Nano-Mechanical Properties

INTRODUCTION

The production of powder coatings has undergone a substantial increase in recent years worldwide, with Europe being the leader for their usage.¹ The use of powders provides unique advantages such as the non-emission of solvents, significant energy savings, excellent adhesion to many substrates, and the production of a good finish. Although the coatings are generally fairly smooth, the classical “orange peel” appearance is still present in many cases. Also, additional defects may be present such as pinholes, impurities, etc. It is also unclear if the surface topography of powder coatings correlates with their mechanical properties.

The recent development of nano-techniques has allowed a more accurate analysis of the intrinsic mechanical properties of the surfaces of such coatings. Among the various types of investigation, scratching techniques have proved especially useful in evaluating the potential of a particular coating to avoid the development of relatively fine, visually apparent scratches that spoil the coating’s appearance, which is usually termed “mar resistance.” Moreover, the scratching techniques, along with more conventional indentation procedures (often performed with the same equipment), provide useful information about deformation in the coatings (e.g., whether elastic, plastic or viscoelastic), as well as their roughness and mechanical constants (e.g., their hardness and elastic modulus).

As early as 1952, Schallamach¹ used scratching techniques to evaluate the mechanisms of friction and abrasion of elastomeric materials, albeit on a macroscopic scale. Even now, this work is a valuable reference on the response of soft and highly elastic surfaces to scratching.

More recently, the scratch hardness of glassy, thermoplastic polymers under a number of contact conditions was studied by Briscoe et al.³ The same group used the compliance method and a calibration technique to ac-

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Both nano-scratching and nano-indentation techniques have been used to evaluate the mechanical properties of the surface of acrylic coatings, with and without added pigment. The coatings were formed from thermosetting, acrylic powders. Both types of coatings—clear and pigmented—do not exhibit any significant differences in their hardness with an increase in baking time from 7 to 15 min. According to the scratching profiles, the deformation induced at the surface is virtually elastic. Introducing the pigment causes a slight increase in the elastic modulus but no significant variation in hardness. In all coatings, the computed hardness and the elastic modulus values are higher near the surface (perhaps as a result of tip geometry effects), but these readily reach plateau values that are consistent with other work available in the literature. A large range-surface profiler, which provided two-dimensional and three-dimensional topographical maps of the coating surfaces, reveals undulations in the surface with a wavelength on the order of 2-4 mm. Moreover, the topography of the pigmented coating is significantly smoother than that of the clear coating in which shallow pits (about 100 μm in diameter) are randomly distributed at the surface. The nano-mechanical properties within these pits are similar to the bulk of the coating.
Table 1—Characteristics of the Epoxy Functional Acrylic Terpolymer (GMA1)

<table>
<thead>
<tr>
<th>Component</th>
<th>Equivalent weight (g/mol)</th>
<th>Density (g/cm³)</th>
<th>Solubility</th>
<th>Miscibility (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Epoxy equivalent</td>
<td>394</td>
<td>1.07</td>
<td>Inherent</td>
<td>95.6</td>
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<tr>
<td>M₄ (PS equivalent)</td>
<td>5720</td>
<td></td>
<td>Insoluble in water</td>
<td></td>
</tr>
<tr>
<td>M₅ (PS equivalent)</td>
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<td></td>
<td>Insoluble in water</td>
<td></td>
</tr>
<tr>
<td>Polystyrene</td>
<td>840</td>
<td></td>
<td>Insoluble in water</td>
<td></td>
</tr>
<tr>
<td>M₆ (PS equivalent)</td>
<td>42</td>
<td></td>
<td>Insoluble in water</td>
<td></td>
</tr>
<tr>
<td>CI CI P:Viscosity</td>
<td>1.06 x 10⁶ (Polymer)</td>
<td>20</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

count for the tip geometry in a study of several glassy thermoplastic surfaces. Scratch hardness measurements were also used to investigate the effects of plasticization by solvents upon the mechanical properties of glassy polymer surfaces.

For many decades, indentation techniques have been used to determine the hardness of coatings. Recent work has shown that the conical stylus, sometimes used for those indentation tests, may provide a useful means of differentiating between different types of deformation processes (i.e., elastic, plastic, and elastic-plastic) induced in the system. Although values for the hardness of the coating, as well as estimates of the adhesion to the substrate, may be obtained, the conical stylus method shows limitations in assessing the appearance of very discrete scratches on the coating. AFM may successfully be used for such a purpose. In one of the first studies of its kind, Courrier applied the AFM method to clear, cross-linked acryllic coatings. Values for the Young's modulus as a function of depth of penetration were obtained. The work also presented scratching maps over relatively large distances (3 mm) and low penetration depths (ca. 20 µm). The same author also provided an interesting correlation between the coating mechanical properties and the corresponding "hardness"

Related investigations of the wear behavior of polymer surfaces using micro- and nano-scale testing have also been reported. In one example, the work of the nano-mechanical techniques characterized the surfaces of organic coatings, and the effects of induced pigment have been largely unexplored.

In the present study, nano-indentation techniques were used for studying both clear and pigmented, cross-linked, acrylic coatings. Until now, there has been no systematic study that has aimed to determine the effects of pigment, if any, on the mechanical and chemical properties of coating surfaces. Moreover, this work aims to determine if variations in surface topography lead to systematic variations in nano-mechanical properties.

The current study: (1) provides information about the proportion of elastic, viscoelastic, and fracture deformation during the nano-scratching of the coatings. It is well known that low applied forces, upon removal of the load, will not be apparent permanent damage or deformation to the coating. If the normal force is increased or a sharper indentor is used in the process, then the coating will yield or fracture according to its intrinsic mechanical characteristics. If the extent of the contact deformation exceeds the yielding potential, the material undergoes some permanent deformation (e.g., a "valley" with "hills" along the sides in produced), or fractures are generated (in the case of severe environments).

In this work, the scratches showed essentially a complete recovery of the cross-linked acrylic surface under investigation, indicative of an elastic (not plastic) behavior, which is characteristic of elastomeric coatings.

EXPERIMENTAL

Work reported here used an experimental solid epoxy functional acrylic terpolymer (referred to as GMA1) supplied by 3M. The terpolymer was synthesized from methyl methacrylate, butyl methacrylate, and glycidyl methacrylate. The properties of the GMA1 terpolymer were reported in a previous work. The GMA1 resin was the binder in both a standard clearcoat formulation (Formulation A) and a standard high gloss white formulation containing titanium dioxide pigments (Formulation B), from Kureha (Formulation A). In both formulations, a multifunctional isobutylene hardener based upon hexamethyldisilazane, Celeno VP LS 2325, from Bayer, and an amino-functional hardener based upon hexamethyldisilazane, Celeno VP LS 2325, from Bayer, were used. The curing agent with a solid value of 465 mg KOH/g and a functionality of 2.3) functioned as the crosslinker and was used in a GMA1/crosslinker weight ratio of 2.84:1. The formulations contained benzoyl peroxide as an anti-pigment-killer. Table 2 gives full details of the formulations. Formulations were extruded at 200 rpm and 70 torr via a Cavan’s Extruder with a barrel temperature profile of 50/110°C. The mill output was 2.9 mm mesh extrudate was applied on 0.9 mm phosphated boradite steel using a PCG spray gun (Gema, Volstic Industry Powder Systems, Switzerland).

The average particle size and shape can be seen in Figures 1 and 2, which show representative scanning electron micrographs of the clear and pigmented powder coatings, respectively. (Experimental details about the SEM analyses are provided in the next section.) Both types of powder have a rather broad particle size distribution with particles being irregular in shape and highly faceted. There are no major differences in appearance between the two formulations.

Figure 1—SEM micrograph of Formulation A (clearcoat) powder in its as-received state. A wide distribution in size is apparent. The shape of the particles is irregular with sharp edges. The bar indicates 50 µm.

The substrates with the deposited powder were introduced into a preheated oven at 150°C for the various baking times of 7, 11, and 15 min. (Note that 15 min in the standard, recommended baking time for Formulations A and B.) After curing, the coating thicknesses were in the range of 120-180 µm for the clearcoats and 50-70 µm for the pigmented samples. Spraying conditions of the powders were the same for both types of sample. The difference in final thickness values is attributed to different charge transfer efficiencies of the two formulations.

Thermal Analysis

Modulated temperature differential scanning calorimetry (MDSC) was used to determine the extent of crosslinking that occurs in the acrylic powders below the baking temperature. MDSC is a relatively new calorimetric technique5,6 that relies on the basic principles of conventional DSC but with the major difference being that it uses a heating ramp containing a sinusoidal signal. In recent years, it has been used successfully for the investigation of structural phase transitions of both thermochromic characterization of multicomponent systems,8 separation of thermal processes with different kinetics or mechanisms,9,10 and more accurate measurement of heat capacity.11 This additional information may provide further insight into the structure and behavior of materials. In the case of powder coatings, conventional DSC is routinely used for the measurement of the thermal transitions.22 Very little work has been published on MDSC performed on thermosetting powders12,13 in general and with even less on thermosetting powders. MDSC analysis is superior to conventional DSC in the analysis of cross-linked acrylic powders, because it can demonstrate the peaks corresponding to the glass transition of the polymer, the melting of the cross-linker, and the cross-linking of the polymer, thereby allowing a more accurate determination of these temperatures.

Chemical Analysis

The flow properties of the powders (both Formulations A and B) were measured using a 2502 TA Instruments (Leatherhead, UK) calorimeter with a heating rate of 1°C/min.

Topographical Analysis

The surface topography of the coatings' surfaces was obtained with a surface profilometer (Dektak, V200-Si). Areas as large as 1 cm x 1 cm were analyzed. Additional information was gained from scanning electron microscopy, a Hitachi S5000 instrument, typically with an accelerating voltage of 20 kV. The samples were coated with a thin layer of gold prior to analysis.

Scratching Experiments

The same instrument was used for both the scratch experiments and indentation experiments (Nano indenter II, supplied by Nano-Instruments Inc., Oak Ridge, TN). The test configuration was a scratch across the coating and indentation experiments.
count for the tip geometry in a study of several glassy thermoplastic surfaces. Scratch hardness measurements were also used to investigate the effects of plasticization by solvents upon the mechanical properties of glassy polymer surfaces.4

For many decades, indentation techniques have been used to determine the hardness of coatings. Recent work has shown that the conical stylus, sometimes used for both indentation and scratching, may provide a useful means of differentiating between different types of deformation processes (i.e., elastic, plastic, and elastic-plastic)5 in the systems. Although values for the hardness of the coating, as well as estimates of the adhesion to the substrate, may be obtained, the conical stylus method shows limitations in assessing the appearance of very discrete scratches on the coating. AFM may successfully be used for such a purpose.6 In one of the first studies of this kind, Corder7 applied the stylus method to clear, crazed acrylic coatings. Values for the Young's modulus as a function of depth of penetration were obtained. The work also presented scratching maps over relatively large distances (3 mm) and low penetration depths (ca. 20 µm). The same author also provided an interesting correlation between the coating mechanical properties and the corresponding "scratch modulus".8

Related investigations of the wear behavior of polymer surfaces have been conducted on micro- and nano-scale testing. There have also been reports of experiments using low energy electrons published, however, on the use of nano-mechanical testing methods to characterize the surfaces of organic coatings, and the effects of included pigment have been largely unexplored.

In the present study, nano-indentation was used for studying both clear and pigmented (i.e., color-filled) acrylic coatings. Until now, there has been no systematic study that has aimed to determine the effects of pigment, if any, on the mechanical and optical properties of such coating surfaces. Moreover, this work aims to determine if varia-
tions in surface topography lead to systematic variations in nano-mechanical properties.

The current study is aimed at providing information about the proportion of elastic, viscoelastic, and fracture deformation during the nano-scratching of the coatings. It is well known that low applied forces, upon re-
moval of the load, will not result in permanent damage or deformation to the coating. If the normal force is increased or a sharper indenter is used in the process, then the coating will yield or fracture according to its intrinsic mechanical characteristics. If the extent of the contact deformation exceeds the yielding potential, the material undergoes some permanent deformation (e.g., a "valley" with "hills" along the sides is produced). In this work, the scratches showed essentially a complete geometric recovery of the cross-linked acrylic surface under investigation, indicative of an elastic (not plastic) behavior, which is characteristic of elastic coatings.

**Experimental**

Materials

Work reported here used an experimental solid epoxy functional acrylic terpolymer (referred to as GMA1) supplied by Ciba Geigy. The terpolymer was synthesized from methyl acrylate, butyl methacrylate, and glycidyl methacrylate. The physical properties of the GMA1 monomer have been characterized.9

The GMA1 resin was the binder in both a standard clearcoat formulation (Formulation A) and a standard high gloss white formulation using titanium dioxide pigments (Formulation B).10,11 From Kayaks, Formulation A in both formulations, a multifunctional carboxylic acid hard-
er used upon hexane, and Dicyan, VPS LS 2125, from Bayer, with an amino value of 465 mg KOH/g and a functionality of 2.3) functioned as the crosslinker and was used in a GMA1/crosslinker ratio of 2.841. The formulations contained benzoin as an anti-
photooxidant, and Table 2 gives full details of the formulations.

Formulations were extruded at 200 rpm and 70 torr via a Corning 1800 die (with a barrel temperature profile of 60/110°C). The extrudate was croped (1.75 mm mesh) extruded onto a 0.9 nm phospho-
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The substrates with the deposited powder were intro-
duced into a preheated oven at 180°C for the various baking times of 7, 11, and 15 min. (Note that 15 min is the standard, recommended baking time for Formulations A and B.) After curing, the coating thickness were in the range of 120-180 µm for the clearcoats and 50-70 µm for the pigmented samples. Spraying conditions of the powders were the same for both types of sample. The difference in final thickness values is attributed to differ-
ent curing conditions.

**Thermal Analysis**

Modulated temperature differential scanning calorimetry (MDSC) was used to determine the extent of crosslinking that occurs in the acrylic powders below the baking temperature. MDSC is a relatively new calorimetric technique,5,13 that relies on the basic principles of conventional DSC but with the major difference being that it uses a heating ramp containing a sinusoidal per-
turbation. In recent years, it has been used successfully for the investigation of structural phase transitions,6 thermal characterization of multicomponent systems,8 separation of thermal processes with different kinetics or mechanisms,9 and more accurate measurement of heat capacity.10 This additional information may provide further insight into the structure and behavior of materials. In the case of powder coatings, conventional DSC is routinely used for measuring the characteristics of the thermal transitions.12 Very little work has been published on MDSC performed on thermosetting powder systems in general and with even less on thermosetting powders. MDSC analysis is superior to conventional DSC in the case of the non-crosslinking acrylic powders, because it can deconvolute the peaks corresponding to the glass transition of the polymer, the melting of the cross-
linker, and the crosslinking of the polymer, thereby al-
lowing a more accurate determination of these tempera-
tures. Typically, the crosslinker "melts" endothermically and acrylic "cure" exotherm occur simultaneously and would not be easily interpretable with a standard DSC experiment. With MDSC, however, the melt and cure stages are readily resolved in the reversing and non-reversing signals. The pigmented and non-pigmented powders were both analyzed using a 2920 TA Instruments (Leatherhead, UK) calorimeter with a heating rate of 1°C/min.

**Chemomechanical Analysis**

The flow properties of the powders (both Formula-
tions A and B) were recorded on a Rheometrics RDSII dynamic rheometer. The instrument was operated at 10% strain using a parallel plate geometry with a 2 mm gap and a frequency of 10 rad/s. Strain sweep measurements showed no evidence for non-linearity under these conditions, and the maximum temperature ramp rate was 10°C/min for all experiments.

**Topographical Analysis**

The surface topography of the coatings' surfaces was obtained with a laser interferometer and contact meter (Dektak, V200-Sx). Areas as large as 1 cm x 1 cm were analyzed. Additional information was gained from scan-
ing electron microscopy with an Hitachi S2000X instru-
ment, typically with an accelerating voltage of 20 kV. The samples were coated with a thin layer of gold prior to analysis.

**Scratching Experiments**

The same instrument was used for both the scratch tests and the indentation experiments (Nano Indenter II, supplied by Nano Instruments, Oak Ridge;
TN, USA). The instrument uses a compliance indentation system, capable of operating at loads in the microgram range and with a theoretical depth resolution on the sub-nanometer scale. It provides data on the Young’s modulus and hardness of the coating. Unlike conventional hardness testers, the instrument does not require an optical measurement of the area of the indentation to calculate the hardness. The position of the indenter relative to the surface of the specimen is monitored and therefore, from a knowledge of the geometry of the tip, the area of the indentation is then calculated.

The Nano-Indentor II is essentially a load-controlled system, where the applied load is continuously monitored. The indenter tip is in the shape of a three-sided diamond pyramid, machined so that the sides make an angle of 65.3° with the normal to the base. The indentations appear as straight triangular lines, and the length of a side of an indentation is approximately 7.4 times its depth. The depth of an indentation, h, is equal to 0.113 times the diameter of the circle that circumscribes the indentation made on a surface. Attached to the top end of the indenter rod, there is a coil held in a magnetic field. Thus, the passage of a current through the coil can be used to apply a force to the indenter. The “zero point” contact for the present system was chosen where the machine stiffness becomes equal to 1.5 times its typical value. More details about the apparatus components are presented elsewhere.5,2

Scratches were made on the coating surface up to a depth of ca. 1.5 µm. This penetration depth, being less than one-tenth of the thickness of the coating, avoids the so-called substrate effects. Since the theoretical depth resolution of the instrument is ≥0.04 µm, the indenter has the advantage of providing information about the very near-surface region.

Each complete scratch procedure had five steps as follows. First, the surface is pre-scratched at a very low constant applied load of 20 µN over 300 µm with a constant penetration of 10 nm/s. This first step provides a reference for the calculation of the scratch penetration. Then the stylus returns for a distance of 100 µm with the same velocity. Next, the scratch is performed deep in the coating with the same velocity of 10 nm/s. After releasing the load, the stylus returns to the initial position. In the final step, the surface is profiled again as in the first step, in order to check for plastic deformation.

In addition, the nano-indentor can record the frictional drag force during scratching, which allows the calculation of the coefficient of friction between the stylus and sample surfaces. Two scratches of different depths were performed for each formulation.

**RESULTS AND DISCUSSION**

**Thermal Analysis**

MTS-DSC curves for the non-pigmented and pigmented acrylic powder (Formulations A and B) are presented in Figures 3 and 4, respectively. The reversing heat flow curves (which are given by the cyclic heat flow within the sample) show a glass transition for the non-pigmented acrylic at ca. 40°C. There is an increase in the value by only 1°C when the powder contains the pigment. These values of the glass transition temperature for the formulations are slightly higher than that obtained for the neat OHA resin (38°C, as shown in Table 1). In both Figures 3 and 4, a melting peak of the crosslinking agent centered around 100°C may be identified. Also, the non-reversing heat flow curve (which is given by the subtraction of the total heat flow of the cyclic heat flow within the sample) shows a peak for the crystallization (i.e., curing) process at around 120°C. These results reveal that the introduction of the pigment does not significantly influence the thermal constants of the acrylic and therefore the baking conditions.

**Chemo-Rheology**

From the determination of the viscosity/temperature profile of a thermoset powder coating, it is possible to characterize both the flow and cure processes.7 Figure 5 shows the result for formulation A, with analogous results being also obtained for pigmented Formulation B. The measured minimum viscosity is 2.7 Pa s. The onset temperature for rapid cure appears at about 150°C resulting in a limiting creep strain as given by the ratio of the storage modulus at full cure, as defined by the plateau in the viscosity/temperature curve, to the yield stress of the powder. Based on the MTSDS and chemo-rheology measurements, it was determined that 150°C is adequate to use...
The hardness and Young’s modulus were measured by performing an indentation experiment to a depth of ca. 700 nm deep into the surface. Each complete hardness test was performed via the following procedure:

First, the stylus is lowered at a velocity of 10 nm/sec until the stiffness of the spring becomes 100 N/m, which is equal to 1.2 times the spring support stiffness of 84 N/m. At this point, the contact load is considered to be reached. The load is increased at a rate of 3 μN/sec over a distance of 700 nm and then held for 60 sec. (The velocity of indentation was 3 μm/sec; the load is then decreased at the initial rate to 80% of the final displacement, at which point the load is held for 60 sec. Finally, the load is released at 300 μm/sec).

Six indentation tests were performed on each sample surface, and these measurements were averaged. There is a slight variation in the range of indentation for the clear and pigmented coatings since the experiment is controlled by an upper limit of the permitted force on the cantilever. Any observable defects on the surface of the clear coatings were avoided and not included when finding the averages.

The continuous stiffness method was used for the evaluation of the Young’s modulus and hardness. This method continuously measures the stiffness of contact between the indenter tip and the sample. During the loading procedure, an oscillatory mechanical force of known magnitude is applied to the mechanical contact junction between the indenter and the sample. An indication of the stiffness of contact between the tip and the sample is given by simultaneously measuring the phase shift between the force and the amplitude of the resulting oscillatory displacement between the tip and the sample. The Poisson’s ratio (ν) was taken as 0.25 in the data analysis, which is a standard value used for glassy polymer surfaces. In any case, the calculated values of nano-hardness and elastic modulus scale inversely with (1 - μ²), and thus the calculated values are not particularly sensitive to the value of μ used.

RESULTS AND DISCUSSION

Thermal Analysis

MTS/TA curves for the non-pigmented and pigmented acrylic powder (Formulation A and B) are presented in Figures 3 and 4, respectively. The reversing heat flow curves (which are given by the cyclic heat flow within the sample) show a glass transition for the non-pigmented acrylic at ca. 48°C. There is an increase in the value by only 1°C when the powder contains the pigment. These values of the glass transition temperature for the formulations are slightly higher than that obtained for the neat Oxa resin (28°C as shown in Table 1). In both Figures 3 and 4, a melting peak of the crosslinking agent centered around 100°C may be identified. Also, the non-reversing heat flow curve (which is given by the subtraction from the total heat flow of the cyclic heat flow within the sample) shows a peak for the crosslinking (i.e., curing) process around 120°C. These results reveal that the introduction of the pigment does not significantly influence the thermal constants of the acrylic and therefore the baking conditions.

Chemo-Rheology

From the determination of the viscosity/temperature profile of a thermoset powder coating, it is possible to characterize both the flow and cure processes. Figure 5 shows the results for Formulation A, with analogous results being also obtained for pigmented Formulation B. The measured minimum viscosity is 2.7 Pa s. The onset temperature for rapid cure appears at about 150°C resulting in a limiting crosslink density as given by G° C° (i.e., the storage modulus at full cure, as defined by the plateau in the viscosity/temperature curve) of 10³ Pa. Based on the MTS/TA and these rheology measurements, it was determined that 150°C is adequate to use.
as the reference cure temperature. Heating both formulations to this temperature apparently produced the same glossy coatings for cure times of seven minutes or more.

Coating Topography

Visual inspection of the coatings reveals a marked unevenness in the surface finish that detracts from its appearance. The non-pigmented coatings also contain small defects, barely visible to the unaided eye, that are suggestive of the presence of "pinholes." Figures 6 and 7 show the topographical profiles of clear and pigmented coatings, respectively. In both, there are variations in coatings thickness extending laterally over several mm. That is, no undulations are apparent at the surface with a wavelength on the order of ca. 2-4 mm. The peak-to-valley height of the undulations are up to 20 mm. In the case of the clear coatings (Figure 6), dimples with an average diameter of about 100 μm are randomly distributed over the surface. A closer examination with SEM at a lower magnification (Figure 7) has revealed that the dimples are very shallow, with no morphological differences in comparison to the rest of the film. It was also found by SEM that the dimples have oval shapes. These shallow dimples are presumed to be the defects visible to the eye and which were mistakenly considered to be pinholes. There is no evidence from the topography shown in Figure 7 that the pigmented particles are present at the surface. Additionally, the morphology observed with SEM at low magnification does not reveal any separate pigment phase at the surface but shows only binder.

The relationship between the formation of the "bills" and "valleys" on the surface (Figure 8) and the inefficient flow following the application of the powder is often described in the literature.222222 It has been suggested that large agglomerates of powder particles resulting from the spray process lead to the formation of undulations or the surface, as observed here. The length scale of the surface undulations (2-4 mm) are at least an order of magnitude greater than the powder particle size (20-100 μm), which is consistent with the concept of particle agglomerates as their source.

Other workers have observed "micro-pinholing" in powder coatings, and they attributed it to vapor trapped within the powder particles.2 The micro-dimples formed at the surface of the clearcoat are relatively the same now and therefore, although having a visual appearance of pinholes, are clearly not this type of defect. The fact that no morphological differences can be seen also suggests that these "defects" belong to the class of "orange peel" features.

The fact that these dimples are not present in the case of pigmented coatings might suggest a more uniform deposition of the powder on the substrate in the presence of pigment. Theories of surface flattening22 predict that surface undulations in thicker coatings should level to a plane at a faster rate than thicker coatings. As the clearcoat is about twice as thick as the pigmented coating, it is surprising that the thick clearcoat is less flat. Theory22 also predicts that small undulations—such as the micro-dimples—will flatten faster than larger waves at the surface. The origin of the dimples is therefore unlikely to be the poor levelling of pre-existing surface defects in the powder layer. Instead, lateral flow of the polymer network during processing is being impeded or prevented. One explanation could be localised variations in viscosity or surface tension.

Nano-Scratching

Figures 8 and 9 show the responses to the various scratching cycles performed on the clear and pigmented acrylic coatings, respectively, both with baking times of 11 min. The general response of the coatings is consistent with the microscratches being relatively smooth. Over distances of 15 mm, there is an average deviation of ± 40 nm from the central line, and the deviation is ±150 nm over lateral distances of 500 μm.

The actual scratches show a slight systematic difference in curvature between the clear and pigmented coats. The slightly more abrupt slope of the curve in the case of the pigmented coating suggests a somewhat harder coating. It should be noted that scratching is a continuous measurement and, hence, gives no information about the coating as a continuum. Comparison of the results shown here with other measurements reveals that no significant differences between the samples with other baking times (7 and 15 min) for the same coating type are detected. That is, baking time does not affect the mechanical properties as reflected in the scratch profiles.

The post-scratch complete surface profiles are very similar to the initial profiles, thus indicating a nearly perfect elastic recovery after scratching for this level of deformation. Also, the roughness of the surfaces is found to remain within the initial, pre-scratch limits for all samples investigated (Note that a perfectly elastic deformation would not leave a visible mark on the surface.) One would expect elastic behavior if the acrylic was fully-croslinked at its surface so as to create an elastic network. By comparison, non-crosslinked acrylic surfaces scratched with nano-indentation show plastic deformation.

For the pigmented coatings, in the region of very low applied loads, the coefficient of friction was found to be ca. 0.35. A slightly higher value of ca. 0.4 was found for the linear region of the clearcoat.

Nano-Hardness

Figures 10 and 11 show the variation of the elastic modulus and hardness, respectively, as a function of indentation depth for both the clear and pigmented coatings after 11 min of baking time. These data are the result of averaging over six measurements. Both curves show a very steep decrease in the computed values at the beginning of indentation, which is attributed to the imperfections in the tip geometry.23 Recent publications have emphasized that defects in the indentor tip might be of a size that is comparable to the depth of indentation, and are caused by the roughness and edge sharpness of the tip geometry.23 The tip geometry was calibrated against a fused silica substrate, as described elsewhere.23 Without edge inaccuracies can arise in the tip calibration for penetration depths below 100 nm. After the initial drop near the surface, constant values for the two mechanical constants are obtained. That is, there is no evidence in, contention of hardeness or elastic modulus on depth into the coating. The average value of elastic modulus for the clearcoat (3 GPa) is slightly lower than for the pigmented coating (4 GPa). Both coatings approach an average nano-hardness value (plastic flow) of ca. 0.3 GPa. No significant differences in modulus or hardness were found in samples having other baking times. For the range of times studied here, an increasing baking period (from 7 to 11 min) does not increase the coating surface hardness or stiffness. The implication of this finding is that the extent of crosslinking changes insignificantly after the first seven minutes of baking.

The values obtained here for the elastic modulus are very similar to those obtained elsewhere from nano-indentation analysis of crosslinked acrylic coatings. Broseta et al.24 have reported a decrease in hardness and elastic modulus with increasing depth in glassy poly(methyl methacrylate) (PMMA) surfaces. In their data analysis, they specifically considered the effects of tip geometry, but they cannot rule out the effects of undefined indentations in the calibration procedure. At penetration depths greater than about 1000 nm, the elastic modulus of the PMMA approached 4 GPa, which is the value expected for amorphous poly(methyl methacrylate). The hardness of PMMA was reported to approach about 0.25 GPa at depths beyond 1000 nm, which is likewise similar to values obtained elsewhere.24 Courbez25 has reported previously that the modulus of crosslinked acrylics decreases with depth. An attempt was made to correlate the modulus depth dependence with a higher croslink density at the surface. It is not clear if this work was also subject to the error induced by the effects of the tip geometry. Research using atomic force microscopy has likewise concluded that the modulus of non-pigmented polyester and polyurethane coatings showed a depth dependence. Our finding of a uniform modulus with increasing depth differs from these other reports.

Scratching and nano-indentation analyses measure properties of material surfaces that are not expected to be the same as in the bulk. Nevertheless, for comparison to the data presented earlier, it is relevant to note that MEK double rub tests were performed on both the clearcoat and the pigmented coating. For both, there was no visual effect after 100 MEK double rubs. Macroscopic hardness tests were also performed. The Koen hardness
as the reference cure temperature. Heating both formulations to this temperature promotes the thickness of the glossy coatings for cure times of minutes or more.

Coating Topography

Visual inspection of the coatings reveals a marked unevenness in the surface finish that detracts from its appearance. The non-pigmented coatings also contain small defects, barely visible to the unaided eye, that are suggestive of the presence of "pinholes." Figures 6 and 7 show typical topographic profiles of clear and pigmented coatings, respectively. In both, there are variations in coatings thickness extending laterally over several mm. That is, deformations are apparent at the surface with a wavelength on the order of ca. 2-4 mm. The peak-to-valley height of the undulations are up to 20 μm. In the case of the clearcoating (Figure 6), dimples with an average diameter of about 100 μm are randomly distributed over the surface. A closer examination with SEM at a glancing angle has revealed that the dimples are very shallow, with no morphological differences in comparison to the rest of the film. It was also found by SEM that the dimples have oval shapes. These shallow dimples are presumed to be the defects visible to the eye and which were mistakenly considered to be pinholes. There is no evidence from the topography shown in Figure 7 (pigmented coating) that the pigment particles are present at the surface.

Additionally, the morphology observed with SEM of the dimples does not reveal any separate pigment phase at the surface but shows only binder.

The relationship between the formation of the "bills" and "valleys" (Figure 5) and their configuration (interstices) and the inefficient flow following the application of the powder is often described in the literature. It has been suggested that gas agglomerates of powder particles resulting from the spray process lead to the formation of pinholes. The liquid phase of the spray is not able to fill these spaces completely, due to their small size. However, the exact mechanism of pinhole formation is still not fully understood. The presence of pinholes can affect the mechanical properties and overall performance of the coatings. The removal of pinholes is crucial for obtaining a high-quality finish and improving the durability of the coatings.

Nano-Scratching

Figures 8 and 9 show the responses to the various scratching cycles performed on the clear and pigmented acrylic coatings, respectively, both with baking times of 11 min. The scratch depths (n) and the track lengths (l) are relatively smooth. Over distances of 15 μm, there is an average deviation of ±40 nm from the central line, and the deviation is ±150 nm over lateral distances of 500 μm.

The actual scratches show a slight systematic difference in curvature between the clear and pigmented coatings. The slightly more abrupt shape of the curve in the case of the pigmented coatings suggests a somewhat harder coating. It should be noted that scratching is a continuous process, and it is difficult to obtain information about the coating as a continuum. Comparison of the results shown here with other measurements reveals that no significant differences between the samples with different baking times (7 and 11 min) for the same coating type are detected. That is, baking time does not affect the mechanical properties as reflected in the scratch profiles.

The post-scratch complete surface profiles are very similar to the initial profiles, thus indicating a nearly perfect elastic recovery after scratching for this level of deformation. Also, the roughness of the surfaces is found to remain within the initial, pre-scratch limits for all samples investigated. The data show that the elastic behavior of the acrylic coating was fully recovered at the surface so as to create an elastic network. By comparison, non-cracklinked acrylic surfaces subjected to nano-indentation show plastic deformation.

For the pigmented coatings, in the region of very low applied loads, the coefficient of friction was found to be ca. 0.35. A slightly higher value of 0.34 was found for the linear region of the scratch.

Nano-Hardness

Figures 10 and 11 show the variation of the elastic modulus and hardness, respectively, as a function of indentation depth for both the clear and pigmented coatings. After 11 min of baking time. These data are the result of averaging over six measurements. Both curves show a very steep decrease in the computed values at the beginning of indentation, which is attributed to the imperfections in the tip geometry. Recent publications emphasize that defects in the indenter tip might be a source of error in the measurement of indentation depth, and they might, therefore, cause significant errors in the hardness evaluation. To minimize such effects, special care was taken in the choice of the indentation geometry for all indentations. The tip geometry was calibrated against a fused silica substrate, as described elsewhere. Without care, inaccuracies can arise in the tip calibration for penetration depths below 100 nm.

After the initial drop near the surface, constant values for the two mechanical constants are obtained. That is, there is no observed change in the elastic modulus or hardness with depth into the coating. The average value of elastic modulus for the clearcoating (3 GPa) is slightly lower than for the pigmented coating (4 GPa). Both coatings approach an average nano-hardness value (plastic flow) of ca. 0.1 GPa. No significant differences in modulus or hardness were found in samples having other baking times. For the range of times studied, an increasing baking period from 7 to 15 min does not increase the coating surface hardness or stiffness. The implication of this finding is that the extent of crosslinking changes insignificantly after the first seven minutes of baking.

The values obtained here for the elastic modulus are very similar to those obtained elsewhere from nanoindentation analysis of crosslinked acrylic coatings. Brisbane et al. have reported a decrease in hardness and elastic modulus with increasing depth in glassy poly(methyl methacrylate) (PMMA) surfaces. In their data analysis, they specifically considered the effects of tip geometry, but they did not report the effects of unidenated impressions in the calibration procedure. At penetration depths greater than about 100 nm, the elastic modulus of the PMMA approached 4 GPa, which is the value for bulk acrylic. The nano-hardness of PMMA was reported to approach about 0.25 GPa at depths beyond 1000 nm, which is likewise similar to values obtained here. However, it is not clear if this work was also subject to the error induced by the effects of the tip geometry. Research using atomic force microscopy has likewise concluded that the modulus of non-pigmented polyester and polyurethane coatings showed a depth dependence. Our finding of a uniform modulus with increasing depth differs from these other reports.

Scratch- and nano-indentation analyses measure properties of materials surfaces that is not expected to be the same as in the bulk. Nevertheless, for comparison to the data presented earlier, it is relevant to note that MIE double rub tests were performed on both the clearcoating and the pigmented coating. For both, there was no visual effect after 100 MIE double rubs. Macroscopic hardness tests were also performed. The Konig hardness

Figure 10—Elastic modulus of the clear (a) and pigmented (b) acrylic powder coatings as a function depth into the surface.

Figure 11—Hardness of the clear (a) and pigmented (b) acrylic powder coatings as a function of indentation depth.
value obtained for the clearcoat formulation is 40 sec, whereas the pigmented coating has a value of 155 sec. Thus, there is an increase in the bulk hardness as a result of pigment addition, whereas there is no difference in the nanohardness values.

As shown previously in Figure 6, the clearcoating surfaces displayed "micro-dimples." Experiments were performed with the aim of determining if these variations in topography could be correlated with mechanical properties. Indentation within the micro-dimples of the clearcoating showed no significant differences in either the hardness or the elastic modulus of these regions in comparison to the smooth regions of the same sample. Thus, in summary, we see uniform mechanical characteristics at the sample surface—both laterally and with depth—and these characteristics are independent of the storing time and only slightly sensitive to the presence of pigment.

CONCLUSIONS

Recently developed and improved techniques in thermal analysis, surface profiling, nano-scratching, and indentation were used to determine the properties of crosslinked acrylic powder coatings. Data regarding the effects of pigment addition on the curing, the visual appearance, and the near-surface mechanical properties were obtained. Several specific conclusions may be drawn.

Although the standard, as-recommended baking time for these acrylic formulations is 15 min, the nano-mechanical properties obtained after a baking time of seven minutes do not change significantly with additional baking times at the same temperature. The presence of the pigment increases the modulus of the coating surface slightly from 3 GPa to 4 GPa. Although the scratching experiments suggested that the pigmented coating has a slightly higher hardness than does the clearcoat, indentation experiments find no significant difference but an average value of 0.1 GPa in both. All of the coatings, regardless of their baking time or the presence of the pigment, showed extensive elastic recovery after the scratching and no significant extents of plastic deformation.

A decrease in elastic modulus was seen near the coating surface that is attributed to the effects of the stylus tip geometry. After this initial drop, the modulus remains constant. Thus, the data indicate that curing is complete at the surface, so that a fully elastic network is formed with a modulus that does not change significantly with penetration into the surface.

A smoother coating surface is achieved upon the addition of pigment to the acrylic. The non-pigmented acrylic coating displayed many "micro-dimples" (ca. 100 μm in diameter) at its surface. The appearance of the film surface within these dimples does not differ from the rest of the coating. Moreover, the hardness and elastic modulus of the coating within these dimpled regions is identical, within experimental error, to the properties outside these regions. Thus, there is no evidence for non-uniformity in the amount of crosslinking laterally in the coating that can be correlated with the dimple formation.

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A decrease in elastic modulus was seen near the coating surface that is attributed to the effects of the styrene tip geometry. After this initial drop, the modulus returned to constant. Thus, the data indicated that curing is complete at the surface, so that a fully elastic network is formed with a modulus that does not change significantly with penetration into the surface.

A smoother coating surface is achieved upon the addition of pigment to the acrylic. The non-pigmented acrylic coating displayed numerous "micro-dimples" (ca. 100 μm diameter) at its surface. The appearance of the film surface within these dimples does not differ from the rest of the coating. Moreover, the hardness and elastic modulus of the coating within these dimpled regions is identical, within experimental error, to the properties outside these regions. Thus, there is no evidence for non-uniformity in the amount of crosslinking laterally to the coating that can be correlated with the dimple formation.

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