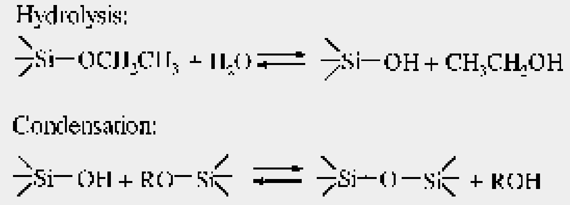
Morphology of Hybrid Coatings Based on Polyester, Melamine Resin, and Silica and the Relation with Hardness and Scratch Resistance

S. Frings, C.F. van Nostrum, and R. van der Linde[**]—Eindhoven University of Technology[*]
H.A. Meinema and C.H.A. Rentrop—TNO-TPD[†]

The morphology of hybrid coatings based on polyester, melamine resin, and various amounts of silica has been investigated, and the hardness and scratch resistance were determined. By increasing silica content, an increase of silica particles in size and number was observed. Small silica particles were preferentially present at the surface. The influence of the silica content on the König hardness, indentation hardness, and elastic modulus was minor. The improved scratch resistance determined for a hybrid coating with 11.4 wt% silica, compared to a similar organic coating without silica, was attributed to small silica particles preferentially present at the surface.

INTRODUCTION

Organic-inorganic hybrids are materials in which the organic and inorganic compounds are combined on a molecular level to benefit from the properties of both components in one material. These hybrid materials are prepared by the synthesis of inorganic components in the presence of organic components using the sol-gel process. The sol-gel process is a method in which inorganic materials can be synthesized by chemical reactions at temperatures far below the temperatures used in conventional methods.[1] This method makes it possible to synthesize inorganic materials in the presence of organic materials, resulting in hybrid materials. In the sol-gel process, metal alkoxides are hydrolyzed followed by condensation reactions to form metal-oxides.[2,3] This is illustrated in *Scheme* 1 for tetraethoxysilane (TEOS). TEOS is often used for the formation of hybrid materials, since the hydrolysis and condensation reactions are relatively slow and therefore well controllable.



$$\equiv Si-OCH_2CH_3 + H_2O \rightleftharpoons \equiv Si-OH + CH_3CH_2OH$$

$$\equiv Si-OH + RO-Si\equiv \rightleftharpoons \equiv Si-O-Si\equiv + ROH$$

SCHEME 1—Sol-gel reactions of tetra-ethoxysilane ($Si(OCH_2CH_3)_4$).

Hybrid materials cover a wide range of materials that can either be based on inorganic glassy materials, in which organic compounds are incorporated to improve, for example, the flexibility[4,5] or on organic materials, which are modified with inorganic compounds for reinforcement[6-8] or to improve properties like heat resistance.[9,10] Several studies have been reported on the structure-properties relation of bulk hybrid materials, using small-angle X-ray scattering and dynamic mechanical analysis.[6,7,11,12] These techniques are less accessible for coating characterization, due to the necessity of uniform and thick samples and preferably free films. Hybrid coatings are mainly under study to improve the scratch resistance of polymer surfaces like polycarbonate, polyethyleneterephtalate, and polymethylmethacrylate. Both inorganic[13-15] -based and organic[16-18] -based hybrid coatings have been studied for this purpose. The scratch resistance in these studies was tested by the Taber abraser test or the Vickers hardness test, however, no direct relations to the coatings morphology were reported.

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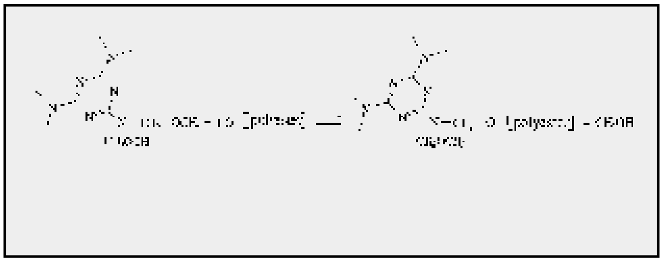
[*] Dept. of Polymer Chemistry and Coatings Technology, P.O. Box 513, 5600 MB Eindhoven, The Netherlands. e-mail: S.Frings@tue.nl, C.F.v.Nostrum@tue.nl, R.van.der.Linde@tue.nl

[†] Materials Division, Dept. of Materials Chemistry and Coatings, P.O. Box 595, 5600 AN Eindhoven, The Netherlands. e-mail: Meinema@tpd.tno.nl, Rentrop@tpd.tno.nl

[**] Author to whom correspondence should be sent.



The aim of this investigation is to study the influence of the chemical composition on the resulting morphology and the mechanical properties of polyester based hybrid coatings, potentially suitable for coil coating applications. These applications display two important features uncommon for the hybrid materials described so far. Firstly, under coil coating conditions coatings are cured fast at a high temperature. Secondly, it is very important that such coatings remain flexible, since precoated metal sheets must be shaped afterwards. Since the flexibility is obtained from the organic phase, polyesters with a low glass transition temperature (T_g) were used. TEOS was used as a precursor in the sol-gel reaction to form hard silica incorporated within the organic matrix. To be able to cure the coatings fast and at high temperature, TEOS was prehydrolyzed before it was added to the organic coating mixture. This prehydrolyzation step was found to be necessary because otherwise most of the TEOS evaporated during curing.[19,20] The polyester resin was crosslinked with hexakis(methoxymethyl)melamine (HMMM) to form an organic network. The reaction, which is acid catalyzed, is displayed in *Scheme* 2.[21] In addition to this reaction, self-condensation of HMMM can take place.[22]

Under acidic conditions the hydrolysis of TEOS is faster than the condensation reaction.[2,23] This results in a large amount of silanol groups that slowly react to form Si-O-Si by condensation, finally resulting in a branched network of silica. In the presence of hydroxyl-terminated polyester and HMMM, the silanol groups can also react with these compounds, although the so formed Si-O-C bonds are sensitive to hydrolysis. In this paper the influence of the amount of silica in the acid-catalyzed polyester-HMMM system on the morphology and the relation with the hardness and scratch resistance of the coatings is described.

EXPERIMENTAL

Materials

A trifunctional hydroxyl-terminated polyester resin was synthesized from diols, triols, and diacids by conventional methods.[24] The molar monomer composition consisted of 35% isophthalic acid, 12% adipic acid, 33% neopentylglycol, 12% of an esterdiol $(HOCH_2C(CH_3)_2CH_2OC(O)C(CH_3)_2CH_2OH)$, 6% trimethylolpropane, and 2% 1,4-cyclo-hexanedimethylol. The polyester was characterized by endgroup titration, gel permeation chromatography (GPC), and differential scanning calorimetry (DSC). The characteristics are summarized in *Table* 1. The HMMM resin: Resimene 745, supplied by Monsanto, was used as received. Tetraethoxysilane 98% (TEOS, Acros), 1-methoxy-2-propyl acetate (MPA, Merck), ethanol 99.8% (Biosolve) and ethyl acetate 99.8% (Biosolve), were used as received. P-Toluenesulfonic acid monohydrate 99% (pTSA, Acros) was recrystallized from ethyl acetate, then dried and dissolved in MPA.

Coating Preparation

All coatings were prepared by dissolving the polyester resin, HMMM, and prehydrolyzed TEOS in MPA to obtain a transparent viscous solution. TEOS was prehydrolyzed ex situ, overnight, in ethanol (25 wt%) with two equivalents of water, at a pH of 2 (pTSA). The molar ratio of HMMM:polyester was 1.5, but to see the influence of a less dense network in the morphology study, a ratio of 0.75 was applied. To the mixture pTSA (1 wt% based on the solid content of the coating) was added. The coating mixtures were applied on acetone cleaned glass plates with a 90 µm doctor blade and on aluminum plates with a wirebar having a pitch of 0.8 mm. After a flash off time of 5 min the coatings were cured in an air-circulation oven at 200°C for 10 min.

Table 1—Characteristics of the Polyester Resin

Acid value[a] (mg KOH/g)	OH value[a] (mg KOH/g)	Mn[a] (g/mole)	Mn[b] (g/mole)	D[b]	T_g[c] (°C)	fn[d]
0.2	83.8	2004	2647	2.9	13	3

(a) Determined by endgroup titration.
(b) Determined by GPC (two Shodex KF-80M (linear) columns, using a refractive index detector (Waters 410), THF as eluent with a flow rate of 1ml/min), based on polystyrene standards.
(c) Determined by DSC (Perkin-Elmer DSC7, 20 °C/min from –40 to 80 °C).
(d) Calculated from composition.
Mn = number average molecular weight, D = polydispersity index, fn = functionality.

Table 2—Calculated and Measured Silica Content in the Polyester-HMMM Coatings Systems of Two Molar Ratios HMMM: Polyester, with Various Amounts of Silica, Determined by TGA

calc. wt% SiO_2	3	4	5	6	8	10	11	12	14
Wt% SiO_2, ratio HMMM:PE 0.75	2.7		5.5			10.5		12.4	14.6
Wt% SiO_2, ratio HMMM:PE 1.5		4.2		6.1	7.5		11.4		15.4

Characterization

The layer thickness of the coatings on glass substrates was determined by a micrometer (Coatchecker VC-2, Evano Instruments). On aluminum substrates the layer thickness was measured with the eddy current principle (Twincheck, List Magnetik). The silica content of the coatings was determined by thermal gravimetric analysis (TGA, Perkin-Elmer TGA7), with a heating rate of 20°C/min from 50 to 800°C. With scanning electron microscopy (SEM, Cambridge, Stereoscan 200) cross sections of the coatings on glass substrates were studied. The samples were etched for 30 min with an oxygen plasma (Nanotech Plasmaprep 100) and then sputtered with Pd/Au for 3 min (BioRad SEM Coating System). With transmission electron microscopy (TEM, Philips CM200 TEM) cross sections with a thickness of 100 nm of coatings on aluminum substrates were studied. The samples were microtomed (Reichert Ultracut E/FC-4D) at –50°C and subsequently floated on a dimethyl sulfoxide/water mixture. The hardness of the coatings was determined with the König pendulum apparatus (Pendelhärteprüfer Model 299/300, Erichsen) according to ASTM D 4366, and with the pencil hardness tester (Ritzhärteprüfer nach Wolff-Wilborn Model 291, Erichsen) according to ASTM D 3363.

Micro-indentation was performed on a homebuilt nano-indenter, with a Berkovich pyramid indenter. The force and displacement of the indenter perpendicular forced with a constant speed in (loading) and out (unloading) the coating surface was measured. From the maximum applied force (F_{max}) and the indented surface area (A), determined by SEM, the indentation hardness (H) was calculated[25]:

$$H = \frac{F_{max}}{A}$$

The reduced elastic modulus (E_r) was determined from the initial slope (S) of the unloading curve and the indentation area (A) by[25,26]:

$$E_r = \frac{\sqrt{\pi}}{2} \cdot \frac{S}{\sqrt{A}}$$

In fact, A in the calculation of E_r should be the indented area at initial unloading, but since this area could not be determined directly, the area after unloading, as determined by SEM, was applied. This resulted in an overestimation of E_r.

Micro-scratching was performed on a homebuilt micro-scratcher, using a diamond tip. A normal force, perpendicular to the coating surface, was applied and scratches were made with a speed of 10 μm/s. The frictional force was measured, and the scratches were studied directly afterwards with AFM (Nanoscope 3100, Digital Instruments). Both the micro-indentation and the micro-scratching methods were performed with forces in the mN range. In this way the influence of the substrate on the measurements was limited. The small indentations and scratches were not visible by the eyes.

RESULTS

The influence of the amount of silica on the morphology of the hybrid coatings based on hydroxyl-terminated polyester and HMMM was studied, and the hardness and the scratch resistance were determined. Therefore, polyester-HMMM coatings with various amounts of prehydrolyzed TEOS were prepared, and the final silica contents were measured by TGA. The results are shown in *Table* 2. The determined amounts of silica were in good agreement with the calculated amounts. The coatings appeared hazy at a silica content of 10.5 wt% and higher for the hybrid coating with an HMMM:polyester ratio of 0.75 and above 11.4 wt% for hybrid coatings with an HMMM:polyester ratio of 1.5.

Morphology of the Hybrid Coatings

To investigate the morphology of the hybrid coatings SEM was used. In *Figure* 1a-f the results of the cross sections of the coatings with an HMMM:polyester molar ratio of 1.5 and with various amounts of silica are shown. The SEM photograph of the pure organic coating (*Figure* 1a) showed an area with small pits, due to the 30 min of oxygen etching. In coatings with an increasing amount of silica up to 6 wt% (*Figure* 1c) silica could not be

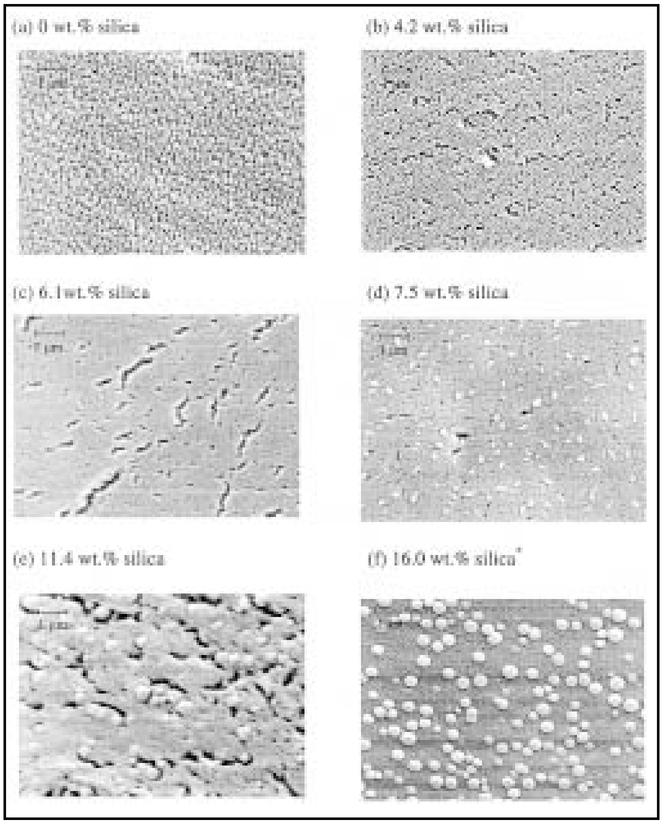


*Figure 1a-f—SEM photographs of cross sections of polyester-HMMM hybrid coatings with a molar ratio HMMM:polyester of 1.5 and with various amounts of silica. *Hazy coatings.*

(a) 0 wt% silica, (b) 4.2 wt% silica, (c) 6.1 wt% silica, (d) 7.5 wt% silica, (e) 11.4 wt% silica, (f) 15.4 wt% silica.

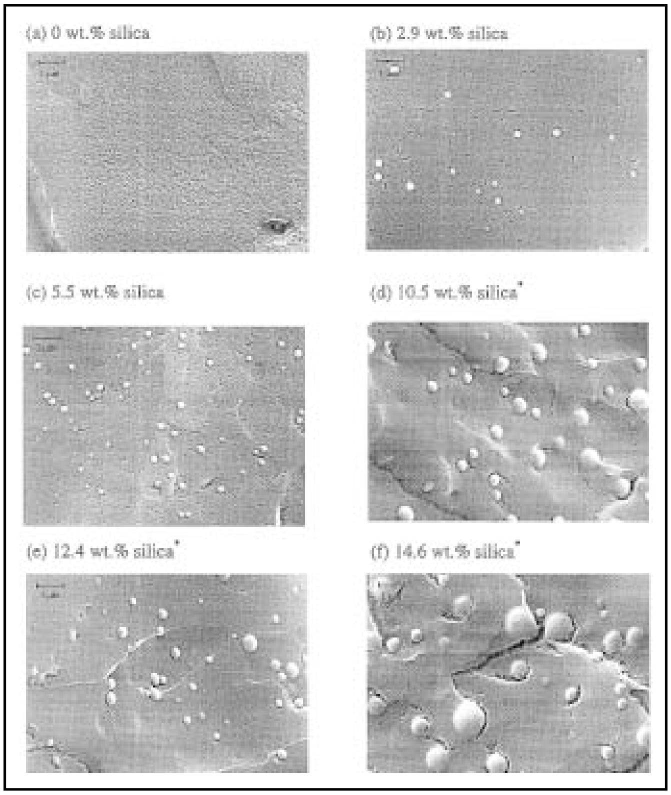


*Figure 2a-f—SEM photographs of cross sections of polyester-HMMM hybrid coatings with a molar ratio HMMM:polyester of 0.75 and with various amounts of silica. * Hazy coatings.*

(a) 0 wt% silica, (b) 2.9 wt% silica, (c) 5.5 wt% silica, (d) 10.5 wt% silica, (e) 12.4 wt% silica, (f) 14.6 wt% silica.

distinguished from the organic matrix. At a silica content of 7.5 wt% (*Figure* 1d) silica particles began to appear. In a transparent coating containing 11.4 wt% silica (*Figure* 1e), smooth round particles with a diameter of around 300 nm were clearly present. The hazy coating with 15.4 wt% silica (*Figure* 1f) showed a large number of round silica particles around 500 nm in an organic matrix, causing scattering of light and resulting in the observed haziness. The particle size increases with increasing silica content, ultimately leading to the hazy coatings. The small cracks that are visible in all SEM photographs are caused by the oxygen etching. When a less dense organic network was formed as in the coatings with an HMMM:polyester molar ratio of 0.75, the effect of increasing silica particles with increasing size is even more pronounced, as shown in *Figure* 2a-f.

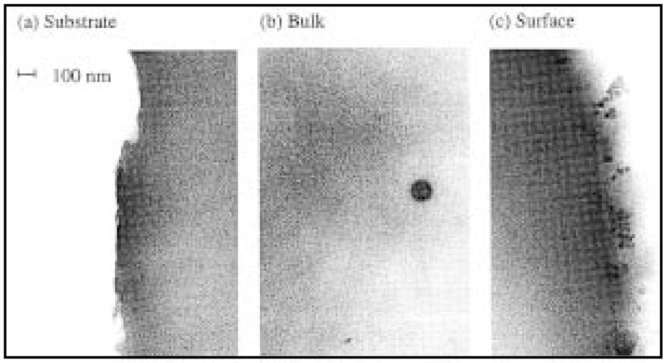


Figure 3a-c—TEM photographs of cross sections of a polyester-HMMM hybrid coating with 6.1 wt% silica. (a) Substrate, (b) bulk, (c) surface.

To study the morphology in more detail, a hybrid coating with 6.1 wt% silica and an HMMM:polyester molar ratio of 1.5, which did not reveal silica in SEM, was examined by TEM. The results are shown in *Figure* 3a-c. There are two remarkable features. Firstly, in the bulk, few smooth round particles with a size of around 100 nm were observed, showing that already at lower silica content, particles have been formed. Secondly, it was clearly shown that on the surface of the coating, small silica particles were present at higher concentrations. From the results gained by SEM and TEM, it can be concluded that in the hybrid polyester-HMMM-silica hybrid coatings under investigation, silica particles are formed increasing in size and number upon increasing silica content. This effect was more pronounced in coatings with a less dense organic network.

Hardness and Scratch Resistance

The hardness and scratch resistance were studied by the König hardness test and the pencil hardness test, and the results were compared with the micro-indentation test and the micro-scratching test, which test the properties on a micro-scale with well defined parameters (see Experimental section). The König hardness is described as comparable with micro-indentation, however, especially at very low and very high hardness, the indenta-

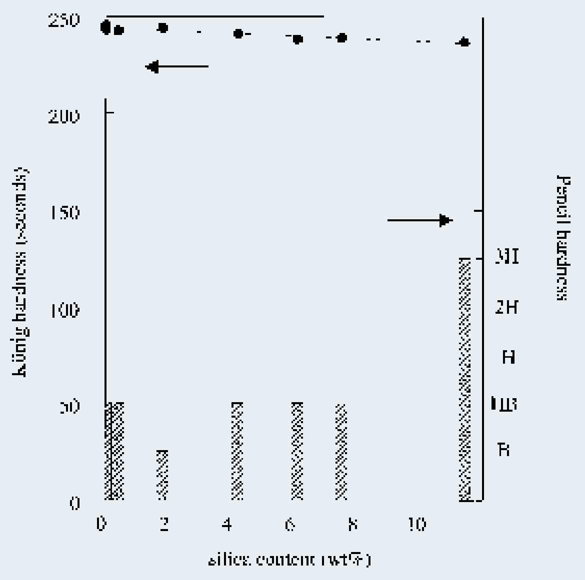


Figure 4—The König and pencil hardness as function of the silica content of polyester-HMMM hybrid coatings. The drawn line is only a guide for the eye.

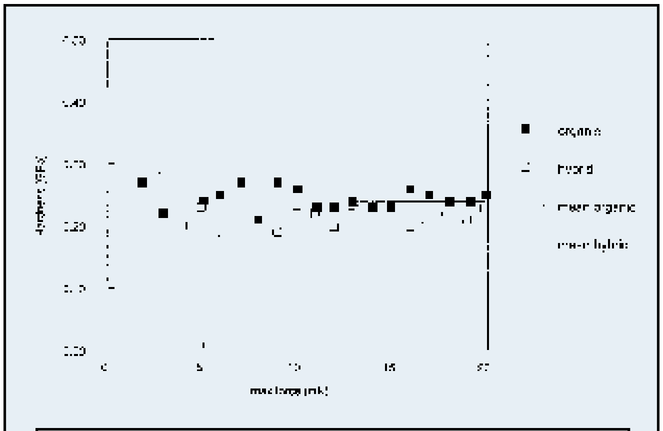


Figure 5—Indentation hardness at various forces (F_{max}) for the polyester-HMMM coating, without (organic) and with 11.4 wt% silica (hybrid).

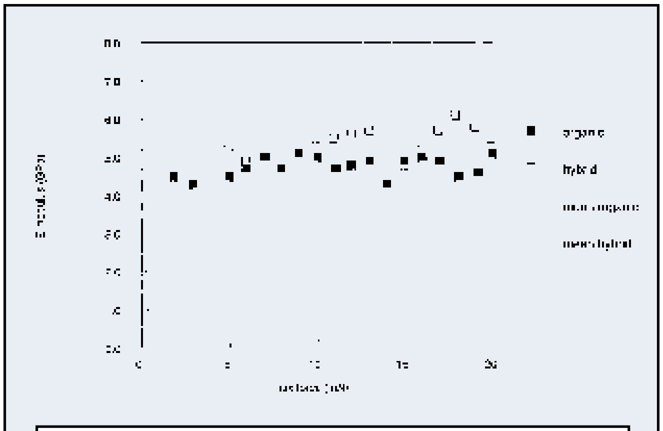


Figure 6—Reduced elastic modulus at various forces (F_{max}) for the polyester-HMMM coating, without (organic) and with 11.4 wt% silica (hybrid).

tion method differentiates better.[27,28] The properties have been studied on the polyester-HMMM hybrid systems with a molar ratio HMMM:polyester of 1.5.

König Hardness and Pencil Hardness: The König hardness and pencil hardness of the polyester-HMMM hybrid coatings with various amounts of silica have been determined on coatings with a dry layer thickness of 21 ± 3 μm on glass substrates. The results are plotted in *Figure* 4. The König hardness of the coatings was close to 250 sec, which is the value of the reference glass. According to ASTM standards, a layer thickness of at least 25 μm is required to minimize the influence of the substrate. Nevertheless, it is known from former measurements on these types of coatings that also with a layer thickness of 21 μm the substrate effect is not dominating. A gradual decrease in hardness of less three percent was found with increasing silica contents up to 11.4 wt%. Also the pencil hardness was not markedly influenced by the silica content. Only the hybrid coating with 11.4 wt% silica showed a higher pencil hardness.

Micro-Indentation: Micro-indentation measurements have been performed on coatings applied on aluminum. The pure organic polyester-HMMM coating was compared with the hybrid polyester-HMMM coating containing 11.4 wt% silica. For various applied forces, the indentation hardness and the reduced elastic modulus were determined, and the results for the hybrid and organic coating are plotted in *Figures* 5 and 6. The maximum indentation did not exceed 10% of the film thickness to rule out the substrate influence.[27] There is a small difference in hardness and elastic modulus between the organic and hybrid coating. The lines in the plots indicate the average values. The organic coating has an average hardness of 0.24 GPa, while the hybrid coating's mean value is 0.21 GPa (*Figure* 5). It can be seen in *Figure* 6 that the elastic modulus of the hybrid coating is higher (mean value of 5.2 GPa) than that of the organic coating (mean value of 4.7 GPa).

Micro-Scratching: Micro-scratching tests have been performed on coatings applied on aluminum. The pure organic coating without silica and the hybrid polyester-HMMM coating with 11.4 wt% silica were compared. Six scratches have been made with normal forces increasing from 0.23 to 4.7 mN. The frictional force as a function of the applied normal force is plotted in *Figure* 7, and the AFM images of the scratches are shown in *Figure* 8, together with their average height profile perpendicular to the scratch direction. There is a remarkable difference in behavior between the organic and the hybrid coating. The frictional force measured on the hybrid coating is less than for the organic coating, and also the AFM images clearly show that the scratches

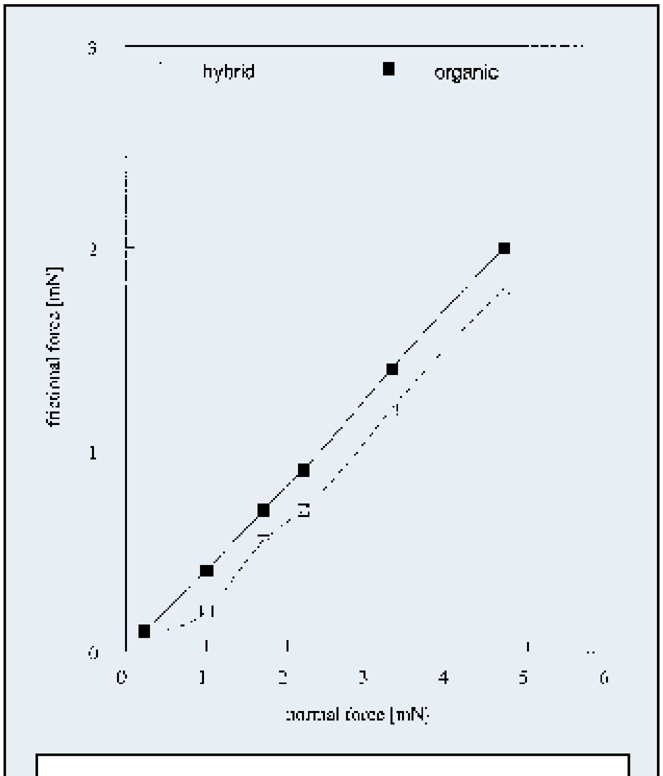


Figure 7—Micro-scratch test: the frictional force as a function of the normal force for the polyester-HMMM coating without (organic) and with 11.4 wt% silica (hybrid).

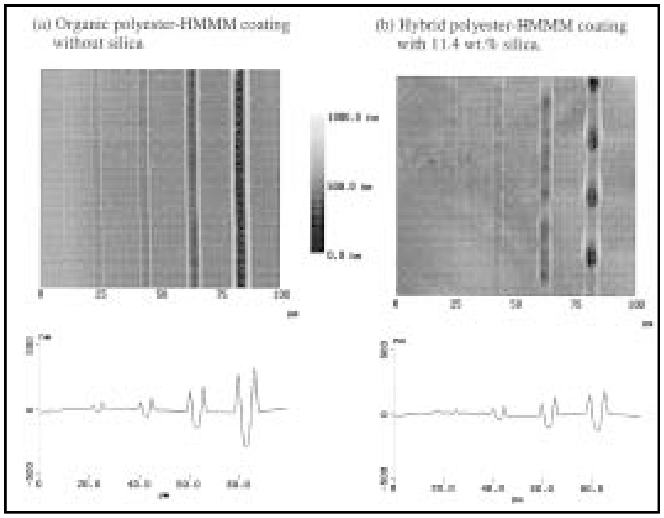


Figure 8a-b—AFM images of scratches and average height profile, from left to right with 1, 1.7, 2.2, 3.3 and 4.7 mN normal force.

(a) Organic polyester-HMMM coating without silica, (b) hybrid polyester-HMMM coating with 11.4 wt% silica.

made with the same force are deeper in the organic coating than in the hybrid coating. Both the lowering of the frictional force and the reduced depths of the scratches demonstrate the improved micro-scratch resistance of the hybrid coatings with 11.4 wt% silica compared to the purely organic coatings.

DISCUSSION

From the chemical composition of the hybrid system, it was expected that both the organic and inorganic phase would form a network: the organic phase by crosslinking of polyester and HMMM and the inorganic phase by polymerization of the silanol groups. Together an interpenetrating network was expected. The morphology obtained, though, showed the formation of particles increasing in size and number with increasing silica content. It is thought that the poor compatibility and the lack of interaction between the organic and inorganic phase are the causes of increased phase separation with increasing silica content, resulting in smooth round silica particles. The interaction between the organic and inorganic phase in this system can occur through Si-O-C bond formation of silanols with polyester or HMMM. In previous research the interaction via hydrogen bonding was excluded.[19] The Si-O-C bond formation apparently cannot compete with the organic crosslinking reaction. The Si-O-C bond can be formed, but due to sensitivity towards hydrolysis, it can also be broken easily, giving opportunities for the more stable polyester-HMMM bonding. The particle formation was less pronounced for the hybrid coatings with a denser organic network. It is assumed that the particle formation, as a result of phase separation, is stopped sooner in the denser crosslinked system because of a higher decrease of mobility within the system, compared to the less dense crosslinked system. The silica is finally trapped in the organic matrix. The improved pencil hardness and micro-scratch resistance can be explained by the increased concentration of silica observed at the surface of the coating (*Figure* 3c). Silica, as a hard compound compared to the organic matrix, was expected to improve the hardness, but from the indentation measurements it has become clear that these effects are not dominating. More important appears the increased smoothness of the hybrid coating with 11.4 wt% silica, as could be judged by visual inspection. The presence of siloxane containing compounds is known to lower the surface tension of coatings[29,30] and in this way they can smooth the surface, which can improve the scratch resistance. The lowered surface tension can also be the drive for the small silica particles to move to the surface, especially when there is a lack of interaction in the bulk of the coating.

CONCLUSIONS

The morphology of hybrid coatings based on polyester, HMMM, and various amounts of silica has been determined and the hardness and scratch resistance were measured. With increasing silica content the number and size of silica particles in the organic matrix in the bulk of the coatings were increased. The effects were more pronounced for hybrid coatings with a less dense network. Furthermore, it was shown that small silica particles were preferentially present at the surface. Both effects may be ascribed to the lack of interaction between the organic and inorganic phase, causing phase separation and diffusion of particles. With increasing silica content, a decrease in König hardness, indentation hardness, and an increase of elastic modulus was observed. The improved scratch resistance of the hybrid coating with 11.4 wt% silica may be attributed to the improved smoothness of the surface as a result of the silica being preferentially present at the surface. Finally, it is concluded that the results obtained with König and pencil hardness test are in good agreement with the micro-indentation and micro-scratching results, respectively.

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