APPLICATION OF NANOTECHNOLOGY FOR ANTI-FRICTION COATINGS

Marco ENGER, Pavel BLAŠKOVITŠ

ABSTRACT

Different slide-active coatings for thermoplastic surfaces, based on a new binder technology, were investigated for their use as slide element in the automobile interior. The main focus of this paper is the determination of the sliding behaviour of the coated thermoplastics in direct comparison to the uncoated variants. The coatings showed clearly different slide motion properties concerning their friction coefficient and stick-slip behaviour. In a direct comparison with the currently used polymers a clear improvement of slide properties could be achieved.

KEY WORDS

slide-active coatings, thermoplastics, friction, solid lubricants, stick-slip, nano-structured particles

INTRODUCTION

Thermoplastic materials are indispensable for many technical applications as they combine many important properties. They can be easily processed and feature a low specific weight. Additionally, their physical properties can be adapted for specific applications. The application of plastics in the car industry is immense and is growing continuously with increasing comfort, safety standards and quality requirements. Especially plastics have established themselves in the car interior for example as dashboards, levers or cover parts [1, 2].

For these components thermoplastic polymers such as ABS, PC, polymer blends or reinforced polymer blends for components requiring a higher material stiffness are often used. Due to danger of contamination there is no possibility to use conventional lubricants (greases and oils). Under dry friction conditions these polymers show a high stick-slip tendency and have high friction level, which can cause disturbing noise emission and also stiff movement of the different plastic components [3-6].

A solution to improve the frictional behaviour of these thermoplastics is dry lubrication with solid lubricants. Solid lubricants are materials which are able to separate two contacting

Marco Enger, M.Sc., Hochschule Mannheim, Kompetenzzentrum Tribologie, m.enger@hs-mannheim.de
Prof. Ing. Pavel Blaškovitš, DrSc., Slovak University of Technology in Bratislava Faculty of Materials Science and Technology, pavol.blaskovits@stuba.sk

surfaces in relative movement to improve their friction and wear behaviour. If solid lubricants are used, the question arises how these materials can be fixed to the contacting surfaces. Anti-friction coatings are a possibility for the fixation of these materials. In general anti-friction coatings consist of a solid lubricant, a binder and a solvent.

Fig. 1 Friction behaviour of various amorphous thermoplastics

Within this research thesis new anti-friction coatings should be developed on the basis of a new binder technology (Silixane) for thermoplastic surfaces. The present paper shows some research results of the last years. Some of the results were also published on other conferences and scientific journals.

EXPERIMENTAL DETAILS

Coating systems

Various slide-active coatings based on the new Silixan binder technology [7, 8] were prepared for this study and applied on different polymeric surfaces. The binder system was slide-modified with typical solid lubricants (PTFE, h-BN, graphite) at different concentrations. The main steps of the coating process are described below. First, the fine solid lubricant particles (PTFE, h-BN, graphite) were homogeneously dispersed in a system containing a Silixan binder and a solvent. Second, the substrate surfaces were pre-treated (degreased and roughened) to improve the adhesion behaviour between coating and substrate. Third, the mixture was applied onto the specimen surfaces by spray application (spray gun). Finally, the coatings were cured in a furnace at a temperature of 80 °C for one hour. The coating process is the same for all coatings. Table 1 gives an overview of the composition of the investigated coatings.

COMPOSITION OF THE DIFFERENT COATING SYSTEMS

Table 1

Solid	Concentra	Size	Bind
PTFE	10/20/40%	4 μ m	Silixa
Graphite	10/20/40%	8 – 28	Silixa ⁿ
h-BN	10/20/40%	3 μ m	Silixa ⁿ

Silixan binders are currently used for nano-based scratch-resistant coatings. The innovative characteristic of the new binder class is the creation of nano-scaled SiO_2 -particles during the curing phase. Figure 2 shows a structural model of a hardened Silixan binder system. The particles distribute homogenously in the binder. They build a strengthening phase in the cured coating system [9] which could have a positive effect on the tribological properties.

Fig. 2 Structural model of a hardened binder system with nano-structured formation between hard glass-like and soft polymer-like zones [9]

In [10] the influence of nanostructured SiO_2 -particles on the sliding behaviour of anti-friction coatings was investigated. Therefore, conventional anti-friction coatings were modified with SiO_2 -particles in terms of powder at different concentrations. The results showed the positive influence of SiO_2 nano-scaled particles on the tribological property profile of anti-friction coatings. Primarily, a significant increasing of the coating durability could be achieved with those particles.

Within the framework of this paper, portfolios of this new class of binders are to be extended regarding their application as binder for slide-active coatings.

Test matrix

For estimating the suitability of the new developed slide-active coatings for the application as slide element, an extensive test program is needed.

Adequate adhesion between coatings and plastic surfaces is essential for the subsequent function as sliding element. Therefore, the bond strength as well as the resistance against mechanical influences will be investigated with the cross-cut and scratch test.

The main focus of the investigation is the tribological characterisation of the coating systems in direct comparison to typical used uncoated thermoplastics.

The investigation of the friction behaviour was run on the Universal-Micro-Tribometer (UMT). The following factors of influence were tested:

- Various p,v-values
- Solid lubricant concentration.

The schematical illustration of the test device is given in figure 3. The test configuration was ball on disk. The temperature and the humidity of the atmosphere were nearly constant during the complete test matrix.

Fig. 3 UMT test rig (ball on disc configuration)

RESULTS AND DISCUSSION

Particle dispersion

The first investigation step was the determination of the particle dispersion of the different slide-active particles in the Silixan matrix. Inhomogeneous particle dispersion can have a negative influence on the adhesive and cohesive as well as on the sliding properties. The results are given in the following micrographs.

The PTFE particles distribute homogeneously in the matrix. No influence of the particle concentration is observable. The graphite particles distribution is very homogeneously independent form the particle fraction in the matrix. For the BN particles a significant particle agglomeration in the matrix is given with the highest agglomeration rate for the lowest solid lubricant concentration (Figure 4, 5 and 6).

Fig. 4 Particle dispersion of the PTFE-particles in the matrix:
a: 10 % PTFE, b: 40 % PTFE

Fig. 5 Particle dispersion of the graphite-particles in the matrix:
a: 10 % graphite, b: 40 % graphite

Fig. 6 Particle agglomeration of the BN-particles in the matrix:
a: 10 % BN, b: 40 % BN

Furthermore, a cross-linking catalyst was used to reduce the agglomeration of the BN particles in the polymeric matrix resulting in a better particle distribution. However, the BN particle agglomeration cannot be completely eliminated.

Bond strength and scratch resistance

Adhesion behaviour

Adequate bond strength between coating and substrate is an important property of the coating for the further use as slide element. To get a first information about the bond strength of the coating systems different thermoplastic (PCABS, ABS, PC, PCABS+GF) materials with various topographies ($R_z = 0,5$ to $16 \mu\text{m}$) were coated with slide-modified Silixan binders. The adhesion between the substrate and the coating systems were measured with the cross-cut test (DIN EN ISO 2409). The cut surfaces were examined with a scanning electron or a digital microscope to more clearly detect a possible coating failure (e. g. coating delamination).

The following figures show the surface analysis for a PCABS substrate with two representative topographies coated with a PTFE-system. No laminar coating failure is observable. Only in the areas of the "cuts" is a marginal damage of the coating apparent.

Fig. 7 Overview cross-cut: a: polished polymer surface, b: blasted substrate surface

The complete results of the influence of the surface topography on the bonding strength of the coatings are given in table 2. All coatings in the test showed a good bond strength independent from the topography that argue for a good chemical (covalent bonding) and mechanical bonding between binder and the substrate surface. This suggests that a sufficient adhesion between binder and base substrate is given. All coatings show similar adhesion behaviour determined with cross-cut test. No coating failed in the cross-cut test through insufficient bond strength.

INFLUENCE OF THE SUBSTRATE TOPOGRAPHY
ON THE ADHESION BEHAVIOUR
(PTFE COATING APPLIED ON PCABS)

Table 2

Substrate topography		Bonding strength
Polished	$R_z \leq 1$	Rating 5: no peeling or removal
	$R_z = 1$	Rating 5: no peeling or removal
Grinded	$R_z = 3$	Rating 5: no peeling or removal
	$R_z = 5$	Rating 5: no peeling or removal
Blasted	$R_z = 8$	Rating 5: no peeling or removal
	$R_z = 16$	Rating 5: no peeling or removal

Scratch test

In the scratch test, an indenter is moved over the coated surface under continuously increasing load with a constant slide velocity. The scratching point produces an increasing elastoplastic deformation of the coating-substrate systems until a coating failure (coating chipping and spalling, coating flaking, coating breakthrough or distinctive cracking) occurs which can have an adhesive or cohesive nature.

Fig. 8 Schematic illustration of the scratch test method

The point at which an incipient or a complete coating failure occurs can be read off directly by using SEM analysis. The corresponding forces which are responsible for the coating failures can be derived directly from the linear relationship between applied force and travelled distance and are named as critical load L_c or failure load L_f (Figure 8). The test parameters were: maximum load = 7,5 N, distance = 10 mm, duration of the test is 1 min.

Fig. 9 SEM-analysis of the scratch track of a BN based coating applied on PCABS:
a: load = 1 N, b: load = 1,6 N, c: load = 2,2 N

Detailed investigations of the scratch tracks are carried out on the scanning electron microscope. Figure 9 represents exemplary SEM micrographs of a BN-based coating applied on PCABS substrate. An extensive plastic deformation of the substrate coating composite is visible in the SEM micrographs, which increases with an increasing load. In spite of the significant plastics deformation of the coating and substrate no coating failure is detectable. This indicates good bond strength between coating and substrate.

Furthermore, cracking was established in the scratch track at a critical load induced by the deformation of the soft substrate. If the coating cannot deform accordingly it will crack. Thereby the typical crack patterns are observable: angular cracks, conformal cracking and tensile cracking. Conformal and tensile cracks are typical for coatings which remain fully adherent on the substrate. The damage increases significantly with increasing load, and a distinctive crack network is formed. No complete coating failure (e. g. coating chipping or a coating breakthrough) is observable. All investigated coatings show similar behaviour.

On the basis of the SEM-analysis the critical failure load was defined for each coating. In this context the critical load represents the load at which a distinctive crack network is visible in the scratch track. The results are given in the following bar diagram (Figure 10).

Fig. 10 Critical load determined with the scratch test

The BN coating system shows the earliest failure of the investigated coating systems. The values for the critical load range between 1,3 and 2,2 N. The highest resistance against mechanical influences was performed by the PTFE-based coating system. For the PTFE coating the average value for the critical load is 1,7 to 3,7 N. The critical load (1,8 to 2,9 N) of the graphite system lies between the other two coating systems. The substrate materials possess a significant influence on the scratch resistance of the coatings. The highest critical loads were determined for the PCABS and ABS substrate. Applied on substrates with a lower deformability (PC, PCABS+GF) all coatings show a premature coating failure.

Tribological behaviour

Friction behaviour

The next tests encompass the tribological behaviour of the coatings under oscillating friction conditions. The results are shown in the figure 11. The given values represent an average of a minimum of three replicate measurements. The error bar indicates the corresponding maximum and minimum measured value. During the tests, the main parameters were chosen as follows: constant slide velocity of 10 mm/s, the normal load varied from 1 and 3 N, corresponding to the maximum Hertzian contact stress 30 and 45 MPa.

Fig. 11 Friction behaviour

The BN coating shows a very low friction level for each investigated p,v-value. The PTFE coating system features a good sliding performance for the complete p,v-spectrum. The graphite based system exhibits a higher coefficient of friction than the other two coating systems. All coatings show a decreasing coefficient of friction with higher loads. The coefficient of friction for uncoated samples is much higher. These findings suggest the three coatings can effectively reduce the friction level under oscillating movement.

Long-term behaviour

To be able to make a statement about the long-term behaviour of the different coating systems an endurance test was carried out for two specific p,v-values (contact stress = 45(85) MPa, velocity = 20(50) mm/s, duration = 48 h). The results are illustrated in figure 12 and 13.

For the description of the durability of the coatings two times are necessary. First, the instant of time at which the coating system is completely intact (steady-state coefficient of friction). This point also defines the time at which the first discontinuities such as short-term peaks in the coefficient of friction curves and/or an increase of the friction coefficient to a higher level can be identified, which are indicators for a partial coating failure. Second, the elapsed time till the coating failed through a complete breakthrough.

Figure 12 Durability at low p,v-values

Fig. 13 Durability at high p,v-values

The PTFE coating shows the best long-term behaviour. The graphite coating also exhibits good durability for the low p,v-combination. The BN based coating performs an insufficient durability for both investigated p,v-values. All coatings show a significant reduction of their durability for an increasing collective stress. As in all coating systems, the same pre-treated

substrate is used and all parameters of the coating process are the same. The different durabilities can be ascribed to the influence of the various solid lubricants. The BN coating builds two phases during the curing phase, which cause a degradation of the adhesive and cohesive properties of the coating leading to a premature coating failure.

Influence of the solid lubricant concentration

The friction and wear behaviour of slide-active coatings depends strongly on the coating composition. In particular, the fraction of the solid lubricant can have a significant influence on the tribological properties.

The variation of the friction level of the different coating systems against the solid lubricant concentration is shown in the following diagram.

The solid lubricant concentration does not significantly affect the friction behaviour of PTFE and graphite based coating systems. Both coating systems possess a constant tribological performance independent from the used solid lubricant fraction in the coating matrix. For the BN modified coating a significant influence of the solid lubricant on the sliding behaviour is given. The BN coating shows a premature coating failure for the lower solid lubricant concentrations due to the high agglomeration rate of the BN particles in the polymeric matrix.

Fig. 14 Influence of the solid lubricant concentration

CONCLUSION

Within this work different slide-active coatings for thermoplastic surfaces, based on a new binder technology, were developed to improve the sliding behaviour of thermoplastic surfaces. These coatings were slide-modified with typical solid lubricants (h-BN, PTFE, graphite) at different concentrations. The first focus of the investigations was the determination of the adhesion behaviour as well as the behaviour against mechanical influences. The friction properties under oscillating movement conditions against different parameters were investigated. Furthermore, the long-term behaviour of the coating was determined. The coatings showed clearly different slide motion properties concerning their friction as well as the long-term behaviour. All coating substrate composites possess good bond strength determined with the cross-cut test. All coatings feature a good resistance to mechanical influences. The results of the friction and wear tests showed that these coatings can effectively reduce the stick-slip tendency and the friction level of amorphous thermoplastics and can also improve their wear resistance. The PTFE coating possesses the best friction behaviour. The endurance test performed on the coatings reveal different wear

lives for each coating. The best long-term behaviour was shown from the graphite and PTFE based coatings.

REFERENCES

1. T. L. HENSEL. 2004. *Globale Marketingstrategien für technische Kunststoffe*. Ticona GmbH, Kelsterbach.
2. Kunststoffe im Automobil: Einsatz und Verwendung. Verband Kunststoffherstellende Industrie e.V. (VKE), Frankfurt/Main
3. N. S. EISS, J. HANCHI. 1998. Stick-Slip friction in dissimilar polymer pairs used in automobile interiors. *Tribology international: the technology of lubrication, wear prevention and friction control*.
4. N. S. EISS, B. P. McCANN. 1993. Frictional Instabilities in Polymer-Polymer Sliding. *Tribology Trans.* 36.
5. N. S. EISS, J. HANCHI. 1998. Friction Instabilities in Plastics Used in Automotive Interiors. *Industrial and Automotive Lubrication. 11th International Colloquium*.
6. H. ENDO, E. MARUI. 2004. Fundamental studies on friction and wear of engineering polymers: *Industrial Lubrication and Tribology*.
7. S. SEPEUR, N. LARYEA. 2008. Silixane – Basis für die Lacke der Zukunft.
8. S. SEPEUR, N. LARYEA, F. GROSS, S. GOEDICKE. 2008. Nanotechnologie: Grundlagen und Anwendungen. Farb und Lack Edition. Vincentz Network.
9. N. LARYEA, S. SEPEUR, C. THURN, M. Mönkemeyer. 2010. Damit das Auto noch lange glänzt: Hochkratzfeste Klarlacke mit neuem Bindemittelkonzept, *Farbe und Lack*, Ausgabe 7.
10. R. ZECHEL, S. HARTL, P. STAUB. 2010. High-Performance Verschleißschutz mit nanopartikelhaltigen Gleitlacken, 51. *Tribologie Fachtagung: Reibung, Schmierung und Verschleiß: Forschung und praktische Anwendungen*, Band 2.
11. W. STEHR. 2002. Stick-Slip Verhalten von Polymeren. 13th International Colloquium *Tribology*, TAE-Esslingen.