Mechanical Surface Characterization: A Promising Procedure to Screen Organic Coatings

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Two ductile coating materials were subjected to a combined indentation and scratch test procedure designed to screen a predetermined pattern of many small sample surfaces in a limited time. The screening of 50 surface spots ordered in a matrix pattern on the surface was carried out in 4.5 hr. The test provides reproducible data in terms of indentation modulus, elastic recovery, scratch penetration depth, and scratch residual depth, and also offers the possibility of detecting critical mechanical transitions such as rupture. The presented procedure produces sufficient data in a limited time scale to fulfill the requirements for a fast method to screen coating compositions.

INTRODUCTION

Combinatorial approaches have been used for over a decade now in pharmaceutical R&D to screen large numbers of compositions and formulations. In recent years, demands for coatings with lower environmental impact and retained or improved performance have awakened greater interest in the issue of improved development procedures. To replace existing high-performance formulations, improved resin knowledge is required, which can only be accomplished by introducing more efficient ways to synthesize, blend, apply, and evaluate resin compositions. For obvious reasons, the concept of high-throughput screening has been given extensive attention in the field of coatings R&D,[1,2] though it is still little practiced.[3,4] Applied to coating development, a desirable setup would include instrumental techniques that are adaptable to automation and feasible for the production and screening of ranges of resin compositions on a milligram scale. For decorative coatings, the appearance is essential. Consequently, mechanical properties preserving the appearance are important. Nanocontact techniques that are also promising for the controlled screening of mechanical performance on a microscale have recently become available and found use in many applications.[5-9]

Contact tests are particularly suitable in the coating industry, since surface properties are of primary concern. The relationship between bulk properties and surface properties is poorly understood. The occurrence of stratification, i.e., a gradient difference between bulk and surface properties, appears to be an issue in coating film layers. Commonly utilized tests measuring polymer bulk properties, such as tensile tests, are less appropriate if coatings stratify.[10,11]

The objective of this preliminary study was to evaluate nanotesting techniques applied to polymer coatings and their feasibility for combinatorial development and use. Within this objective, the main priority was to put up a procedure that would be sufficiently accurate to rank materials in terms of mechanical performance. For this reason, finding appropriate contact parameters, which describe mechanical performance to such extent that compositions can be ranked, is highly desirable. The intention was to mechanically screen microscopic spots distributed in a matrix pattern on a macroscopically well-defined surface. In the presented study, multiple tests were carried out in a predetermined pattern

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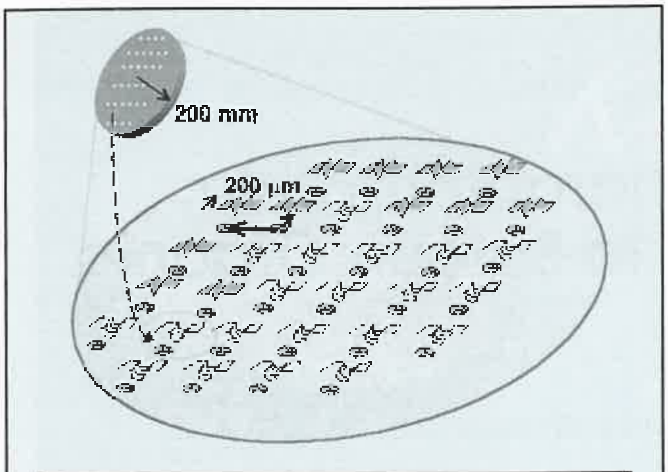

Figure 1—Multiple nanocontact testing as a tool to screen organic coatings.

on uniform and homogeneous surfaces of a single composition. A microcontact test device, which provides both indentation and scratching, was selected for this purpose. The utilized procedure resembles high-throughput screening conditions where various materials, synthesized in a combinatorial procedure, are blended and deposited on a single surface and subjected to individual testing (*Figure* 1).

Focus was on the accuracy and reproducibility of the test procedure and the possibility to achieve acceptable results with a reduced number of tests and time. The accuracy issue concerns instrumental capabilities: the use of progressive load tests and, in particular, the procedure of profiling the surface with the same geometry that is utilized to impose the surface deformations. Instrumental reproducibility is required to obtain sufficient information about the nature of material response with a minimum number of tests.

EXPERIMENTAL

Materials and Sample Preparation

A solventborne isocyanate coil coating and a flexible powder coating were applied and cured on galvanized steel substrates and subjected to mechanical testing. Both coatings had been characterized by standard coil coating tests, such as T-bend and deep-drawing tests, and were considered as ductile materials. The samples had been stored prior to testing at 23°C and 50% RH for 260 days, *Table* 1.

Free-standing films of the top layers of each material had previously been characterized mechanically by quasi-static and dynamical uniaxial testing.[11] Parameters describing the mechanical and viscoelastic behavior are given in *Table* 2. Each parameter value corresponds to an average of at least six test results.

Material **A** exhibits higher stiffness, higher strength, and higher resistance to yield, but Material **B** is superior in ductility in terms of energy to yield and elongation to break. According to the considerably lower glass transition temperature for Material **B**, this material can be assumed to behave with more viscoelasticity than Material **A** (at room temperature).

Instrumentation

The instrument used was a CSM Nano-Scratch Tester® (NST) with a standard force cantilever suitable for forces between 100 µN and 100 mN. The NST device shares a high-resolution x-y-translation table with a microscopy head. The tested sample surfaces were profiled using the test contact geometry (scratch indentor). The indentor position during prescan, a loaded scratch-scan, and postscan measured the penetration and residual depths, *Figure* 2. Hence, initial contact conditions in terms of load and penetration can be correlated to the residual deformation at the same position.

The instrument translation table was equipped with a friction stage thus offering, in addition to indentor position and normal load data, friction force measurements. Additional surface imaging of the residual deformation was carried out with Optical Microscopy (OM) and Atomic Force Microscopy (AFM). Both were mounted onto the same microscopy head on the NST frame. The test setup is described in detail elsewhere.[6]

Procedure

The nano testing was performed both in scratching and in indentation mode using the same contact geometry. The combined use of both test modes is desirable to

Table 1—Data of the Studied Coatings

Material	Layer 1 Primer	Layer 2 Top	Crosslinker-Resin (Layer 2)	Comments
A	—	75-90 µm	TGIC-COOH-polyester	Powder/solid clearcoat
B	12 µm	25 µm	Isocyanate-OH-polyester	Solventborne clearcoat

Table 2—Mechanical Properties of the Free-Standing Films

Sample Name	Young's Modulus (MPa)	Energy to Yield (mJ)	Strength (MPa)	Strain to Break (%)	T_g (°C)
Material **A**	**2830** ± 747	**4.52** ± 1.03	**58** ± 1.0	**28** ± 32	**70**
Material **B**	**1725** ± 640	**0.68** ± 0.13	**30** ± [illegible].0	**320** ± 150	**45**

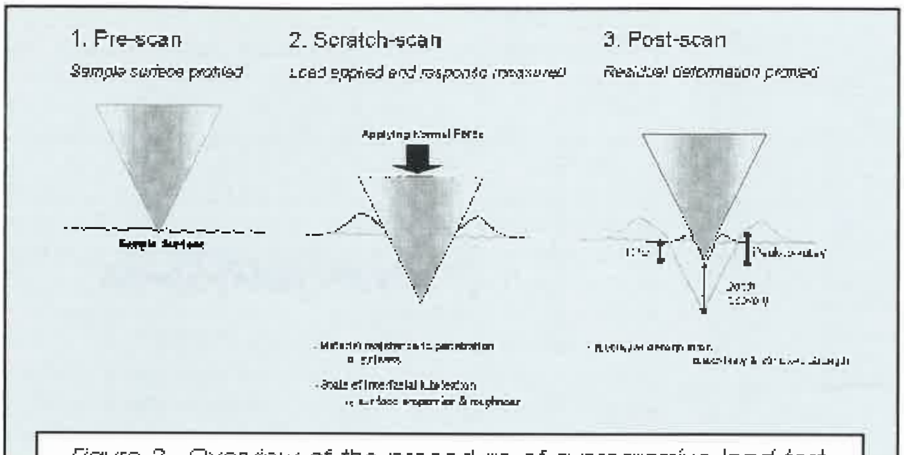

Figure 2—Overview of the procedure of a progressive load test, determination of the magnitudes of immediate and residual deformation, and interpretation of the results.

produce a complete picture of the mechanical response of an arbitrary material. The indentation mode provides a direct value of stiffness (assuming the Poisson's ratio is constant and equal for the range of tested materials). Indentation testing also gives satisfactory information on elastic and plastic response.[12] Rupture transitions and failure modes can only be studied through scratch testing.[9,12,13] A Rockwell-geometry with 90°-cone angle and 2 µm-tip radius was used for both indentation and scratch testing. The indentation tests were performed to an indentation depth of 1 µm using a loading/unloading rate of 5 mN/min. Poisson's ratio was assumed to be constant and 0.30 for both materials, which, in general, is a reasonable assumption for polymers in their glassy state. The scratch tests were performed over a scratch length of 100 µm at scratch speeds between 0.18 mm/min to 1 mm/min. A progressive load test procedure was utilized.[6,7] Initial contact conditions in terms of positional values of load and penetration can, over the whole scratch length, be correlated to the residual deformation at the same position. Hence, a single progressive load test can replace the use of many constant load tests to examine the material response over a range of loads, in accordance with the concept of scratch mapping.[12,14] The progressive load test data give information about scratch hardness, plasticity, deformation (work) hardening, and substrate-coating interactions. In addition, the initiation of a mechanical rupture transition with increased load is believed to relate to the fatigue toughness of the material.

The indentations were arranged in five lines, each with 10 indentations, spaced 200 µm between lines and indentation points. The 50 scratches were spaced by 200 µm. The indentor was not cleaned or separately treated to avoid contamination between the individual contact tests during the screening of test spots. The tests were carried out at 21°C and 40% RH.

RESULTS AND DISCUSSION

Screening Indentation Testing

INDENTATION TEST RELIABILITY AND REPRODUCIBILITY: A typical indentation test curve obtained for a conical indentor on a viscoelastic surface is shown in *Figure* 3a. This is the 17th test on Material A in a series of 50 tests simulating screening conditions. The presented stiffness values were calculated using the initial slope of the unloading curve and an estimate of the contact area based on indentor and displacement data. The stiffness estimation for a multiple test of 50 indentations distributed over a single-material surface is shown in *Figure* 3b for Material A and Material B.

Excluding the five first tests (encircled data in *Figure* 3b and *Figure* 4a-b) in the first line of 10 indentations on

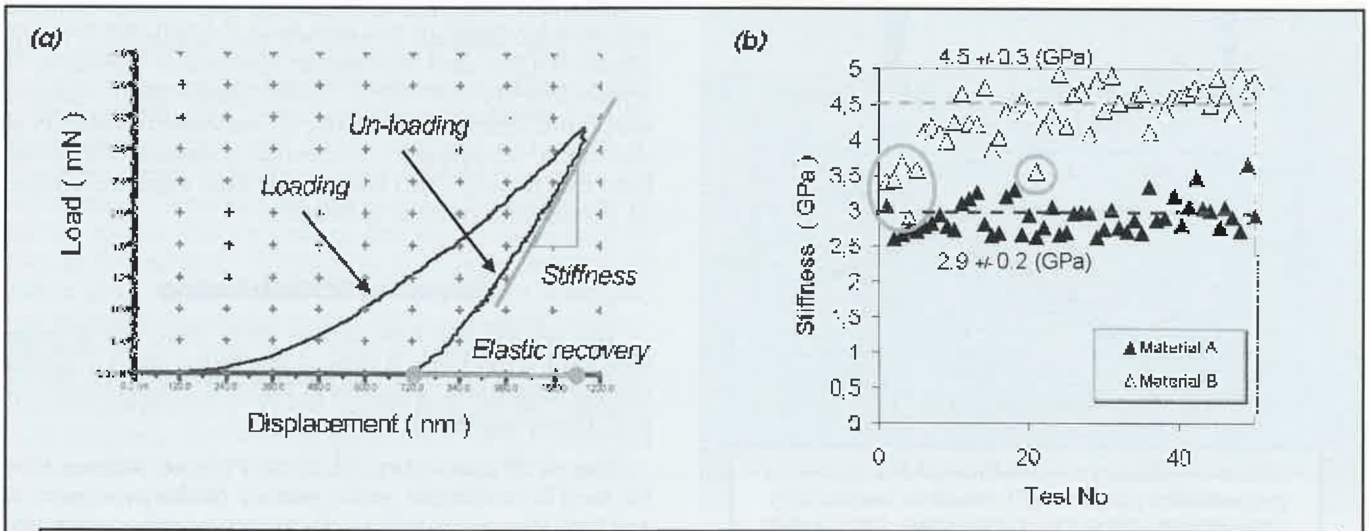

*Figure 3—(a) Indentation test curve on Material **B** at 15 mN/min to 1 µm, and (b) the reproducibility of stiffness data in a multiple test.*

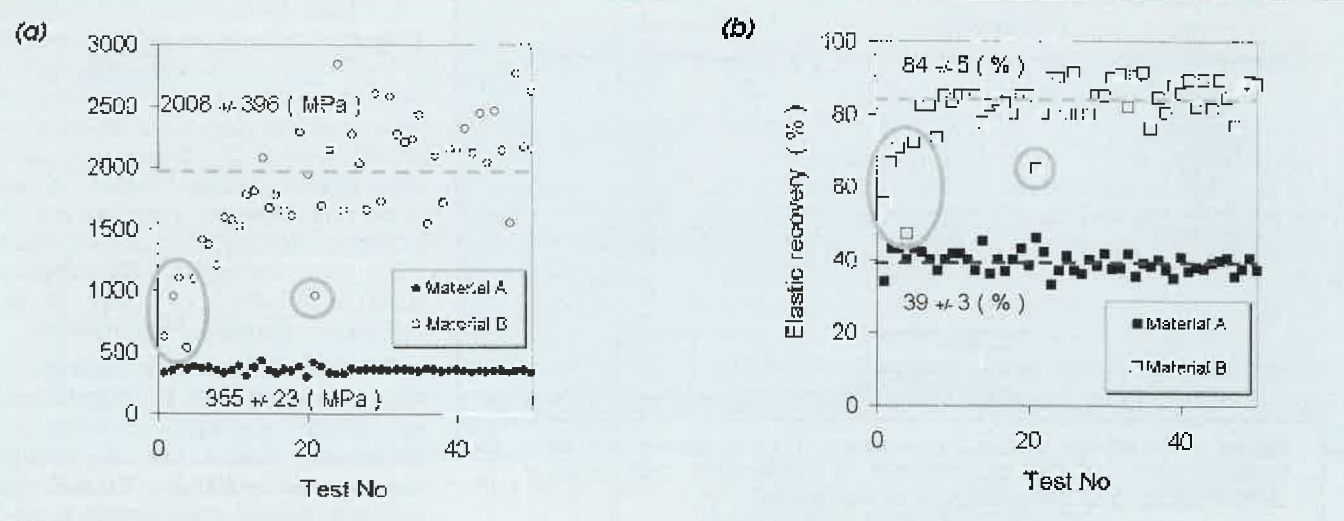

Figure 4— Reproducibility of (a) hardness data, and (b) elastic recovery in a screening indentation test.

Material **B** and the 21st test, regarded as noninstrumental artifacts and probably due to a local surface heterogeneity, the overall reproducibility was high.

Correlation Between Indentation Response and Tensile Parameters: The indentation stiffness of Material **A** agreed well with the measured tensile modulus. Apparently, Material **B** can be considered a heterogeneous layer concerning the different material ranking in stiffness with respect to the tensile test on free-standing films. Material **B** has a stiffer and more elastic surface compared to the bulk of the very same material. Similar observations have been reported recently in literature for other crosslinked polyurethanes.[9,18-19] This observation illustrates the difficulties in correlating intrinsic bulk properties to surface performance for this family of materials. In addition, it serves as a good example for the necessity of using contact tests to predict common wear in crosslinked coatings. Additional data on indentation hardness and degree of (immediate) elastic recovery is presented in *Figure* 4. Individual test results do not deviate (from the mean value) significantly enough to have impact on comparisons between the materials.

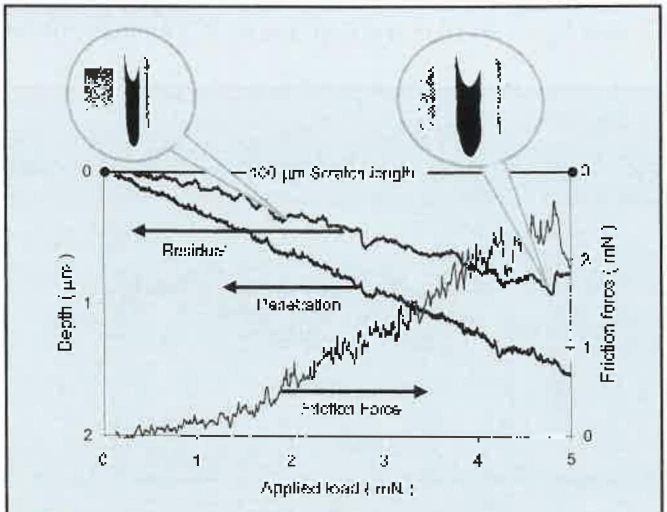

*Figure 5—Response of Material **B** in terms of penetration depth, d(P), residual depth d(R), and friction force to a progressive load test in the interval 0.1-25 mN utilizing a 90° cone at 0.1 mm/min scratch speed.*

Effect of Test Parameters on Indentation Response: The time for the indentation part of the screening test, including 50 indentations in the predetermined test pattern, was three hours. The same surfaces were subjected to a multiple test at a slower loading rate, 2 mN/min, to the same depth, 1 µm. In this test, as expected, the shape of the test curves was different due to viscoelastic creep and, consequently, different mean values were obtained for both materials due to their individual viscoelastic response. The individual ranking in stiffness was changed as the low T_g-coating Material **B** exhibited a response with a dramatically reduced stiffness and hardness, 0.87 GPa and 300 MPa, respectively. Material **A** remained glassy with stiffness values (also difficult to estimate due to extensive creep) above 3 GPa and somewhat decreased hardness to approximately 240 MPa. These observations suggest that rapid indentation testing (15 mN/min) presents an additional advantage if compared to the use of a slower load rate (2 mN/min) besides the time aspect: the effect of viscoelastic creep is reduced.

Screening Scratch Testing

The second test type in this work concerns progressive load scratching. A typical test curve from a scratch test on Material **B** is shown in *Figure* 5. Interpretation of test data is explained in *Figure* 2.

Use of Scratch Indentor to Profile Sample Surfaces: The reliability and accuracy of the procedure to analyze the residual surface topography with the scratch indentor was first investigated on different coatings to confirm its validity. Would this procedure result in great underestimation of the residual deformation? To overcome this uncertainty, progressive load tests were performed on five different ductile coatings, (*Figures* 6-8). These formulations have been described elsewhere[11] and are, for the sake of simplicity, denoted as Material $\mathbf{A}_{clear}$, $\mathbf{A}_{white}$, $\mathbf{B}_{clear}$, $\mathbf{B}_{white}$, and $\mathbf{B}_{black}$. Material $\mathbf{A}_{clear}$ and Material $\mathbf{B}_{clear}$ correspond to Material **A** and **B** but were stored for less time (Material $\mathbf{A}_{clear}$ and $\mathbf{B}_{clear}$ were stored for 70 days and Material A and B were stored for 260 days) which changed these materials significantly. With time both coatings became more brittle, they gained strength and, consequently, gained higher resistance to rupture, i.e., higher L_r, and increased penetration resistance.[20] Material $\mathbf{A}_{white}$, $\mathbf{B}_{white}$, and $\mathbf{B}_{black}$ are the white- and black-pigmented counterparts to the clearcoats. The TiO_2-pigmented coating formulations of Material **A** and **B** contained roughly the same amount of pigmentation ($PVC_A = 36\%$ and $PVC_B = 33\%$), while the carbon black-pigmented formulation of Material **B** contained only 5.6%. The residual scratch ditch was estimated first by performing a postscan with the indentor geometry, and then carrying out in-situ surface imaging with the AFM-objective. The residual data, *d(R)*, were compared with 2D data from AFM, *d(Ditch)*, for the clear coatings (*Figure* 6), and for the pigmented coatings (*Figure* 7).

Obviously, the determination of the ditch by indentor profiling was sufficiently accurate for the studied ductile coatings. Thus, using the indentor to profile the surface can be considered a reliable method to determine the depth magnitude of the ditch. However, there was a considerable plastic build-up in all the studied systems that this estimate failed to determine. The height of the piles was observed, for loads less than the rupture transition, to be roughly the same as the depth of the ditch. This issue is significant for ductile polymers but can be disregarded for more brittle/glassy polymers in which pile formations at the scratch boundaries are negligible features in the residual deformation pattern.

Use and Interpretation of Friction Data: Additional information concerning the type of response is given by comparing the evolution of friction coefficient (the ratio between the normal load and the tangential force) for the materials.[11] The tangential force is governed by the stiffness of the material and the amount of plastic build-up in the front edge of the scratching geometry, i.e., the plastic contribution to the total imposed deformation. However, surface friction and scratch response are interrelated. Generally, an increase of the coefficient of friction causes the location of the plastic zone to shift toward the surface[21,22] resulting in a larger amount of plastic flow on the surface. Consequently, at comparative penetration depths and conditions where no rupture events are present, a scratch response involving higher friction can be interpreted as generating more plastic pile build-up at the boundaries of the contact. Such response is therefore associated with a material with predominantly plastic deformation. This hypothesis was evaluated in the tests shown in *Figure* 6. Frictional data and surface imaging data (AFM) for these tests are shown in *Figure* 8. Frictional data in the progressive load tests were compared with penetration

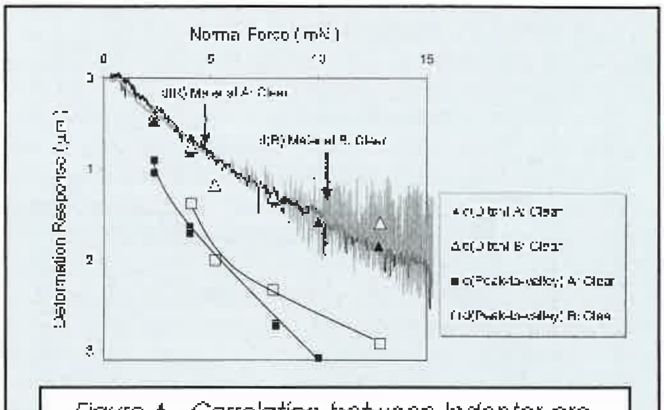

Figure 6—Correlation between indentor profiling, d(R), and AFM, d(Ditch), for Material $\mathbf{A}_{clear}$ *and Material* $\mathbf{B}_{clear}$ *(data on peak-to-valley height are included).*

data (represented by a continuous line) and estimations of effective contact depth data (represented by markers) in *Figure* 8. The effective contact depth was estimated by profiling the residual scratch (with AFM) and projecting the contact geometry between the pile-up peaks.[10,13] Material $\mathbf{B}_{clear}$ exhibited higher friction coefficient compared to Material $\mathbf{A}_{clear}$, thus was expected to deform with more plastic build-up. However, neither the estimated effective contact depth data, *Figure* 8, nor the total residual deformation depth data, *d(Peak to valley)* in *Figure* 6, supports this interpretation. The probable explanation is that a considerable amount of build-up and ditch support on the front edge is due to viscoelastic deformation that recovers with time to a great extent. The location of glass transition close to room temperature for Material $\mathbf{B}_{clear}$ consolidates this explanation. In conclusion, the experiments presented here do not support the use of frictional data solely to rank the degree of plastic response.

Scratch Test Reliability and Reproducibility: The screening progressive load tests in *Figure* 5 were performed at 0.2 mm/min scratch speed and a load rate of 5 mN/min utilizing the same indentor geometry. The scratch length was, as depicted in *Figure* 5, only 100 µm

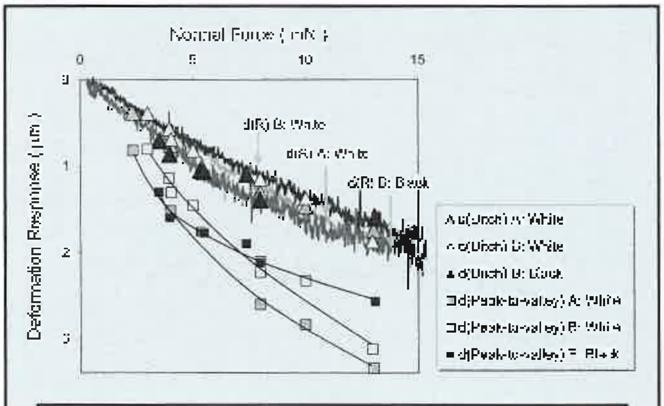

Figure 7—Correlation between indentor profiling, d(R), and AFM, d(Ditch), for Material $\mathbf{A}_{white}$, $\mathbf{B}_{white}$ *and* $\mathbf{B}_{black}$ *(data on peak to-valley height are included).*

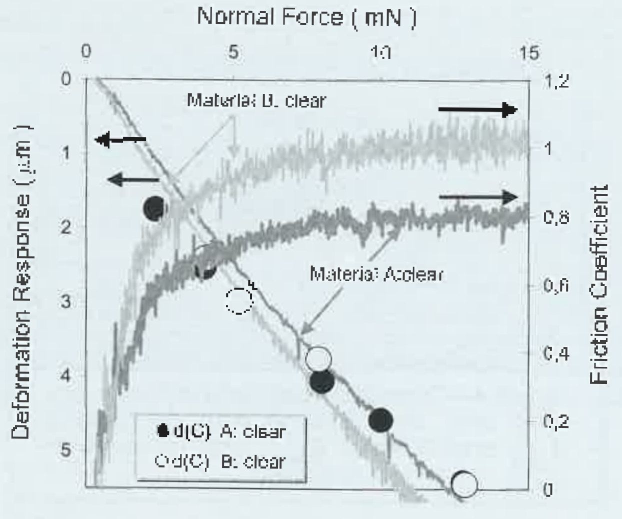

Figure 8—Friction coefficient, penetration depth, and effective contact depth for Material A_{clear} *and Material* B_{clear}

to fulfill the dimensional restrictions in a screening test where care has to be taken to avoid heterogeneity on the boundaries of the deposited samples. This is the fifth test of the total 50 scratch tests carried out on this sample surface of Material **B**. Neither test data nor AFM-imaging showed any presence of rupture events for this test range of loads. This observation also holds for Material A. An estimate of the elastic recovery can be obtained for a certain load by subtracting the residual depth, *d(R)*, of the scratch ditch from the penetration depth, *d(P)*. *Figure* 9 shows the results for 2 mN and 4 mN normal load, respectively, in a screening test with 50 individual progressive scratch tests carried out on different spots on Material **B**. Apparently, comparing the scratch response at 1 µm penetration depth (at a load of 3 mN) with the response in the indentation test at the same depth, *Figure* 4b and *Figure* 9, the elastic recovery is 50% lower if the indentor geometry is sliding forward.

The 50 scratch tests took three hours, the same amount of time as the indentation tests. Good reproducibility of the studied parameters (penetration depth, residual depth, and elasticity) was obtained. The reproducibility and standard deviation was of the same order of magnitude (or better) as observed for corresponding parameters in traditional tensile tests of free coating films (stiffness, elasticity, and stress-strain-relationship). Testing on the surface of Material **B** showed again proof of local heterogeneity or instrumental instability (encircled data, *Figure* 9), which illustrates a risk with contact testing on a nanoscale. Positively, the evolution and shape of the test data curves accounting for these divergent results (not shown here) very clearly indicated that the response was not representing a constitutive response of a homogenous viscoelastic surface (which is a prerequisite in contact testing). Thus, it is simple to avoid taking such data into account in further analysis. The last remark also holds for two of the total six divergent indentation data shown in *Figure* 4 (tests 4 and 21).

Effect of Test Parameters on Scratch Response: The selection of scratching geometry is an issue that has been subjected to comprehensive study.[13,14] In short, blunt contact geometries correspond to small contact strains while a sharper contact, i.e., increased attack angle between indentor and adjacent material on the front edge, involves increased contact strains. In order to improve the possibility of inducing failure responses in ductile materials (thus providing more information on the material behavior) and reduce the screening test time, a sharper geometry was utilized: a 60° cone with a 2 µm tip radius, and the translation speed was increased 10× to 1 mm/min. Increasing the load rate from 5 mN/min to 133 mN/min and increasing the scratch length from 100 µm to 200 µm (the scratches still fulfill the dimensional requirements of the screening test), resulted in an increased load range (from 5 mN to 30 mN). Hereby, 50 tests could be carried out in less than 1.5 hr. The resulting response for Material **B** subjected to this test is shown in *Figure* 10, where data

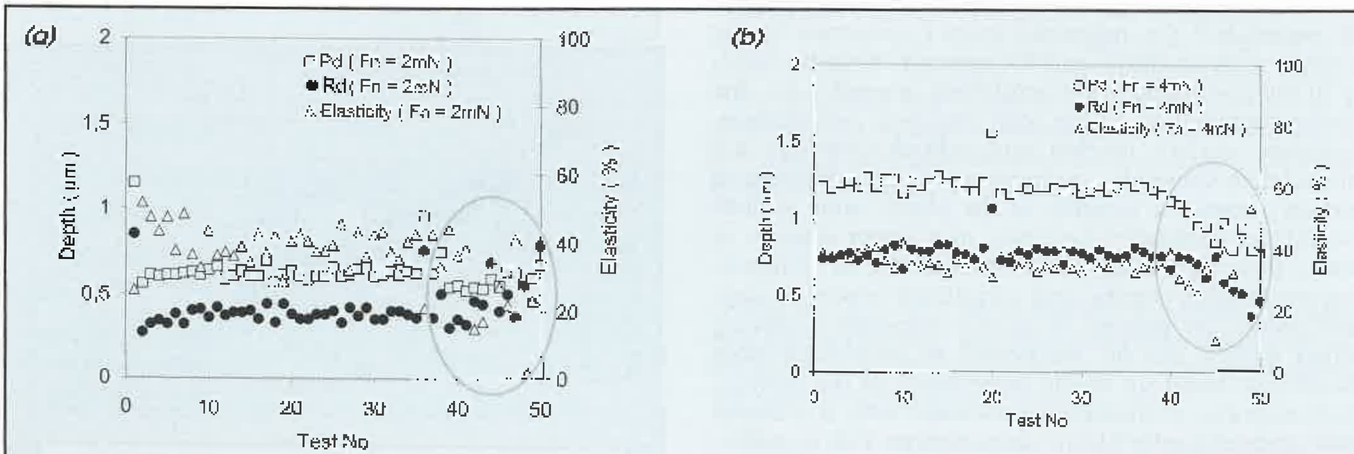

Figure 9—Reproducibility in a screening scratch test utilizing a 90°-cone at 0.1 mm/min scratch speed. The scratch response of Material ***B*** *was measured in terms of penetration depth, residual depth, and elastic recovery at (a) 2 mN and (b) 4 mN.*

from a slower test at 0.2 mm/min with a blunter cone (90°) in the load range 0-5 mN also is included for comparison. A failure response at 5 mN normal load was detected in terms of rapid change in test data (penetration depth, residual depth, and friction force). Optical microscopy (500× magnification) confirmed the above interpretation of a mechanical transition (*Figure* 10). The overall characteristics of the rupture, such as smooth and continuous borders, suggested a ductile failure. This transition, denoted by a critical load, L_c, is frequently suggested as a key parameter of material performance, since it is often accompanied by a marked increase in visibility of the residual damage pattern for glassy polymers.[6,7]

The reproducibility of the load, penetration depth, and residual depth in this test is good, in fact better, than the previously described test performed at slower speed with a blunter tip (*Figure* 11a). Positively, no divergent data were found for this set of test parameters. More surprisingly, the detection of a critical load, L_c, from test data, for which a transition from plastic response to failure response occurred, showed little variation (*Figure* 11b).

Correlation Between Scratch Response and Tensile Parameters: The effective strain is supposed to be proportional to the semicone angle for a conical geometry, thus, the strain can be considered approximately constant, independent of depth, at depths deeper than the height of the tip, assuming the absence of substrate influence (no change in stress state). Hence, the critical loads would be directly related to the strength of a material. The presented test data, *Figure* 11b, ranked Material **A** as somewhat more resistant and cohesive than Material **B** in terms of L_c, which is in agreement with tensile data. Penetration depth can, under certain circumstances, be used as a qualitative inverse measure of stiffness.[21,22] Penetration depth is, however, a more sensitive measure for low modulus materials. In short, the test ranked Material **A** as somewhat stiffer, i.e., more penetration resistant, and more resistant to cohesive failure (corresponding to higher strength in tensile testing). The individual ranking of the two materials in terms of penetration resistance holds for the whole range of loads (not shown). These findings are in agreement with the uniaxial tensile data (*Table* 2).

Microscopic Analysis of Failure Pattern: A slightly more comprehensive (and time consuming) procedure involves a further evaluation step in terms of an optical inspection of the characteristics of the residual deformation pattern, in particular the shape of the ruptures at loads above L_c. When the progressive scratch test was used to scratch various types of amorphous organic materials,[23] ranging from rubbery and ductile thermosets to glassy thermosets, the residual scratches (at loads above L_c) revealed a few characteristic features, which are summarized in *Figure* 12. Hence, a brief survey of the present ruptures at loads above L_c can provide additional information that facilitates the classification of material responses.

Validity of the Presented Test Procedure

The necessity of combining indentation tests with scratch tests to obtain a more complete picture of the end-properties of materials has been dealt with by Briscoe.[12] The use of a nanocontact device minimizes the influence from substrate on the coating response.[24] Furthermore, the test apparatus and contact asperity utilized here produces deformations that resemble real wear such as the characteristic mar damage observed on automobiles. Consequently, this test procedure provides data that describe both general mechanical performance and a critical coating property, mar resistance, and, thus, complies with the demands in a variety of coating applications on a primary screening method.

The use of indentation tests in a screening test procedure has been demonstrated in this paper. General guidelines and limitations concerning nanoindentation tests on viscoelastic materials have been treated elsewhere.[8,25] The presented indentation data show the significance of indentation rate and the error involved in testing heterogeneous surfaces. The use of scratch tests in a screening test procedure presents a slightly more complicated case. The presented results clearly illustrate the importance of taking extensive care in optimizing the test parameters, i.e., scratch length, load rate, and scratch speed, to obtain the greatest possible load range in respect to the available surface test area. Increased load range improves the probability of detecting mechanical transitions and, thus, of obtaining additional information. As residual depth and rupture have been reported to correlate well with the visibility of scratches for a range of polymers and coatings,[7] the screening scratch test procedure presented here provides sufficient data to rank most materials with respect to scratch resistance. However, for extremely ductile polymers the plastic pile-up plays a significant role for the visibility with the consequence that this procedure will be less accurate. To distinguish between glassy and

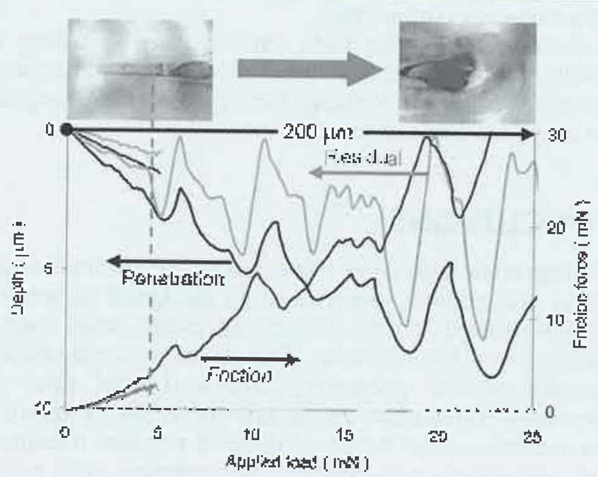

*Figure 10—Response of Material **B** to a progressive load test in the interval 0.1-25 mN utilizing a 60° cone at 1 mm/min scratch speed.*

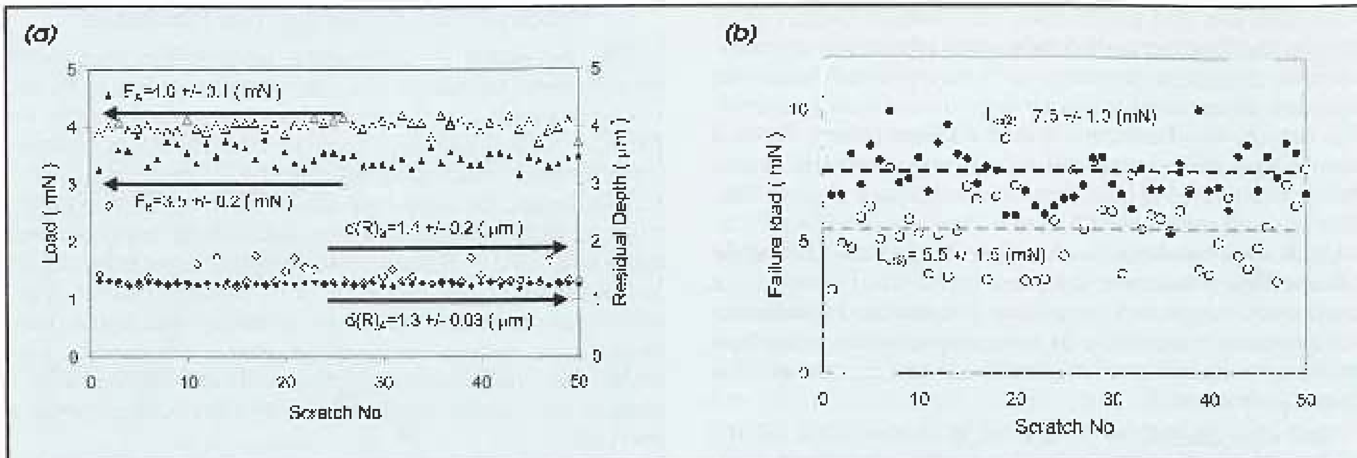

Figure 11—Reproducibility in a screening scratch test with a 60° cone at 1 mm/min scratch speed: (a) force/resistance and residual depth at 2 µm penetration depth; and (b) critical/transition load, L_c. Material **A** (dark) and Material **B** (bright).

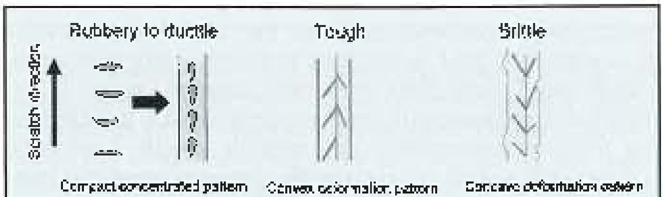

Figure 12—A sketch of characteristic failure pattern for different types of mechanical responses (as seen from above).

ductile response, a correct analysis of the indentor profiling data and the friction data from the screening test plays a key role.[11] Size and shape of the pile-up is preferably measured with surface imaging techniques such as OM, AFM, and interferometer techniques. In the tests presented, no precaution was taken concerning indentor tip contamination. An efficient way to avoid this source of errors is to perform a separate indent in a surface with mechanical or chemical cleaning effect between each contact test.

In conclusion, the tests carried out, including the results presented above, hold mechanical nanocontact testing as a very promising tool for screening ranges of surfaces in a limited time.

CONCLUSIONS

Coating materials were subjected to a combined indentation and scratch test procedure designed to screen a predetermined matrix pattern of many small sample surfaces in a limited time. The use of a combination of sharper contact geometry, increased load rate, and increased translation speed enhanced the outcome of the scratch test in terms of distinct rupture transitions and retained reproducibility. The screening of 50 surface spots was carried out in three hours for indentation testing and one and one-half hours for scratch testing. The combined test provides reproducible data in terms of indentation modulus, elastic recovery, scratch penetration depth, and scratch residual depth, and makes it possible to determine critical mechanical transitions such as rupture. The presented procedure produces sufficient data in limited time to fulfill the requirements for a fast method to screen coating compositions.

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