size in and at the surface of layers and especially on the top layer. The thicknesses of TiO_2 and SiO_2 layers are in the range between 45-55 nm and 65 nm respectively. The crystalline phase of TiO_2 and amorphous phase of SiO_2 nanoparticles were observed by HRTEM. A small reflectance differences between simulated and real interfreence multilayers could be originate from interdiffusion of TiO_2 and SiO_2 nanoparticles at the phase boundaries. This is an issue for the next investigation in which pure TiO_2 and pure SiO_2 layers have to be produced for such an investigation. The purity of layers may allow to investigate the phase boundaries with respect to interdiffusion in detail via michrochemical analysis by HR-TEM.

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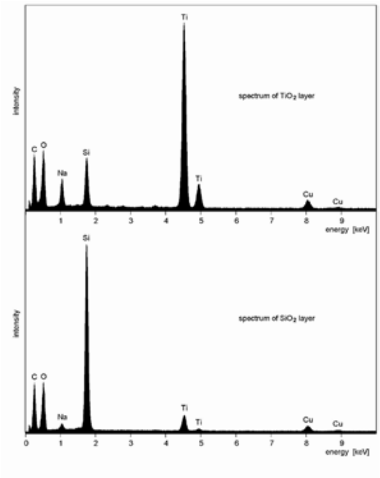

Fig. 7: Energy dispersive x-ray spectra of the TiO_2 and SiO_2 layers

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Investigation on thermal and chemical stability of polymer based easy-to-clean nanocomposite systems

Ralf.Gerdes, Pamela Kalmes, Carsten Becker-Willinger

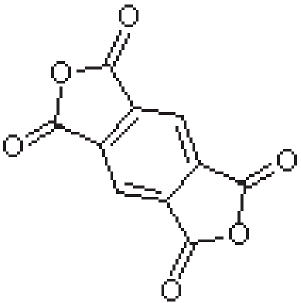
Abstract

Anti-adhesive coatings are of significant importance for many industrial processes such as pigment and paint production as well as also food processing industry, because they can help to significantly reduce the cleaning effort. For this reason, the amount of cleaning chemicals and waste water can be reduced, which should have a remarkable effect on the process costs. In this investigation abrasion resistant low surface free energy coatings based on fluoroalkyl group and SiC particles containing polyimides have been synthesised which show surface properties comparable to PTFE and can be coated like a paint on surfaces. Especially in food production processes a high chemical stability is required for coating materials to withstand the cleaning procedures which are used in order to maintain the hygienic situation in the production facilities. The investigations revealed a high abrasion resistance (weight loss approx. 12 mg after 1000 cycles taber abrader test) and a moderate chemical stability of the coating systems. A chemical attack by sodium hydroxide solution as

well as by oxidising substances such as nitric acid (HNO_3) at elevated temperatures (90°C) led to a fast destruction of the coating performance caused by damage of the organic matrix. Also the exposure with carrot juice and milk at 90°C showed some influence. The contact angles against water decreased by about 20-30% whereas the oleophobic properties remained almost unchanged. On the other hand the polyimide nanocomposites showed a low surface roughness ($R_a \leq 0.2$ µm) and adjustable antistatic properties, what enables to use them in dry food processing (e.g. in flour mills). By using a nanocomposite system filled with 10 wt.-% carbon black FW 200 a resistivity of 1.5x103 Ω and a charge decay time of 0 s were obtained.

Introduction

Since many decades coatings based on polytetrafluoroethylene (PTFE) and its derivatives have been and still are in use to create anti-adhesive coatings for surfaces, which are in contact with food such as e.g. kitchenware and pans [1, 2]. In order to obtain long lasting coatings on this basis, an intensive pre-treatment and the use of primers is necessary to obtain sufficient adhesion to the substrate. The application is followed by a thermal treatment of the surface at temperatures in the range of 400°C, which limits the types of substrate materials and requires an industrial process for the application on parts. For the use of anti-adhesive coatings in food production industry it is important to provide materials, which can be applied on site on already existing equipment and show adhesion to different kinds of substrate materials such as stainless steel, plastics and even sometimes on glass. Starting from the early nineties also thin anti-adhesive coatings based on the sol-gel process and fluorosilanes have been investigated intensively, which combined an excellent adhesion to almost all types of substrate materials with transparency and excellent hydrophobic and oleophobic properties [3, 4]. Besides their interesting base properties these types of materials finally could not be used in food production processes, because they showed a low resistance against mechanical abrasion and high pH cleaning substances such as sodium hydroxide solution at elevated temperature. Some years ago now a new class of organic-inorganic nanocomposite materials has been developed that combines high abrasion stability with alkaline resistance and paint ability [5]. Especially the polyimide



Pyromellitic dianhydride - PMDA [89-32-7]

Fig. 1: Chemical structure of used anhydride compounds

types [6] and polyurethane types [7] based on this approach have been investigated more in detail regarding to abrasion resistance in combination with heat resistance and chemical resistance respectively. The polyimides in particular allow many variations with regard to the monomer composition which enables to vary flexibility, polarity as well as their chemical stability [8-27]. In order to reduce the water uptake of polyimides, many investigations have been carried out to incorporate hydrophobic components, such as fluorine containing hydrocarbons [28-40]. As the above approach [5, 6] described mainly the influence of the type of (nano)particulate filler on the mechanical, thermal and chemical properties, it was of high interest for the present work to investigate the influence of monomer composition and fluorocarbon content of such type of polyimide nanocomposite systems on the anti-adhesive behaviour under technical conditions.

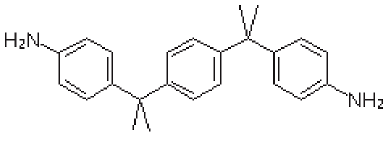
2 Experimental

Materials and preparation procedures

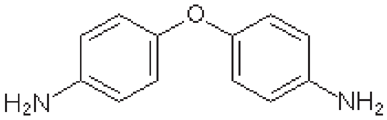
For all coating compositions pyromellitic dianhydride - PMDA (ABCR) was used as anhydride component, SiC (H.C. Starck SiC Grade UF 10, average particle size/ d50: 0.70 μm) as ceramic powder filler and Fluorolink D (Solvay Solexis, average equivalent weight: 1000) as reactive fluoro compound. In order to investigate the influence of the matrix structure on the properties of the polyimide based coatings with respect to the mechanical and chemical stability the different amine compounds Bis(4-aminophenyl)-1,4-disopropyl-benzene – Bisaniline P (Aldrich), 4,4’-Oxydianiline - ODPAm (Aldrich), 3-Aminophenyl sulfone – 3-APS (Aldrich), 4,4’-Bis(3-aminophenoxy) diphenyl sulfone – BAPPS (ABCR) have been used. The chemical formulars of the monomers used are shown in Figure 1 and Figure 2 respectively.

Table 1 gives an overview about the variations in the matrix system. The amount of SiC filler has been kept constant at 40 wt.-% in the solid content. All starting materials were used without further purification.

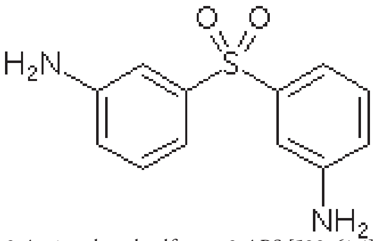
For the preparation of coating materials monomers (PMDA, amine compound, SiC and Fluorolink D) were mixed using a bead mill (Dispermat) in NMP as solvent. For this purpose the starting chemicals were filled together with NMP and glass beads (diameter: 1.7-2.0 mm) in the mil-



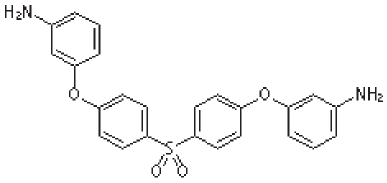
Bis(4-aminophenyl)1,4-disopropyl-benzene – Bisaniline P [2716-10-1]



4,4‘-Oxydianiline -ODPAm [1013-80-4]



3-Aminophenyl sulfone – 3-APS [599-61-1]



4,4‘-Bis(3-aminophenoxy)diphenyl sulfone - BAPPS [30203-11-3]

Fig. 2: Chemical structures of used amine compounds

ling container and were stirred with the corresponding milling tool for 2 hours at 60°C and 2000 rpm. Then the coating material was separated from glass beads by filtration using a sieve to obtain a mixture ready for application. All coating compositions have been applied on stainless steel substrates (1.4301 – dimension: 100x100 mm) using the spray-coating method followed by thermal curing for 2 hours at 200°C.

Measurements

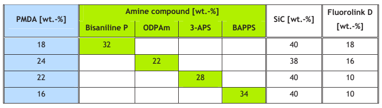
The determination of static contact angles was performed according to the horizontal drop method using a goniometer. For this purpose drops of corresponding solvent (water and hexadecane) with a defined size (about 3 µl) were applied and the angle between the baseline of the drop and the tangent at the drop boundary was measured. The measurement was performed at room temperature (approx. 20°C) and three drops per sample and test liquid respectively were measured.

The determination of surface roughness was carried out by a perthometer, whereas the surface which should be characterized was scanned with a diamond stylus (scan length: 5.0 mm, scan speed: 0.1 mm/ s, stylus force: 15 mg). Afterwards, the different roughness values like Ra, Rz and Rmax were automatically calculated from measured surface data.

The verification of mechanical stability, was performed by Taber Abraser Test according to DIN 53 754. For a further quantification of mechanical stability of the different coating compositions the static contact angles against water and hexadecane were measured by goniometer.

In order to determine the thermal stability the coated substrates were exposed in a convection oven at 150°C for at last 120 hours. After cooling down at ambient temperature (approx. 20°C) the static contact angles against water and hexadecane were measured by goniometer to quantify the thermal stability.

In order to verify the chemical resistance the corresponding test liquids (NaOH 2%, HNO_3 2%, milk (UHT-milk) and carrot juice) were filled in small pots, which were fixed on the coated substrates (cp. figure 3). Afterwards the so prepared samples were put in a convection oven and were exposed for 24 hours at 90°C. After cooling down at ambient temperature (approx. 20°C) the static contact angles against water and hexadecane were measured by goniometer to quantify the chemical stability.



PMDA [wt.-%]	Amine compound [wt.-%]				SiC [wt.-%]	Fluorolink D [wt.-%]
	Bisaniline P	ODPAm	3-APS	BAPPS		
18	32				40	18
24		22			38	16
22			28		40	10
16				34	40	10

Table 1: Investigated compositions of imide based coating materials depending on used amine compound

Fig. 3: Experimental setup for determination of chemical resistance of coatings. Blue pot is filled with corresponding test liquid and fixed on the coated substrate.

3 Results and discussion

3.1 Anti-adhesive polyimide nanocomposite base systems

In order to investigate the influence of the matrix structure in polyimide based anti-adhesive nanocomposite coating systems on the anti-adhesive properties under different loading conditions, different types of aromatic diamine monomers have been chosen to form the intended polyimide structures in combination with pyromellitic dianhydride and carboxylic acid terminated perfluoropolyether (Fluorolink D). As can also be derived from the chemical formulas in Figure 2 the polarity of the diamine monomers increases in the sequence Bisaniline P, ODPAm, 3-APS and BAPPS. It was of interest to investigate the influence of the type of monomer on the initial hydrophobic and oleophobic properties and the stability of the anti-adhesive effect in dependence on the type of external load. Because these monomers have different molecular weight, the variation of the type of diamine should also have an influence on the network density which determines the mechanical surface properties. SiC has been used as nanoparticulate filler at a constant concentration of 40 wt.-%. All monomers and the filler particles have been mixed in a bead mill at 60°C for two hours using NMP as solvent. During this procedure a polyamic acid structure has been formed. This reactive mixture has been coated by spraying technique on stainless steel plates and has been cured at 200°C for again two hours. Figure 4 shows the dependence of the initial static contact angles on the monomer composition in the polyimide nanocomposites on stainless steel.

From Figure 4 it can be derived that all the systems show a behaviour in the contact angle quite comparable to PTFE (contact angle against water/ hexadecane: 118°/ 55°). The observed small differences can be attributed to differences in surface roughness between all the nanocomposite systems and also the PTFE. No distinction can be made also with respect to the monomer composition, which means that the monomer polarity has no influence on the initial static contact angle. This behaviour can be explained by the fact that the Fluorolink D component has enough mobility during the curing process in order to orient its hydrophobic and oleophobic chain to the coating air interface. This enrichment leads to a saturation of the coating surface with perfluorinated carbon chains, which

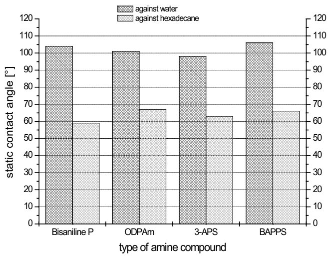


Fig. 4: Initial anti-adhesive properties: Static contact angles (by goniometer) against water and hexadecane depending on used amine compound – substrate material: stainless steel (1.4301) – coating technique: spray-coating – curing conditions: 2 h at 200°C.

Amine compound	Surface roughness [µm]		
	R_a	R_z	R_{max}
stainless steel 1.4301	0,14 ± 0,02	0,93 ± 0,14	1,06 ± 0,08
PTFE	1,35 ± 0,07	9,71 ± 0,54	12,20 ± 1,28
Bisaniline P	0.19 ± 0.05	1.22 ± 0.30	1.93 ± 0.79
ODPAm	0.43 ± 0.07	2.67 ± 0.32	3.51 ± 0.64
3-APS	0.35 ± 0.08	2.25 ± 0.63	4.17 ± 1.98
BAPPS	0.26 ± 0.07	1.63 ± 0.32	2.27 ± 0.85

Table 2: Surface roughness from perthometer depending on used amine compound – substrate material: stainless steel (1.4301) – coating technique: spray coating – curing conditions: 2 h at 200°C.

then dominates the surface properties. To facilitate the interpretation of the contact angle behaviour, table 2 shows the surface roughness of the polyimide nanocomposites from perthometer measurements.

Table 2 shows that smooth surfaces could be obtained with the nanocomposite coatings. The roughness is only slightly higher than that of the stainless steel, whereas the PTFE roughness is about three times higher compared to the nanocomposites. This micro-roughness explains the higher initial contact angle against water of the PTFE. Taking this into account the initial contact angles of the nanocomposites are on a quite reasonable level. In order to use the coatings in practical applications such as food production industry the mechanical resistance of the resulting coated surfaces is of high importance. The durability of the anti-adhesive effect has been investigated using the taber abrader test. Figure 5 shows the percental decrease of the static contact angle after 1000 cycles taber abrader test in dependence on the type of diamine monomer used in the polyimide matrix.

It can be derived from Figure 5 that the monomer composition with the diamine having the lowest polarity also shows the lowest degradation of the anti-adhesive properties after mechanical abrasion. Nevertheless the highest decrease of about 20 % for the system with BAPPS is still tolerable and a sufficient anti-adhesive effect is expected also for this system.

Figure 6 gives additional information about the temperature stability of the nanocomposite systems. This property is especially important if dry processes during the food production are in the focus of the application but also in wet processes such as ultra high temperature treatment of e.g. milk a high temperature stability is required.

From the behaviour of the contact angle in dependence on the duration of temperature load at 150°C in Fig. 6 it can be derived that all the nanocomposites should have enough long term thermal stability with respect to the anti-adhesive effect. The PTFE sample on the other hand does also not degrade in this test.

After these basic investigations it was of interest to obtain information about the behaviour under chemical load conditions. During food production process several cleaning steps are required to be performed by the producer to maintain an uncritical hygienic situation in the components of the production system,

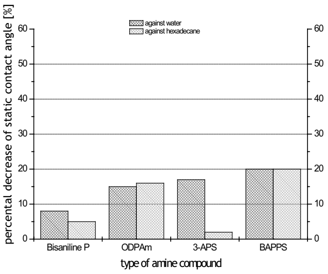


Fig. 5: Percental decrease of static contact angle against water and hex adecane after 1000 cycles taber abraser test – substrate material: stainless steel (1.4301) – coating technique: spray-coating – curing conditions: 2 h at 200°C

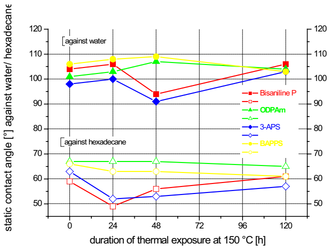


Fig. 6: Static contact angles against water and hexadecane depending on type of amine compound as well as on duration of thermal exposure at 150°C – substrate material: stainless steel (1.4301) – coating technique: spray coating – curing conditions: 2 h at 200°C

which are in direct contact with the food in order to avoid germ formation and growth of bacteria to occur. Of course also the coating materials have to withstand these cleaning conditions even though they have been applied originally to reduce the cleaning effort in order to ensure maximum product safety at any time during the production process. Two typical cleaning agents, sodium hydroxide solution (NaOH, 2 %) and nitric acid (HNO_3, 2 %), have been chosen. The temperature during exposure was chosen to be 90°C to simulate the cleaning step in the facilities. Table 3 shows the results of the cleaning simulation in comparison to two products (milk and carrot juice), which are critical for deposition phenomena in thermal treatment processes.

It is obvious from the results in Table 3 that after 24 h chemical attack by NaOH and HNO_3 at 90°C leads for almost all polyimide systems to destruction of the coating layer. This behaviour was somewhat expected before, because the hydrolytic stability of the imide groupings is limited. In addition to that the HNO_3 has oxidising capability and can attack the organic matrix also by this mechanism. Also the PTFE is not completely unaffected. The real substances milk and carrot juice also show some influence on the remaining anti-adhesive behaviour. The decrease in contact angle against water and hexadecane is more pronounced than in case of e.g. mechanical impact from the taber abrader test, as can also be derived from figure 7 and figure 8, which show the percental decrease of the contact angle after exposure to milk and carrot juice at 90°C respectively.

In the case of milk the oleophobic properties seem to be almost unaffected whereas the hydrophobic properties show a decrease of about 20-30 % during the exposure.

The polyimide nanocomposite comprising BAPPS as diamine monomer shows a significant decrease especially in the oleophobic properties after thermal treatment with carrot juice. It should be mentioned that this coating surface has been visually affected by the carrot juice resulting in discolouration. For this reason, it could not completely be excluded that some deposits of components of the carrot juice have been built, which are responsible for the minimisation of the oleophobic effect. The deposits may have been built especially in the case of the most polar co-monomer BAPPS. This assumption will be further proved by

Amine compound	Contact angle [°] against water/ hexadecane				
	initial	after 24 h NaOH (2%) pH 13	after 24 h HNO_3 (2%) pH 1	after 24 h milk	after 24 h carrot juice
PTFE	118/ 55	86/ 52	77/ 51	118/ 55	115/ 54
Bisaniline P	104/ 59	destroyed	destroyed	84/ 57	84/ 56
ODPAm	101/ 67	80/ 57	destroyed	76/ 65	77/ 64
3-APS	98/ 63	destroyed	71/ 63	71/ 61	68/ 60
BAPPS	106/ 66	destroyed	destroyed	81/ 61	73/ 31

Table 3: Measured static contact angles against water and hexadecane depending on type of amine compound as well as on chemical exposure (NaOH, HNO3, milk and carrot juice) at 90°C for 24 h – substrate material: stainless steel (1.4301) – coating technique: spray coating – curing conditions: 2 h at 200°C

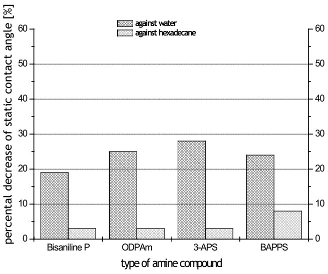


Fig. 7: Percental decrease of static contact angle against water and hexadecane after 24 h of exposure with milk at 90°C – substrate material: stainless steel (1.4301) – coating technique: spray-coating – curing conditions: 2 h at 200°C

additional investigations on the local mechanisms occurring directly at the coating surface.

Overall it can be stated that the anti-adhesive polyimide based nanocomposites obviously have some limitations for the use in wet and hydrolytic environment. For this reason further investigations have been performed to find possible compositions useful for dry processes.

3.2 Influence of modification with carbon black (FW 200) and graphite (KS 6) on the antistatic behaviour of the anti-adhesive polyimide nanocomposites

In dry processes concerning food production such as e.g. flour milling it is important to provide coating systems with antistatic behaviour in order to prevent explosions caused by electrostatic discharge phenomena. From the viewpoint of costs carbon fillers such as carbon black (FW 200, Degussa) and graphite (KS 6, TIMCAL AG) have been dispersed in different amounts in a selected polyimide nanocomposite system from above, in order to elucidate the optimum concentration of these additives for an electrostatic effect while maintaining the abrasion stability of the coatings at the same time. Table 4 shows the results of the charge decay time and the resistivity in combination with the surface roughness for the two different additives in dependence on the concentration. The polyimide system with BAPPS co-monomer has been chosen though the other systems showed slightly better behaviour in the previous testing program, because smooth layers could be created in the unfilled case without carbon filler and the matrix was somewhat more polar, a fact which should be important to provide a good basis for antistatic properties.

From Table 4 it can be derived that beginning with a concentration of 5 wt.-% the resistivity indicates antistatic behaviour of the coating systems. The charge decay time already goes down to 0 s starting from a concentration of 2.5 wt.-% carbon additive. Especially the KS 6 graphite filler seems to have almost no negative effect on the roughness of the coatings. The maintenance of a smooth surface is an important advantage useful for transfer the coating materials towards the practical application. Finally Figure 9 and Figure 10 show the behaviour of the coatings containing carbon black and graphite respectively in the taber abrader test.

It can be concluded from the taber abrader test, that the carbon additives have no negative effect on the

Kind of modifier	Amount of modifier [wt.-%]	Static contact angle [°]		Surface roughness [μm]			Decay time of electric-charge [s]	Resistivity [Ω]
		water	hexa-decane	R_a	R_z	R_{max}		
-	0	106	66	0.26 ± 0.07	1.63 ± 0.32	2.27 ± 0.85	2.9	5.1×10^9
FW 200	2.5	106	63	0.70 ± 0.10	4.21 ± 0.50	5.70 ± 0.82	0	1.3×10^5
	5	107	63	0.75 ± 0.03	4.76 ± 0.47	7.75 ± 1.92	0	1.2×10^6
	10	110	66	0.38 ± 0.096	2.85 ± 0.69	5.45 ± 3.09	0	1.5×10^3
KS 6	2.5	106	63	0.41 ± 0.10	2.64 ± 0.74	4.08 ± 1.49	0	2.3×10^9
	5	107	63	0.24 ± 0.06	1.53 ± 0.40	1.87 ± 0.66	0	1.1×10^5
	10	110	66	0.32 ± 0.01	2.06 ± 0.03	2.71 ± 0.29	0	8.7×10^4

Table 4: Influence of modifier (carbon black – FW 200/ graphite (KS 6) and modifier amount on static contact angles against water/ hexadecane, surface roughness as well as conductivity determined by decay time and resistivity – coating material: PMDA/ BAPPS with 10 wt.-% Fluorolink D and 40 wt.-% SiC – substrate material: stainless steel (1.4301/ 1.4571) – coating technique: spray-coating – curing conditions: 2 h at 200°C

wear resistance of the coatings, even though the additives are soft compared to the SiC filler used. Especially the carbon black FW 200 seems to exert some tribological properties which result in a slight decrease of the percentage decrease in contact angle with increasing FW 200 concentration.

4 Conclusion

The investigations revealed that interesting polyimide based anti-adhesive nanocomposites could be created, which show similar anti-adhesive behaviour like PTFE surfaces. Their big advantage compared to PTFE is their ability to be applied by spray coating on almost every type of substrates and to be cured under comparably mild conditions. Although the chemical stability in wet, hydrolytic environment is quite limited for these types of systems, they show an excellent behaviour which makes them suitable for applications in dry processes. It is important to note, that an antistatic behaviour can be installed without loosing the mechanical stability. Overall a material basis has been worked out which after appropriate optimisation and technology development has a big potential to be used as anti-adhesive surface in industrial processes.

5 Acknowledgements

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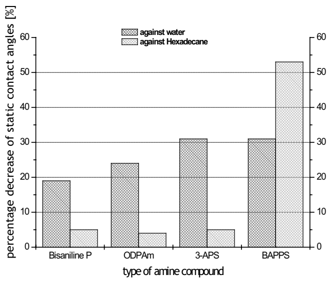

Fig. 8: Percental decrease of static contact angle against water and hexadecane after 24 h of exposure with carrot juice at 90°C – substrate material: stainless steel (1.4301) – coating technique: spray-coating – curing conditions: 2 h at 200°C

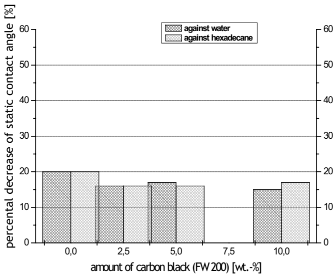

Fig. 9: Influence of the amount of carbon black (FW 200) on wear resistance determined by decrease of static contact angles against water and hexadecane after 1000 cycles taber abrader test respectively – coating material: PMDA/ BAPPS with 10 wt.-% Fluorolink D and 40 wt.-% SiC – substrate material: stainless steel (1.4301) – coating technique: spray-coating – curing conditions: 2 h at 200°C

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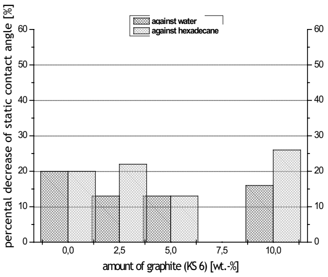

Fig. 10: Influence of the amount of graphite (KS 6) on wear resistance determined by decrease of static contact angles against water and hexadecane after 1000 cycles taber abrader test respectively – coating material: PMDA/ BAPPS with 10 wt.-% Fluorolink D and 40 wt.-% SiC – substrate material: stainless steel (1.4301) – coating technique: spray-coating – curing conditions: 2 h at 200°C

Quantitative spectrochemical Analysis of Na_3AlF_6, $ZrSiO_4$ and InSb with the Analytical Electron Microscope (TEM & SEM)

Eine Reihe zertifizierter natürlicher Mineralien und synthetisierter Zwei- und Mehrelementverbindungen, Kryolith (Na_3AlF_6), Zirkon ($ZrSiO_4$) und Indiumantimonid (InSb) [1] - teilweise in oxidischer Form vorliegend - wurde nach standardfreier Methodik mittels energiedispersiver Rönt-

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[1] Reference Standards for TEM, registered Stand. No. 5998, Science Services München