Colloids and Surfaces A: Physicochem. Eng. Aspects 457 (2014) 297–306

Contents lists available at ScienceDirect

Colloids and Surfaces A: Physicochemical and Engineering Aspects

journal homepage: www.elsevier.com/locate/colsurfa

Stability of oil-based dispersions containing poly(tetrafluoroethylene) micropowder

T. Hoffmann*, C. Bellmann, A. Caspari, U. Geissler, D. Lehmann

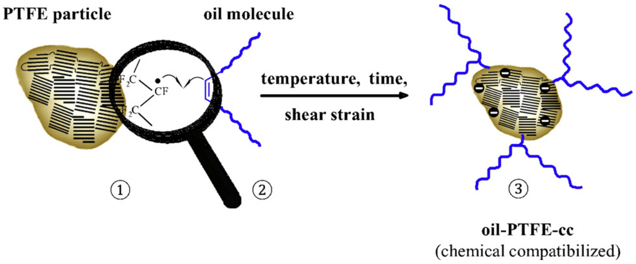
Leibniz-Institut für Polymerforschung Dresden e.V., Hohe Str. 6, 01069, Dresden, Germany

HIGHLIGHTS

- Oil-PTFE-cc dispersions were prepared and their stability analyzed.
- Differences are discussed in terms of particle interactions and stability.
- Concentration of functional groups can be explained by the amount of the zeta potential vs. pH.
- The influence on tribological properties is discussed as well.
- An individual optimum level for both PTFE micropowders in the oil can be derived.

GRAPHICAL ABSTRACT

Stabilization of oil-PTFE-cc dispersion can be achieved by shearing the perfluoroalkyl(peroxy) radicals on the PTFE particle surface (1) and the subsequent reaction with olefinic oil molecules (2) (additional stabilization by negative charges due to functional groups and by the shearing process itself (3).



ARTICLE INFO

Article history:
Received 31 January 2014
Received in revised form 21 May 2014
Accepted 27 May 2014
Available online 4 June 2014

Keywords:
PTFE micropowder
Oil-PTFE-cc dispersions
Chemical compatibilization
Particle interactions

ABSTRACT

Micropowder of poly(tetrafluoroethylene) (PTFE) can be used in base oils to improve the tribological properties significantly, if oil molecules are covalently linked to primary PTFE particles in the dispersion. Enhanced properties are not only determined by the amount of PTFE micropowder added to the oil but as well by the surface charge, radical concentration, and the size and distribution of PTFE particles in the oil phase.

The chemical compatibilization (=cc) between PTFE micropowder and ester oil by the use of two types of PTFE micropowder, which differ in radical concentration and the amount of functional groups is shown. The concentration of PTFE micropowder in the dispersions was varied from 5 to 20 wt%. Both the pure PTFE micropowder and the oil-PTFE-cc dispersions were characterized by ESR and FTIR spectroscopy as well as by zeta potential measurements. Rheological and tribological tests were performed on the ester oil and the oil-PTFE-cc dispersions. Qualitative differences are discussed in terms of particle interactions, dispersion stability, chemical compatibilization efficiency and the amount of functional groups.

A correlation between flow properties and surface charge of the PTFE particles within the dispersions was obtained. The influence on tribological properties is discussed as well.

1. Introduction

Regardless of its excellent chemical resistance, poly(tetrafluoroethylene) (PTFE) is very sensitive to high-energy radiation, such as electron beam and γ- 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.

---

* Corresponding author. Tel.: +49 351 46581012; fax: +49 351 4658 290.
E-mail address: hoffmann-thorsten@ipfdd.de (T. Hoffmann).

http://dx.doi.org/10.1016/j.colsurfa.2014.05.068

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 modification of high molecular weight poly(tetrafluoroethylene) by electron beam irradiation is a well investigated and commercial process that has also been investigated for many years at the Leibniz-Institut für Polymerforschung Dresden e.V. In this way a PTFE micropowder is obtained by partial polymer degradation. 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. These groups then allow a chemical reaction of PTFE micropowder with suitable oil groups as well as with thermoplastics to result in a chemical compatibilization [1].

The irradiation of PTFE has the following effects:

- reduction of the molecular weight due to chain scission,
- formation of persistent perfluoroalkyl(peroxy) radicals,
- functionalization of the PTFE particles with carbonyl fluoride (–COF) and carboxylic acid (–COOH) groups formed upon hydrolysis.

In addition, the irradiation of the PTFE powder generally results in a smaller particle size.

The degradation mechanism of PTFE during irradiation in air has been already discussed in detail in the literature [1–3].

The concentration of radicals in the particles must be $>5 \times 10^{17}$ spin g^{-1} PTFE to achieve a chemical compatibilization with oil molecules.

The perfluoroalkyl(peroxy) radicals on the surface of the PTFE particles react fast with olefinic groups of oil molecules by radical addition reactions during the dispersion process. After this primary compatibilization reaction secondary allylic radicals are formed at the compatibilized molecules as intermediates which are less reactive. Afterwards these secondary radicals can react with further oil molecules at a slower reaction rate or can be stabilized to final products e.g. by recombination.

The effect of functional groups (–COF, –COOH) is rather low because only a small number is located at the surface of PTFE particles. The number of accessible –COOH groups close to the surface of the PTFE particles can be increased by fragmentation of agglomerated PTFE particles. In addition, it was shown that the irradiation also affects the particle size, regardless of the type of radiation and the kind of PTFE (emulsion or suspension polymer) [4].

The chemically compatibilized oil chains are stable 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 (=cc) reaction between PTFE micropowder and olefinic groups of oils to oil-PTFE-cc dispersions has already been described [5,6]. The formation of an electrochemical double layer, e.g. owing to different dielectric constants, causes an electron transfer between a particle surface and organic liquid that can be related to the donor-acceptor interaction forces, has also been discussed [7].

It is known that the strength of the particle particle interaction forces depends not only on the solid volume fraction but also on the specific area. The van der Waals attraction forces lead to agglomeration of particles. Repulsion forces between the particles caused by electrostatic charge resulting in a stabilizing effect on the particles in suspension. Electrostatic repulsion forces arise when particles carry a surface charge. The feasibility of such a chemical compatibilization reaction depends mainly on a sufficient fragmentation of agglomerated PTFE particles to ensure the accessibility of the persistent perfluoroalkyl(peroxy) radicals to the olefinic groups of the oil.

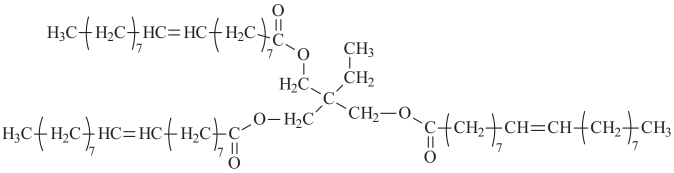


Fig. 1. Chemical structure of trimethylolpropane trioleate (TMP).

Two PTFE micropowders were tested for use in the chemical compatibilization reaction (=cc) with the ester oil and the products were analyzed by ESR and FTIR spectroscopy as well as by rheological and tribological characterizations and by the measurement of the zeta potential. The properties of the resulting dispersions were recorded and the results discussed taking into account the influence of the type and the amount of PTFE. Initial studies of TMP-PTFE-cc dispersions using a commercial PTFE and phosphorus-containing surfactants have already been published [8].

2. Materials and methods

Dispersions of an ester oil and two commercially available types of PTFE micropowder were prepared in varying concentrations (5, 10, 17.5, and 20 wt%). In order to evaluate the influence of the different PTFE micropowders to the dispersion properties, the PTFE micropowders were tested for particle size distribution, surface charge as well as the rheological and tribological properties of the resulting dispersions. The effect of the concentration of PTFE micropowder on the properties of the dispersions was discussed additionally.

2.1. Base oil

The ester oil trimethylolpropane trioleate (TMP) by ILCO-Chemikalien GmbH (Germany) was used. The chemical structure is shown in Fig. 1 in idealized form. Some data of TMP are listed in Table 1. General properties of TMP were already summarized in references [8,9] and are not to be mentioned in detail here.

2.2. PTFE materials

For the chemical compatibilization with TMP two commercial PTFE micropowders from C.H. Erbslöh KG (Germany) were used:

- Zonyl® MP1100 (emulsion polymer, produced and irradiated by DuPont) with a high concentration of functional groups (–COF, –COOH) and a relatively high radical concentration (10^{18} spin g^{-1} PTFE).
- Zonyl® MP1600 (emulsion polymer, prepared by a controlled polymerization technique by DuPont) with nearly no functional groups and a relatively low radical concentration (10^{16} spin g^{-1} PTFE).

The properties of both PTFE micropowders are summarized in Table 2. The amount of perfluoroalkyl(peroxy) radicals was determined by electron spin resonance (ESR) spectroscopy. Fourier transform infrared (FTIR) spectroscopy was used for determination of the number of functional groups according to reference [10]. The listed particle size refers to the d_{50} value at which 50 percent of the particles are equal or smaller than the specified value. Scanning electron microscopy (SEM) was used to determine the morphology of the neat PTFE types. The zeta potential (ζ) of both PTFE micropowders was estimated at pH 5. The characterization