

Functionalization of Irradiated PTFE Micropowder with Methacryl- or Hydroxy Groups for Chemical Coupling of PTFE with Different Matrix Polymers

B. Klüpfel, D. Lehmann

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

Received 23 September 2004; accepted 7 April 2005

DOI 10.1002/app.22885

Published online in Wiley InterScience (www.interscience.wiley.com).

ABSTRACT: This article describes the modification of electron beam irradiated polytetrafluoroethylene (PTFE) material (500 kGy) into a functionalised micropowder, bearing methacrylate or hydroxy groups. The aim of this work is to achieve compatibilization of modified PTFE in a variety of matrix polymers, such as elastomers and duromers. It is well known that irradiation of high molecular PTFE in the presence of air, followed by annealing with water vapor, leads to a functionalization of the PTFE micropowder, containing carboxylic acid groups. For sufficient stability of the coupling of the functional groups that are to be introduced via these acid groups, a transformation into amide groups is necessary, and can be performed by the reaction of the electron beam irradiated PTFE with ϵ -caprolactam in the first step. The corresponding acid-terminated PTFE-oligoamide is then reacted with functional epoxy monomers, like glycidol or glycidyl methacrylate, to obtain the functionalised PTFE micropowders (PTFE-OH and PTFE-MA). As

the number of COOH groups in the electron beam irradiated PTFE is not very high, IR-spectroscopic identification of the functional groups is not very distinct. To find evidence for the existence/reactivity of the additionally introduced functional groups, model reactions have been performed, where PTFE-MA is reacted with methyl methacrylate/AIBN. IR spectroscopic analysis of the reaction products shows characteristic absorption bands of PMMA, indicating successful graft polymerization of PMMA to PTFE-MA. For PTFE-OH, reaction with cyclohexylisocyanate leads to a bisurethane adduct, which shows a strong urethane absorption in the IR spectrum. © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 101: 2819–2824, 2006

Key words: polytetrafluoroethylene (PTFE); electron beam irradiation; functionalization of polymers; compatibilization; matrix

INTRODUCTION

The outstanding properties of polytetrafluoroethylene (PTFE), such as thermal and chemical stability, high toughness at low temperature, weather resistance, a low coefficient of friction etc., provide a broad range of application for the high performance plastic. These extraordinary characteristics are a result of the low polarisability and the high bond energy of the C—F bond (486 kJ/mol) and the perfect shielding of the C—C backbone by the fluorine atoms. As a further special feature, the hydrophobic surface is mentioned, causing serious difficulties for adhesion with other materials. For this reason, it is necessary to modify the surface of the PTFE particles, when compatibilization of PTFE in diverse matrix polymers is desired, which is not possible with the untreated high molecular material. This aim can be achieved in three ways: (a)

covering the unmodified surface with a shell (core-shell particles);¹ (b) modifying the surface with less antiadhesive groups; (c) modifying the surface with functional groups suitable for chemical coupling with the matrix polymer.² Because of the outstanding chemical resistance of this material, modifying the surface of PTFE appears to be difficult and can be achieved chemically by treatment with high reactive alkali metals/-hydrides or organometallic reagents.^{3–6} For several reasons, this method appears to be unsuitable for a modern industrial process.

Besides its chemical stability, PTFE is extremely sensitive to ionizing radiation; thus, another method for surface modification is the treatment of high molecular PTFE with γ -rays⁷ or electron beams.⁸ On this topic, intensive studies have been made,^{9–14} resulting in a broad knowledge of the occurring processes and the change in the material properties. Irradiation of high molecular PTFE in air leads to oxidative degradation by chain scission, which is associated with a decrease of molecular weight and increasing crystallinity. By applying this method, PTFE micropowders are produced, which are commonly used as additives for plastics, inks, coatings, elastomers, or lubricants,

Correspondence to: D. Lehmann (lehmann@ipfdd.de).

Contract grant sponsor: Deutsche Forschungsgemeinschaft (DFG).

thus improving the sliding and nonstick effects coming with an enhanced wear resistance.¹⁵ The surface modification is proven by contact angle measurements of electron beam irradiated PTFE films, since it results in a significant change in the surface energy when compared with the unirradiated PTFE films.¹⁶ This effect is caused by carboxylic acid groups, generated by hydrolysis of C(=O)F groups, which are formed by irradiation of PTFE in the presence of oxygen.^{9–16} Determination of the acid group concentration is achieved by IR spectroscopic end-group analysis¹⁷ or by potentiometric titration.¹⁸ The COOH groups raise the adhesion of PTFE to other materials, but sufficient compatibilization of the micropowder is still not achieved when matrix polymers are blended with PTFE. For some applications, this physical interaction between polymer matrix and PTFE might be satisfactory, but for high performance tribological applications it appears to be not sufficient.

Earlier investigations have shown that carboxylic acid groups of the PTFE micropowder can be used for chemical coupling between PTFE and polyamide 6 by reactive processing.¹⁹ As a possible mechanism, they proposed a scission of the polyamide through cleavage of amide bonds by the COOH groups of the PTFE. This transamidation mechanism was derived from studies on reactive extrusion of polyamide 6 with trimellitic anhydride.^{20,21} Analogous PTFE-PA-6.6 block copolymers showed favorable tribological properties when compared with commercially available PTFE-PA-blends.²² In addition, the coupling of PTFE and polyamide has been proven by FTIR and DSC studies, after eliminating the polyamide matrix by extraction with formic acid. To extend the field of application for compatibilization of PTFE in elastomers (e.g., composition rubber) and duromers (e.g., polyurea, polyurethanes) by chemical coupling, further modification of the carboxylated PTFE micropowder is necessary. In this article, we describe a method for the functionalization of irradiated PTFE with methacrylate or hydroxy groups via the carboxylic acid groups, to provide suitable link options for PTFE and the matrix polymer by chemical bonding in a subsequent reactive extrusion process.

EXPERIMENTAL

Irradiated (500 kGy; 28.8 $\mu\text{mol/g}$ COOH²³) PTFE (Zonyl® MP1100, Du Pont), ϵ -caprolactam (Merck), glycidyl methacrylate (GMA; BASF), and glycidol (Aldrich) were used as received. FTIR measurements were carried out from cold pressed samples on a IFS 66 (Bruker). The spectra were normalized by setting the band at 2365 cm^{-1} (combination band associated with the CF₂ backbone) to a maximum intensity of 1.00.

Preparation of PTFE-oligoamide

In a 500-mL, three-necked flask fitted with a mechanical stirrer and a thermometer, 180 g of ϵ -caprolactam was heated to 150°C, and the melt was degassed by applying vacuum and flushing with nitrogen (three times). Then, 100 g of PTFE was added with intense stirring, the temperature was raised to 240°C, and the melt was then stirred for 4 h. After cooling to 100°C, the melt was poured into 700 mL of ice-cold methanol; the resulting slurry was then filtered. The unreacted ϵ -caprolactam could be recovered by vacuum distillation of the filtrate, after evaporation of methanol. The residue was transferred to a flask, and then 500 mL of methanol was added, and the resulting slurry was heated to reflux for 1 h with intense mechanical stirring, followed by filtration. This procedure was repeated two times to ensure that any free or nonbonded ϵ -caprolactam is removed. The greyish PTFE-oligoamide (PTFE-OA) was then dried in a vacuum oven at 80°C for 6 h.

Preparation of methacrylate functionalised PTFE

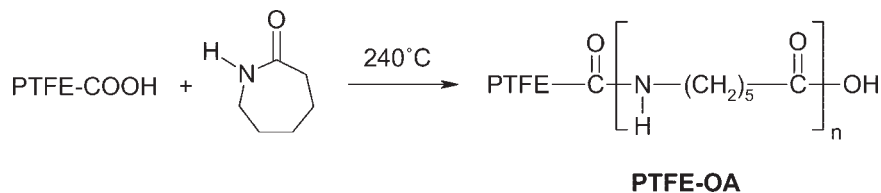
To a suspension of 184 g of PTFE-OA in 1.0 L of DMSO was added 18.4 mL of GMA, 3.70 g of 2,6-di-tert-butyl-4-methylphenol (to avoid polymerization of GMA), and 5.50 g of 2-methylimidazole as basic catalyst, and the reaction mixture was then heated to 188°C for 3 h, with intense mechanical stirring. After cooling to ambient temperature, the reaction mixture was filtered, and the residue was washed three times with 700 mL of methanol by applying intense mechanical stirring. The methacrylate functionalised PTFE (PTFE-MA) material was then dried in a vacuum oven at 80°C for 6 h.

Preparation of hydroxy functionalised PTFE

To a suspension of 228 g of PTFE-OA in 800 mL of DMSO was added 50.0 mL of glycidol and 8.00 g of 2-methylimidazole. The mixture was heated to 160°C for 8 h with intense mechanical stirring. Work-up and drying were similar to the preparation of PTFE-MA, as described earlier.

Reaction of PTFE-MA with methyl methacrylate/AIBN

To a degassed suspension of 8.5 g of PTFE-MA in 180 mL of N,N-dimethylacetamide, 10 mL of methyl methacrylate (MMA) and 0.6 g AIBN were added, and the stirred mixture heated to 95°C for 1 h. Then, the material was separated by filtration and washed two times with N,N-dimethylacetamide and three times with methanol and dried in a vacuum oven at 80°C for 6 h.



Scheme 1 Formation of PTFE-OA.

Reaction of methacrylate-functionalised PTFE with cyclohexyl isocyanate

To a suspension of 8.5 g of methacrylate-functionalised PTFE (PTFE-OH) in 60 mL of acetonitrile, 2 mL of cyclohexyl isocyanate was added, and the mixture was heated to reflux for 4 h. Then, the material was separated by filtration and washed three times with methanol and dried in a vacuum oven at 80°C for 6 h.

RESULTS AND DISCUSSION

Formation and analysis of PTFE-OA

Perfluorinated esters appear less stable toward hydrolysis, as perfluorinated carboxylate acts as a good leaving group similar to the often-used trifluoroacetate group. In contrast, perfluorinated amides should be much more stable under the conditions of a reactive extrusion process. Therefore, direct transformation of the PTFE-COOH groups to ester groups is not practical and is avoided by the introduction of an amide group, directly connected to the PTFE. In addition, another functional group has to be introduced, enabling successful coupling of a reagent bearing diverse functional groups for coupling with a polymer matrix. This aim is achieved by reaction of irradiated PTFE (commercially available Zonyl MP1100, DuPont) with ϵ -caprolactam.

Similar to the formation of PTFE-PA-6 blockcopolymer¹⁹, in which the amide bonds of the polyamide are cleaved and the PTFE-amide bonds are formed, the ϵ -caprolactam ring is opened and the PTFE-OA (Scheme 1) is formed. This modified PTFE material is characterized by a PTFE-linked amide group, as well as a terminal carboxylic acid group, which can undergo further transformations to yield stable derivatives. IR spectroscopic analysis (Fig. 1) of PTFE-OA, in comparison to the starting material Zonyl MP1100 and high molecular PTFE, shows complete disappearance of the COF groups [$\nu(\text{C}=\text{O})_{\text{COF}} = 1883 \text{ cm}^{-1}$], as well as the OH_{COOH} [$\nu(\text{O}-\text{H}) = 3400\text{--}2800 \text{ cm}^{-1}$] groups. Except for a small shoulder at 1768 cm^{-1} , the characteristic COOH absorption bands of irradiated PTFE [$\nu(\text{C}=\text{O})_{\text{COOH}}(\text{free}) = 1811 \text{ cm}^{-1}$, $\nu(\text{C}=\text{O})_{\text{COOH}}(\text{ass.}) = 1776 \text{ cm}^{-1}$] have been eliminated, indicating an almost complete conversion of the acid to amide groups. With irradiated PTFE, decarbox-

ylation can be observed at elevated temperatures⁸ and had to be excluded as a competing reaction pathway here. When the irradiated PTFE was treated under similar reaction conditions, however, with the ϵ -caprolactam substituted by an inert solvent (Malotherm SH), no significant change in the COOH concentration was found by IR spectroscopy. The PTFE-OA is characterized by the characteristic poly(oligoamide) absorptions [$\nu(\text{N}-\text{H}) = 3500\text{--}3100 \text{ cm}^{-1}$, $\nu(\text{C}-\text{H}) = 3100\text{--}2800 \text{ cm}^{-1}$, $\nu(\text{C}=\text{O})_{\text{amide I}} = 1656 \text{ cm}^{-1}$, $\nu(\text{C}=\text{O})_{\text{amide II}} = 1545 \text{ cm}^{-1}$] superposed by the PTFE bands. In addition, an absorption band is found at 1726 cm^{-1} assigned to PTFE bond amide groups, indicating successful chemical coupling of PTFE with ϵ -caprolactam.

To exclude possible formation of clathrate or core-shell materials, an analogous transformation was carried out using another PTFE-type of comparable particle size, but without carboxylic acid groups (Du Pont Zonyl MP1600). Here, no poly(oligoamide) absorptions were found, which confirms chemical coupling as well as the structural considerations discussed earlier.

Functionalization of PTFE-OA: synthesis and analysis of PTFE-MA

As mentioned earlier, for a successful coupling with matrix polymers, functionalization of the PTFE sur-

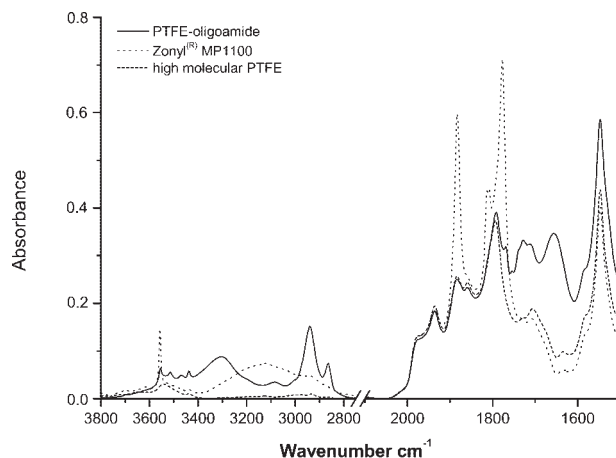
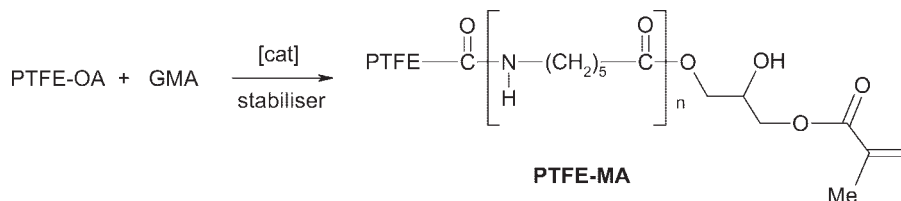


Figure 1 FTIR spectra of high molecular PTFE (dashed line), Zonyl MP1100 (dotted line), and PTFE-OA (full line) in the region of $3800\text{--}2750 \text{ cm}^{-1}$ and $1900\text{--}1500 \text{ cm}^{-1}$.



Scheme 2 Formation of PTFE-MA.

face with diverse groups is required. For chemical coupling of PTFE with composition rubbers, like NBR, introduction of olefinic double bonds is necessary, suitable for reaction with NBR radicals formed during the plastification or vulcanization process. In this context, reaction of PTFE-OA with GMA offers an attractive pathway for the coupling of olefinic double bonds to the PTFE-micropowder surface (Scheme 2).

The base-catalyzed reaction of carboxylic acids with epoxides is a well-known process, leading to hydroxy-functional esters. Two structural isomers are formed, of which only one is shown in Scheme 2. To avoid polymerization of the methacrylic unit, 2,6-di-*tert*-butyl-4-methylphenol has been added as a stabilizing agent. Attempts to use [(Ph)₄P]Br as epoxy activating catalyst for this reaction were not successful, while for the basic catalyst, 2-methylimidazole, a good activity was found. In this case, analysis of PTFE-MA by FTIR spectroscopy is not straightforward, since the concentration of the coupling groups is not very high. In addition, the absorption intensity of the newly introduced groups (OH, C—H, C=C) is not strong. When compared with the spectrum of PTFE-OA, for PTFE-MA, only a small increase in intensity of the O—H and C—H absorption bands is determined (Fig. 2). The main difference is obvious, regarding the ester absorp-

tion band [$\nu(\text{C}=\text{O})_{\text{ester}} = 1729 \text{ cm}^{-1}$], in which a significant increase is observed.

With these indications by IR spectroscopy, it cannot be rigorously proven that functionalization had been successful. As a model reaction that would provide indirect evidence for potentially present olefinic double bonds showing characteristic IR-absorption bands, graft copolymerisation with MMA has been carried out using AIBN as radical initiator. When comparing the FTIR spectra of PTFE-MA and the copolymer, a more intensive ester absorption band [$\nu(\text{C}=\text{O})_{\text{ester}} = 1732 \text{ cm}^{-1}$] becomes apparent (Fig. 2). For the C—H absorption bands, only a slight signal broadening is observed, because of the weakness of the absorption. To exclude any incorrect results caused by possible inclusion of PMMA into the particles or the formation of core-shell materials, the reaction is carried out in *N,N*-dimethylacetamide, a good solvent for PMMA. In addition, when the unfunctionalised PTFE-OA is treated under the same conditions, no graft copolymerisation of MMA is detectable and the PTFE-OA is recovered unchanged.

The successful model reaction proves two important facts: a functionalization of PTFE-OA with olefinic double bonds has occurred, and the PTFE-linked functional groups are reactive with regard to radical-initiated addition reactions. In a next step, processing of composition rubbers with PTFE-MA has to be carried out, followed by verification of the chemical coupling of PTFE to the rubber as well as tribological investigations of the novel materials.

Functionalization of PTFE-OA: synthesis and analysis of PTFE-OH

Functionalization of PTFE with hydroxy groups offers the opportunity for subsequent reaction with isocyanates, the basic material for the production of polyurethanes and polyureas. Chemical coupling of PTFE to such materials should be achieved during the mixing process of diisocyanates, with the alcohol or amine components and the PTFE-OH powder. Synthesis and analysis of PTFE-OH is in accordance with PTFE-MA, where GMA is substituted by glycidol (Scheme 3). As mentioned earlier, two structural isomers are formed, of which only one is shown in Scheme 3. The base-catalyzed opening of the epoxy ring leads to the for-

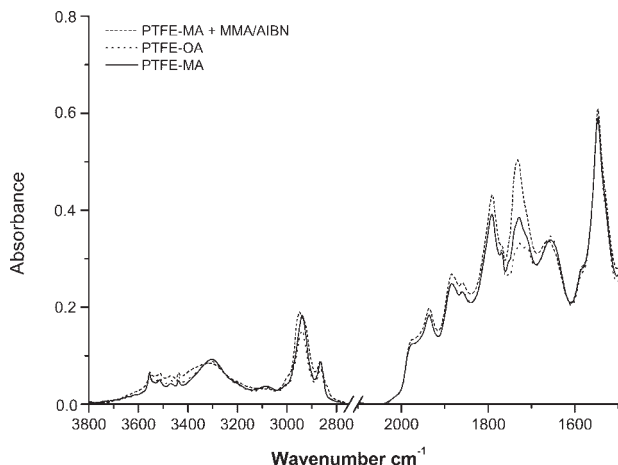
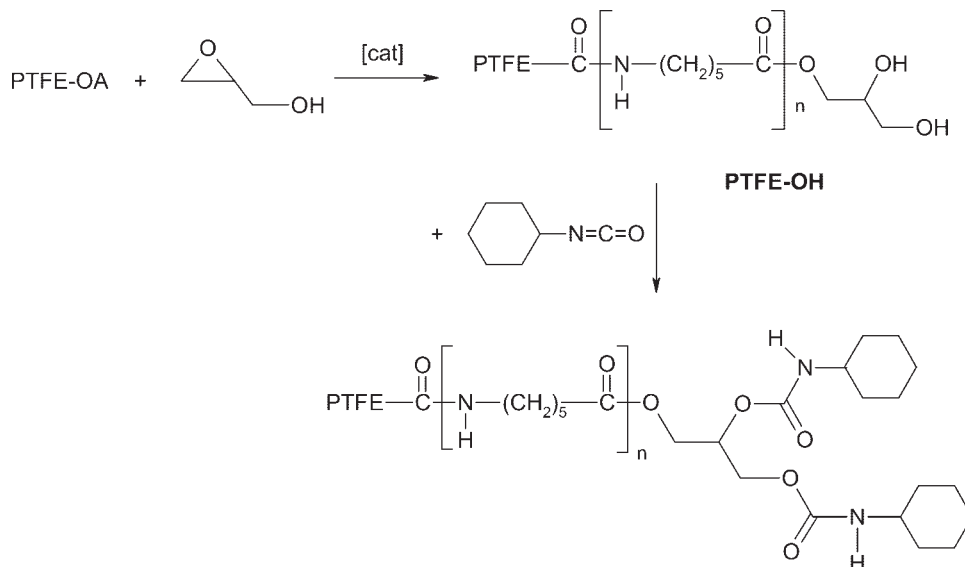


Figure 2 FTIR spectra of PTFE-OA (dashed line), PTFE-MA (full line), and PTFE-MA reacted with MMA/AIBN (dotted line) in the region of $3800\text{--}2750 \text{ cm}^{-1}$ and $1900\text{--}1500 \text{ cm}^{-1}$.



Scheme 3 Formation of PTFE-OH and reaction of PTFE-OH with cyclohexyl isocyanate.

mation of a glycerol monoester. In the FTIR spectrum, the hydroxy functionalities can be clearly identified by the broad O—H absorption band [$\nu(\text{O—H}) = 3600\text{--}3100\text{ cm}^{-1}$], resulting in an increased intensity of all signals in the specified frequency range (Fig. 3). For the C—H and C=O absorption bands, a slightly increased absorption is observed as well.

Again, for additional indications of the structural determinations by IR spectroscopy, model reactions have been performed, taking advantage of the high reactivity of alcohol toward isocyanates to yield urethanes. Thus, PTFE-OH is reacted with cyclohexyl isocyanate, which leads to the formation of a bisurethane adduct, as shown in Scheme 3. Comparison of

its IR spectra to those of PTFE-OH exhibits a characteristic absorption band [$\nu(\text{C=O})_{\text{urethane}} = 1709\text{ cm}^{-1}$], as well as a slight increase of the C—H absorptions. The intensity of the O—H absorption band [$\nu(\text{O—H}) = 3600\text{--}3100\text{ cm}^{-1}$] of PTFE-OH is significantly decreased for the model compound, an additional indication for a conversion of the hydroxy to urethane groups.

Again in this case, a similar treatment of the unfunctionalised PTFE-OA has been conducted, to exclude any misleading results. Here again, after the conversion, no change in the IR spectrum can be observed, which proves a successful functionalization as well as the principle reactivity toward isocyanates. Future projects will deal with the incorporation of the functionalised PTFE micropowder into duroplastic polyurethane or polyurea materials, for tribological testing.

CONCLUSIONS

Modification of electron beam irradiated PTFE micropowder, bearing carboxylic acid groups into a functionalised material is achieved by reaction with ϵ -caprolactam in the first step. The resulting acid-terminated PTFE-OA is then treated with glycidol or GMA in a second step. By applying this method, the surface of the PTFE particles is functionalised with methacrylate or hydroxy groups, which is difficult to verify via IR spectroscopy, because of the low concentration and a small absorption coefficient of the functional groups. Model reactions like the graft-copolymerisation of MMA for PTFE-MA or reaction with cyclohexyl isocyanate for PTFE-OH indicate successful functionalization, concluded from characteristic

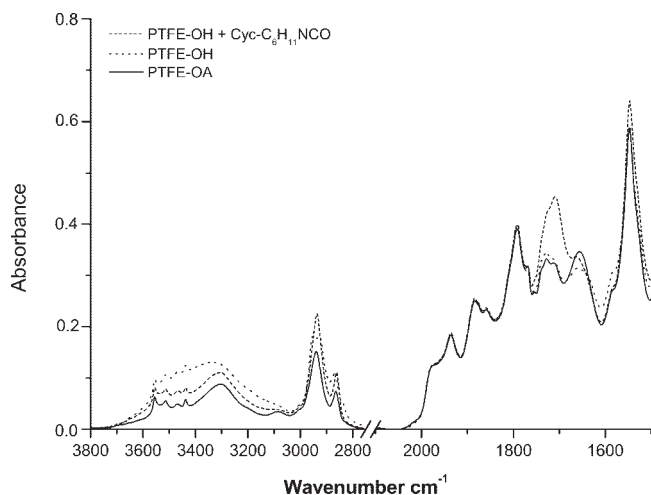


Figure 3 FTIR spectra of PTFE-OA (full line), PTFE-OH (dashed line), and PTFE-OH reacted with cyclohexyl isocyanate (dotted line) in the region of $3800\text{--}2750\text{ cm}^{-1}$ and $1900\text{--}1500\text{ cm}^{-1}$.

absorption bands of the model compounds. The aim of this work is to supply modified PTFE micropowders, which promise good compatibilization in a variety of matrix polymers, such as elastomers (e.g., composition rubber) and duromers (e.g., polyurea, thermoplastic polyurethanes). This compatibilization is intended to be achieved by chemical coupling of PTFE with the matrix polymers during a reactive extrusion process. The model reactions employed for analysis, in particular, have already demonstrated the principal reactivity concerning radical addition (for PTFE-MA) or addition to isocyanates (for PTFE-OH). Future investigations will deal with the reactive processing of matrix polymers with modified PTFE, the proof of a chemical coupling between matrix and PTFE and tribological examinations of the materials, respectively.

References

- Okaniwa, M. *J Appl Polym Sci* 1998, 68, 185.
- Lunkwitz, K.; Lappan, U.; Lehmann, D. *Radiat Phys Chem* 2000, 57, 373.
- Huang, C.; Chiang, W. *Angew Makromol Chem* 1993, 209, 9.
- Noh, I.; Chittur, K.; Goodman, S.; Hubbell, J. *J Polym Sci Part A: Polym Chem* 1997, 35, 1499.
- Marchesi, J.; Keith, H.; Garton, A. *J Adhes* 1992, 38, 185.
- Boittiaux, V.; Boucetta, F.; Combellas, C.; Kanoufi, F.; Thiebault, A.; Delamar, M.; Bertrand, P. *Polymer* 1999, 40, 2011.
- Oshima, A.; Seguchi, T.; Tabata, Y. *Radiat Phys Chem* 1999, 55, 61.
- Lappan, U.; Häußler, L.; Pompe, G.; Lunkwitz, K. *J Appl Polym Sci* 1997, 66, 2287.
- Golden, J. H. *J Polym Sci* 1960, 45, 534.
- Bro, M.; Lovejoy, E.; McKay, G. *J Appl Polym Sci* 1963, 7, 2121.
- Muromcev, V.; Asaturjan, R.; Achveldiani, I. *Usp Khim* 1971, 40, 312.
- Iwasaki, M. *Fluorite Chem Rev* 1971, 5, 1.
- Lunkwitz, K.; Brink, H.; Handte, D.; Ferse, A. *Radiat Phys Chem* 1989, 33, 523.
- Hagiwara, M.; Tagawa, M.; Amemiya, H.; Araki, K.; Shinohara, I.; Kagiya, T. *J Polym Sci Part A: Polym Chem* 1976, 14, 2167.
- Feiring, A. E. In *Organofluorine Chemistry: Principles and Commercial Applications*; Banks, R.E.; Smart, B. E.; Tatlow, J. C., Eds.; Plenum Press: New York, 1994.
- Bürger, W.; Lunkwitz, K.; Pompe, G.; Petr, A.; Jehnichen, D. *J Appl Polym Sci* 1993, 48, 1973.
- Buckmaster, M. D.; Morgan, R. A. *Eur. Pat. EP 0222945 B1* (1992).
- Gleißler, U.; Lappan, U.; Bürger, W.; Lunkwitz, K. *Angew Makromol Chem* 1998, 256, 85.
- Lehmann, D.; Hupfer, B.; Lappan, U.; Pompe, G.; Häußler, L.; Jehnichen, D.; Janke, A.; Gleißler, U.; Reinhardt, R.; Lunkwitz, K.; Franke, R.; Kunze, K. *Designed Monomers & Polymers* 2002, 5, 317.
- Eichhorn, K.-J.; Lehmann, D.; Voigt, D. *J Appl Polym Sci* 1996, 62, 2053.
- Lehmann, D.; Eichhorn, K.-J.; Voigt, D.; Schulze, U. *Kautsch Gummi Kunstst* 1997, 50, 873.
- Staudinger, U. *Diploma Thesis, TU Dresden* 2003.
- Lehmann, D.; Lappan, U.; Hupfer, B.; Häußler, L.; Pompe, G.; Jehnichen, D.; Janke, A.; Simon, F.; Lunkwitz, K. *Makromolekulares Kolloquium, Freiburg, February 22–24, 2001*.