequisite for radical transfer reaction (right).

## MATERIALS AND METHODS

The ester oil trimethylolpropane trioleate (TMP) purchased by ILCO Chemikalien GmbH (Germany) as well as a poly- $\alpha$ -olefin

(PAO) supplied by Lehmann & Voss & Co. KG (Germany) were used as base oils. Oil-PTFE-cc containing additives (LUBOFÉ-additives O, P, and PD) were delivered by *perfluorence* GmbH. The PTFE micropowder

(Zonyl® MP1100) and the extreme pressure (EP) additive diolethylhydrogenphosphite (Duraphos™ AP240L) were purchased from C.H. Erbslöh KG (Germany). All the chemicals were used as delivered.

The investigation of the wear protection suitability of lubricants according to DIN 51819 was carried out on the FAG rolling bearing FE-8 lubricant test bench equipped with two axial cylindrical roller bearings type 81212 under following conditions: axial load = 80 kN,  $\vartheta = 80\text{ }^{\circ}\text{C}$ , duration = 80 hours, speed =  $7.5\text{ min}^{-1}$  (Institut für Maschinenelemente und Maschinengestaltung IME, RWTH Aachen). A very small lubricating film thickness can be formed under the chosen high load and low speed. Furthermore, high demands are made on the wear behavior of the lubricant because of the occurring high slip that was caused by drilling movement of the cylinder rolls.

Figure 3 shows the structure of a FE-8 test head according to DIN 51819, cited from [10]. The required axial load on the test bearing is done with a disc spring set and a spacer disc, which is present in different thicknesses. The stress in the standard test is 80 kN. The test bearings are lubricated via two oil inlets with each  $0.1\text{ L}\cdot\text{min}^{-1}$ . For each lubricant two axial cylindrical roller bearings were used. The LUBOFÉ-additives were

stirred over the entire test period. The oil pumps worked without filters. The wear dimensions (mg) of each bearing was determined from the weight difference of the 15 cylinder rolls before and after the test = wear mass of the roller set. For the lubricants presented here the FE-8 test could be performed only once.

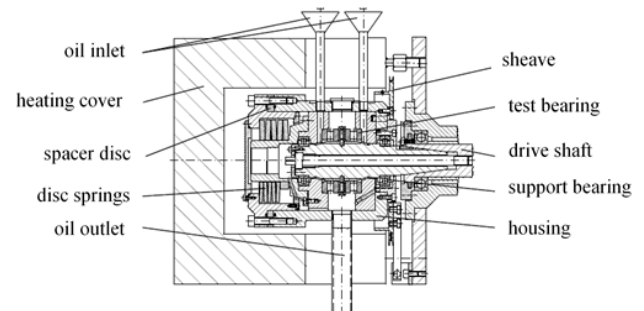


Figure 3. FE-8 test head according to DIN 51819.

## RESULTS AND DISCUSSION

An oil-wear analysis test on cylindrical roller bearings was performed (FE-8 test). The results will be shown in Figure 4 in the form of frictional torque as function of test period (80 hours) in the mixed friction region. The wear dimension of the roller set was determined after the test ends and the results are summarized in Table 1.

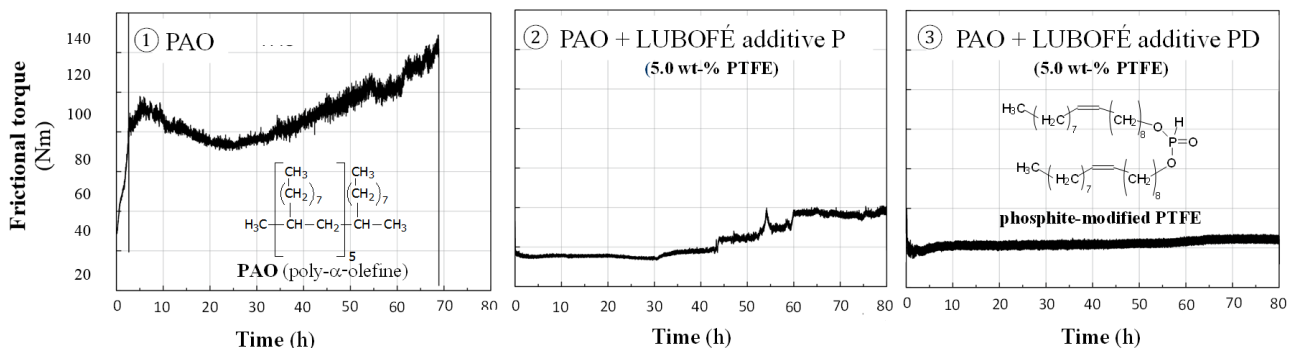


Figure 4. Classification of the anti-wear effect during the FE-8 rolling bearing test of PAO and two PAO grades modified with LUBOFÉ-additives (frictional torque curves dependent on test duration (80 hours) in the mixed friction region).

Table 1. Comparison of the wear dimensions after the FE-8 rolling bearing test depending on the presence of AW/EP additive in PAO.

No.	lubricant/base oil		wear dimensions <sup>1</sup> (mg)	category	frictional torque <sup>2</sup> (Nm)
	base oil	additive			
①	PAO	-	464	very high wear	>120
②	PAO	LUBOFÉ-additive P <sup>3</sup> (5 wt-% PTFE)	316	very high wear	40
③	PAO	LUBOFÉ-additive PD <sup>3</sup> (5 wt-% PTFE)	1	very high resistance to wear	25

<sup>1</sup>Wear dimension of the rolling element set

<sup>2</sup>Corresponds to the frictional torque at the end of the test

<sup>3</sup>Preparation according to EP 2 227528 B1 by *perfluorence GmbH*

Functional groups in the base oil can affect tribological results (particularly the extreme pressure behavior) of test products positively. During the preparation of oil-PTFE-cc dispersions dioleilyhydrogenphosphite (Duraphos<sup>TM</sup> AP240L) can be used additionally. Duraphos<sup>TM</sup> AP240L owns olefinically unsaturated groups as well as a phosphite group and, hence, it can act as surfactant and as EP modifier.

In a mechanical-dynamical test (FE-8) in the mixed friction area on axial cylindrical roller bearings (type 81212) an excellent wear protection could be achieved with this PAO/AP240L-PTFE-cc dispersion (LUBOFÉ-additive PD) after dilution in PAO to 5 wt-% PTFE. The test conditions chosen are 80 kN load at  $\vartheta = 80$  °C, 80 hours test period, and a speed of 7.5 rpm. Under these conditions, only a small lubricating film can be formed. In addition, high slip by drilling movement of the cylinder rolls causes high demands on the wear protection of the lubricant. Wear dimensions of rolling elements were only 1 mg on a constant low frictional torque of 25 Nm until the

entire test period. This low wear dimension is caused by the formation of an effective tribofilm by the adhesion of the PTFE-coupled phosphite group on the metal surface.

The adhesion mechanism of functional groups on metal surfaces using the example of dioleilyhydrogenphosphite is shown in Figure 5 schematically. On this way a rapid transfer movement and a fixation of chemically compatibilized PTFE microparticles (PTFE-cc) on the metal surface can be assumed. After that adhesion process PTFE can act as solid lubricant and as local oil thickener to improve the emergency running characteristics that were observed by VKA measurements.

A stronger linkage of the PTFE micropowder in the friction gap is achieved by a stable fixation/rapid adsorption of the phosphite group on the metal surface via ionic bonds (salt formation) and coordinative bonds, whereby the total migration of the lubricant from the friction gap is avoided [12, 13].

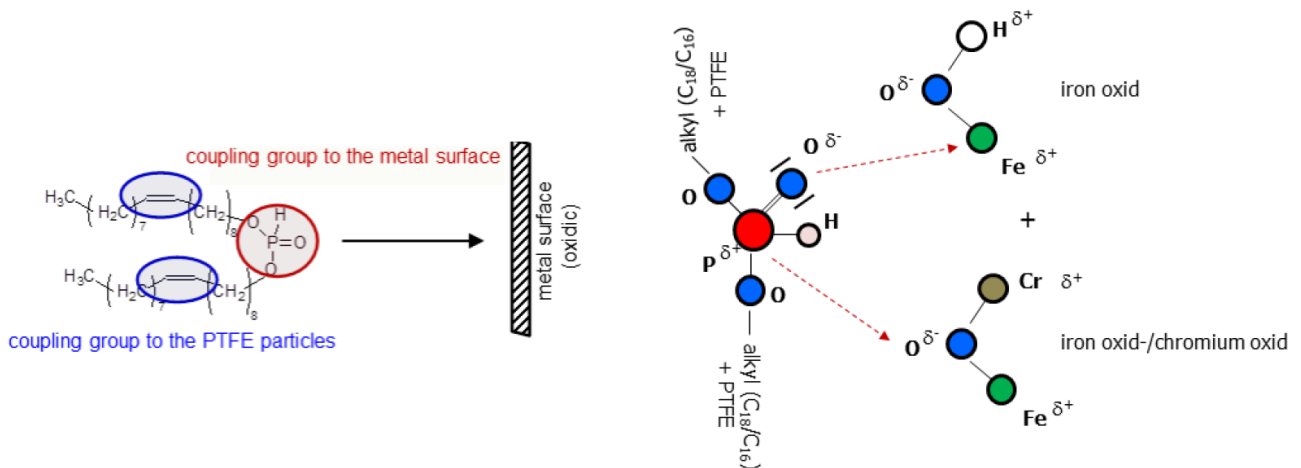


Figure 5. Model for the adhesion mechanism of oil/diolelhydrogenphosphite (Duraphos® AP 240L)-PTFE-cc on a metal surface (assumption: 100Cr6) according to reference [11].

The goal of the current development process is the improved understanding of the interaction mechanism as well as the further rise of the interaction on the substrate surface by the use of various functionalities (phosphonate-/phosphate-/sulfonate-/sulfate- or silane-groups) as a basis for the development of solid lubricants and their subsequent commercialization by *perfluorence* GmbH as novel LUBOFÉ-additives [14].

By means of EDX analysis, the adsorbed oil/AP240L-PTFE-cc layers on the rolling elements from the FE-8 test run No. 3 were detected (Figure 6, Table 2).

In addition to zinc (red layer) which originates from brass cage of the cylindrical

roller bearings, phosphorus was detected as phosphate (green layer). Two rolling elements of the rolling set were treated in methanol/water and in n-hexane to verify the hydrolytic stability of these layers and to analyze the chemical composition. The treatment in methanol/water leads to a partial hydrolysis of the phosphate layer. In contrast, the treatment in n-hexane causes formation of bulky polyphosphate, which was also confirmed by XPS studies.

In addition to the modified chemical composition, the roughness and heterogeneity of the surface layer were also changed by the different hydrolytic stability. This was investigated in first preliminary experiments by examination of the surface topography and by wetting measurements against water.

Table 2. Results of EDX analysis after FE-8 rolling bearing test for No.3 after chemical treatment.

No.	lubricant/base oil		treatment in	results from EDX analysis
	base oil	additive		
③	PAO	LUBOFÉ-additive PD <sup>3</sup> (5 wt-% PTFE)	methanol/water #1	partial hydrolysis of phosphat layer
			n-hexane #2	formation of voluminous polyphosphate layer

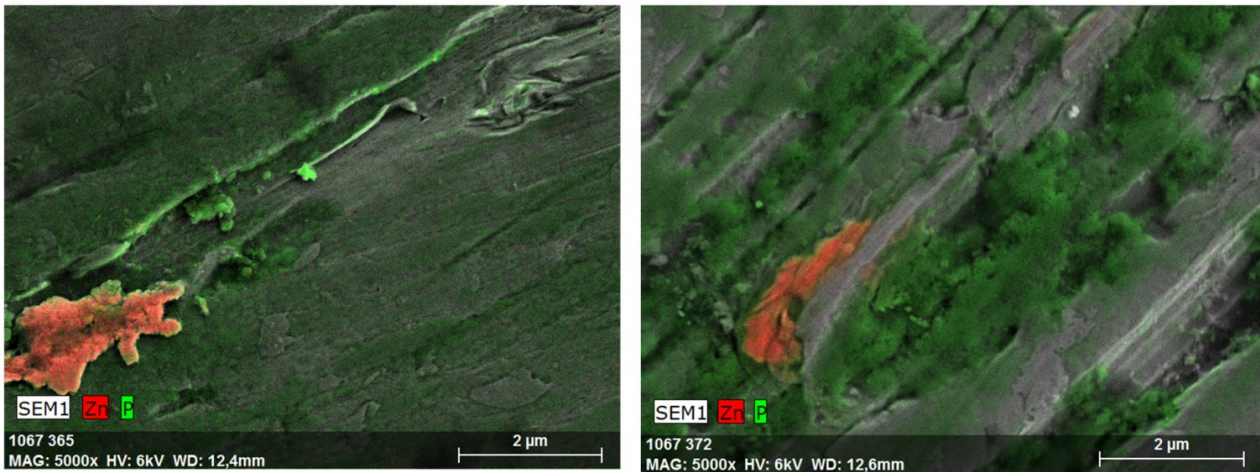


Figure 6. Characterization of rolling elements (from FE-8 test No. ③) after treatment in methanol/water (#1 = left) or n-hexane (#2 = right)); SEM: 5000x enlargement.

## CONCLUSIONS

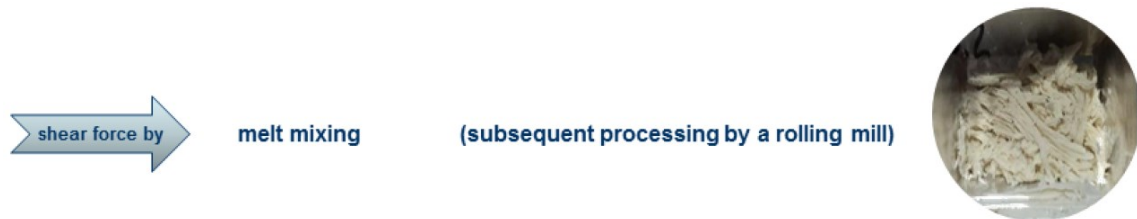
During the irradiation of high molecular weight poly(tetrafluoroethylene) (PTFE) in presence of oxygen perfluoroalkyl(peroxy) radicals and functional groups are formed which allow chemical coupling reactions (cc = chemical compatibilized) with oils and plastics. The radicals are used for the chemical compatibilization reaction with olefinically unsaturated groups of base oils. The tribological properties and the dispersion stability of the resulting oil-PTFE-cc (cc = chemical compatibilized) dispersions are significantly enhanced in comparison to physical mixture of oil and PTFE micropowder. Even up to 25 wt-% of PTFE micropowder in the base oil still lead to stable liquids [6] (see scheme 1). These oil-PTFE-cc-dispersions show primarily anti-wear (AW) properties by fixation of chemical

grafted PTFE particles (PTFE-cg) on the surface. The use of reactive groups (e.g. phosphite groups) in the oil gives the dispersions extreme pressure (EP) properties additionally. The functionalized PTFE particles reach the surface faster and act as solid lubricant and as local oil thickener. This leads even to improved emergency running characteristics.

PTFE-cc additive can be also used as solid lubricant up to 98 wt-% by melt mixing in presence of additives [14] (scheme 2). The homogenization was performed by rolling with additional base oils or with liquid chemicals possess suitable functionalities. Solid lubricants with tailored properties can be developed in this manner.



Scheme 1. Oil-PTFE-cc dispersion (PTFE up to 25 wt-% = liquid).



Scheme 2. PTFE-cc additive as solid lubricant (PTFE up to 98 wt-% = solid).

## ACKNOWLEDGEMENTS

The authors gratefully acknowledged the funding by the Bundesministerium für Bildung und Forschung (Nr. 03FO2172), the BMWi for funding the EXIST research transfer project (grant No. 03EFT8SN34) and the AiF for funding under grant No. KF2954202SL3. Furthermore, the authors thank the employees of Leibniz-Institut für Polymerforschung Dresden and of IME, RWTH Aachen.

## REFERENCES

1. W. Bürger, K. Lunkwitz, G. Pompe, A. Petr, D. Jehnichen, Radiation Degradation of Fluoropolymers: Carboxylated Fluoropolymers from Radiation Degradation in Presence of Air. *Journal Applied Polymer Science* 48 (1993) 1973-1985.
2. K. Lunkwitz, U. Lappan, U. Scheler, Modification of perfluorinated polymers by high-energy irradiation. *Journal of Fluorine Chemistry* 125 (2004) 863-873.
3. D. Lehmann, U. Hupfer, U. Lappan, G. Pompe, L. Häußler, D. Jehnichen, A. Janke, U. Geissler, R. Reinhardt, K. Lunkwitz, R. Franke, K. Kunze, New PTFE-polyamide compounds. *Designed Monomers and Polymers* 5 (2/3) (2002) 317-324.
4. A. Taeger, T. Hoffmann, W. Butwilowski, M. Heller, T. Engelhardt, D. Lehmann, Evidence of chemical compatibilization reaction between PEEK and irradiation modified PTFE. *High Performance Polymers* 26 (2014) 188-196.
5. A. Taeger, D. Lehmann, H. Marks, K. Kunze, Vergleich modifizierter PTFE- und PTFE-Rezyklat-Produkte als Festschmierstoffkomponente in Tribomaterialien. *Tribologie + Schmierungstechnik* 59 (2012) 5-10.
6. Langzeitstabile Öl-PTFE-Dispersion und Verfahren zu ihrer Herstellung. EP 2 227 528 B1 (2010).
7. T. Hoffmann, D. Lehmann, Chemical modification of poly(tetrafluoroethylene) micropowder - basis for special lubricant additives. *Lubrication Science* 24 (2012) 313-327.
8. T. Hoffmann, C. Bellmann, A. Caspari, U. Geissler, D. Lehmann, Stability of oil-based dispersions containing poly(tetrafluoroethylene) micropowder. *Colloids and Surfaces A: Physicochemical and Engineering Aspects* 457 (2014) 297-306.
9. (a) Betriebsanleitung, IKA Ultra-Turrax<sup>®</sup>, T25 digital (2007).  
(b) [http://www.ika.de/ika/pdf/flyer-catalog/Disperser\\_Brochure\\_DE](http://www.ika.de/ika/pdf/flyer-catalog/Disperser_Brochure_DE).
10. G. Burghardt, Untersuchung des Einflusses tribologischer



- Grenzschichten auf das Verschleißverhalten von Wälzlagern bei Grenzreibung. Diplomarbeit RWTH Aachen (2011).
11. J. Schulz, B. Decker, P. Feinle, J. Rigo, Interactions of additives with metal surfaces – New findings. OilDoc. Conference and Exhibition (2013).
  12. Oberflächen mit Öl-PTFE-Schmierstoff und Verfahren zu deren Herstellung. DE 10 2013 216 652 A1 (2015).
  13. D. Lehmann, B. Klüpfel, S. Martens, H. Linke, I. Römhild, Modifizierte PTFE-Mikropulver für Anwendungen in Ölen und Fetten. (54) GfT-Tagung (2006).
  14. Öl-modifizierte PTFE-Festschmierstoffe und Verfahren zu deren Herstellung, PCT/EP 2015/079092 (2015).