Formulation and testing of scratch resistant clearcoats

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The multilayer coating technology, with a clearcoat as a last layer, which evolved in the automotive industry, is already well established in many other industries. The advantage of this technology relates to the application of coatings with special functions in a multilayer coating system, whereas one of requirements toward clearcoats is a high and durable scratch resistance.
At present, several clearcoats with an enhanced scratch resistance are already available on the market. The general rules of the formulation of such coatings are however unknown and there is no agreement upon the usage of defined methods for the evaluation of their scratch resistance. Both issues have been tackled within the frame of the government supported research project at FPL, with a cooperation of the industrial companies.

New polymers and nanoparticles for scratch resistant coatings
It can be supposed that the most influential factors on the scratch resistance of clearcoats are the specific properties of the polymeric binder such as elasticity, hardness, glass transition temperature, mol mass, chemical and spatial structure of the polymer, the crosslinking density and the constitution of the polymer network after curing. By the choice of several new polyurethane polymers for clearcoats (Table 1), these parameters have been varied and tested on their influence on the scratch resistance.

Table 1 Choice of polyurethane polymers for clearcoats

Clearcoat	**Discription**
Bayer-1	Standard formulation, polyacrylate polyol (4.2% OH), functionality 3.5, HDI trimer (21.8% NCO), middle molar mass
Bayer-3	Polyacrylate/polycarbonate polyol (9:1, 4.9% OH), functionality 3.5, HDI trimer (21.8% NCO), higher crosslinking density, more flexible
Bayer-5	Polyacrylate/polycarbonate polyol (9:1, 4.9% OH), functionality 3.5, HDI trimer (21.8% NCO), lower molar mass of the polycarbonate diol
Bayer-7	Polyacrylate polyol (16.5% OH), functionality 4.5, HDI trimer/allophonate (19.3% NCO), high crosslinking density, better self healing

It has been already empirically found that the scratch resistance of coatings can be improved by the addition of nanoparticles [1, 2]. Because the mechanism of action of nanoparticles is not definitely cleared up and understood, it became also a subject of the present research. Several nanoparticle products tested in this work are given in Table 2.

Table 2 Nanoproducts tested in clearcoats

Nanoparticles	**Description**
Al_2O_3	Different spherical, hydrophobic and hydrophilic products with a particle size of 13-20 nm, acronyms: Al-3610D, Al-C, Al-C805
$BaSO_4$	Hydrophilic, spherical product with a particle size of 40 nm
Bentonite	Different plately like hydrophilic and hydrophobic products with a particle size of <1µm, 1 nm, acronyms: Bt-15, Bt-32
SiO_2	Different spherical, hydrophobic and neutral products with a particle size of 12-20 nm, OH or C=C funcionalized, acronyms: Si-3650D, Si-44D, Si-46D, Si-7200, Si-7200D, Si-9200, Si-9200D
ZnO	Different spherical, hydrophilic and hydrophobic products wit a particle size of 25 nm, acronyms: Zn-20D, Zn-Z805D

Testing the scratch resistance

For the evaluation of the scratch resistance of the clearcoats such methods as nanoscratch tester (NST), Amtec-Kistler, Rota-Hub and Crocmeter were utilized. Dynamic Mechanical Analysis (DMA) and internal stress measurements were also carried out.

The data of the nanoscratch test are usually represented as a interdependence between the gloss after scratching and the minimal force needed to produce irreversible scratches. The greater gloss/recovery and the greater force to induce scratches stand for the better scratch resistance. The NST diagram for clearcoats with 10 % w/w of nanoparticle tested is given in Fig. 1.

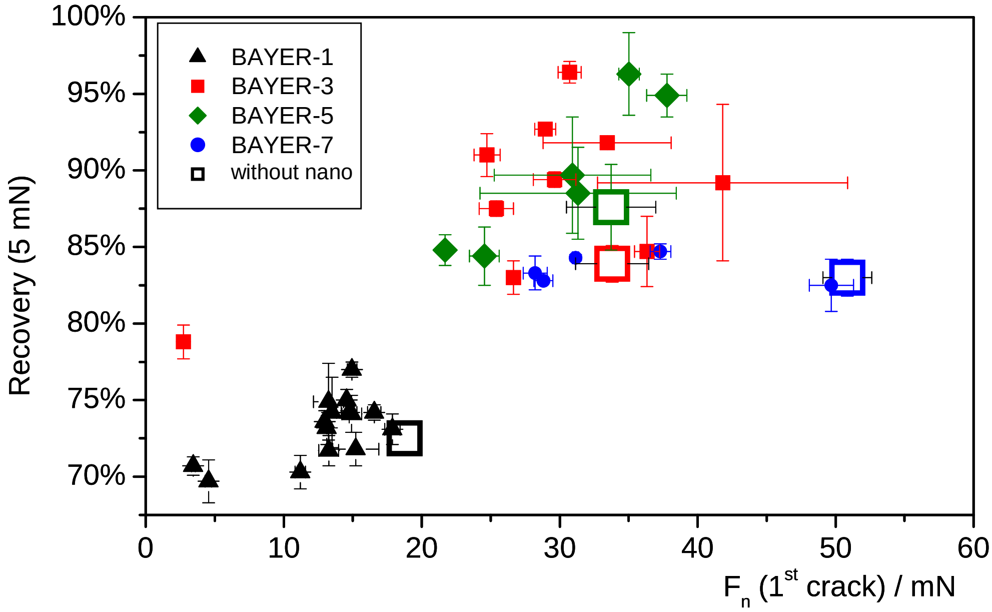

Fig. 1 NST data for clearcoats with nanoparticles

Exemplary data of a Crockmeter evaluation of nanoparticles in a standard formulation are given in Fig. 2.

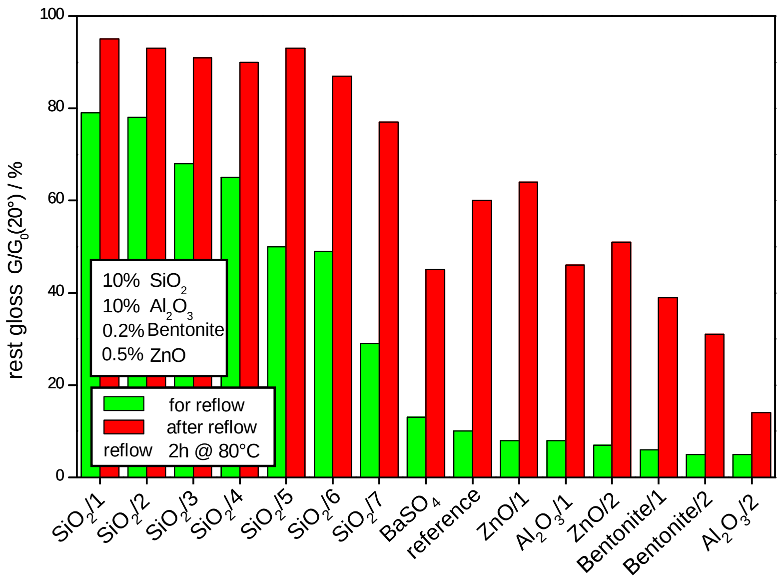

Fig. 2 Crockmeter data for a standard coating formulation BAYER-1 with nanoparticles

In opposite to the NST data, diverse SiO_2 particles showed an essential improvement of the scratch resistance of the standard coating formulation BAYER-1 according to the Crockmeter test. The same effect was noticed also for the remaining coatings. It is therefore obvious that the scratch resistance of coatings can be improved by the addition of nanoparticles but the extend of this improvement is nanoparticle specific and has to be proved from case to case separately. It is also striking that the Crockmeter data differ from the data of NST and allow a better discrimination of nanoparticles. This can be attributed to the methodical differences between both methods.

Nanoparticles in coatings

The interactions of nanoparticles with each other and with the surrounding polymeric matrix seem to be important influential factors on the scratch resistance of coatings too. The SEM micrographs in Fig. 3 depict the distribution of SiO_2 nanoparticles in a standard formulation.

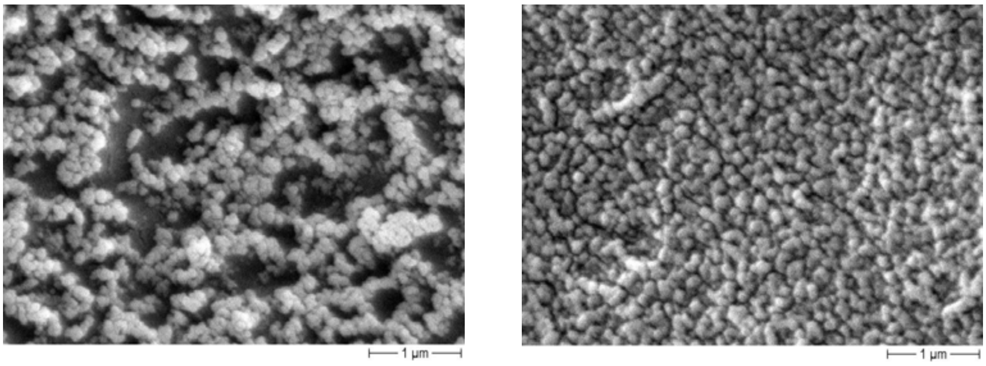

Fig. 3 SEM micrographs of cross sections of a standard formulation with organically treated (left) and untreated (right) SiO_2 nanoparticles

For organically treated SiO_2 a kind of a particle self organization in strings and a build-up of a quasi secondary network within a polymeric network of the binder took place. For these particles a pronounce tendency to improve the scratch resistance of coatings was noticed. In the case of non-treated SiO_2 particles a homogeneous distribution within the coating matrix was noticed.

The exemplary data of the Dynamic Mechanical Analysis (DMA) for the standard formulation with nanoparticles are given in Fig. 4.

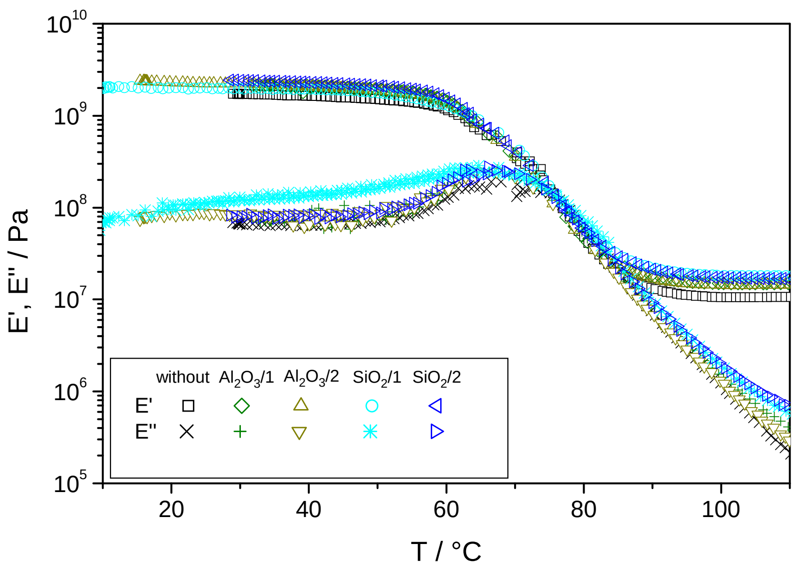

Fig. 4 DMA data for the standard formulation BAYER-1 with 10% w/w of nanoparticles

The small rise of the plateau in a rubber-elastic area can be related to the presence of non-interacted spherical particles with a polymeric matrix, as foreseen by the theory of Einstein and Guth [3].
Nanoparticles can also influence the internal stress of coatings. The exemplary data for the internal stress of two coating formulations with nanoparticles are given in Table 3.

Table 3 Exemplary data for the internal stress of coatings with nanoparticles

10 % w/w nanoparticles	BAYER-1 / MPa	BAYER-3 / MPa
-	1.5	0.2
Al_2O_3/1	0.8	0.1
Al_2O_3/2	0.1	0.1
SiO_2/1	0.5	0.2
SiO_2/2	0.7	0.0

It is evident that nanoparticles reduce efficiently the internal stress in coatings, which could be regarded as a potential factor by their action toward the improvement of the scratch resistance of coatings.

Conclusions

The polymeric binders influence the scratch resistance of clear coats to a great extend. Such polymer properties as a high crosslinking density, accompanied by the enhanced elasticity are of a great advantage.
Nanoparticles can further improve the scratch resistance of clear coats. Their relaxation action toward the internal stress and the aligement in the polymeric matrix boost their action. A direct participation of nanoparticles in the build-up of the polymeric network seem not to be a decisive factor.
Crockmeter test allows a distinct discrimination of clearcoats according to their scratch resistance and correlates well with a nanoscratch test. Amtec-Kistler and Rota-Hub tests utilize a lower loading and exhibit a respectively weaker discrimination power.

Literature

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