Application of the spherical indenter for determination of the elastic modulus of coatings

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Abstract. In this work a study of nanoindentation of the surface of epoxy-polyester-based powder coatings deposited on steel substrates was carried out. The effect of the test method on the identifiable mechanical properties is investigated. The measurement results obtained by using a spherical indenter and a Berkovich indenter are compared. Estimates of reduced modulus of elasticity, Young's modulus and rigidity of coatings are obtained. The experimental data obtained indicate a significant dependence of the determined mechanical properties of the paint and varnish coatings depending on the type of indenter used. In the case of Berkovich indenter, the Young's modulus of coatings (0.6 GPa) is understated in relation to coating properties known from macro experiments (3 GPa). Using a spherical indenter, Young's modulus is overestimated (6.3 GPa). Key words: Modulus of elasticity, indentation, coatings, mechanical properties.

1 Introduction

In recent years, the continuous indentation method, formerly known as the kinetic rigidity method, has been increasingly used to determine the rigidity of materials [1-6]. The essence of the kinetic rigidity method is that an indenter is introduced into the material under study and two parameters are recorded: the load and the depth of introduction of the indenter. Rigidity is determined by dividing the load by the surface area of the indentation or its projection. The EU standards now also provide for kinetic indentation to determine rigidity, and the following levels of rigidity determination are observed [3, 4]:

1. macro level: 2 N < P < 30000 N,
2. micro-level: P < 2 H, h > 200 nm,
3. nano level: h < 200 nm, P < 2 mN

where P is load, h is depth of indentation.

Obviously, level 1 corresponds most closely to the commonly used term macro-rigidity, level 2 to micro-rigidity and level 3 can logically be referred to as nanorigidity.

The basic principles of the analytical model used in the indentation method are [5]:
- the strain at unloading is fully elastic;
- the relation between the stiffness of the specimen and the indenter can be obtained as follows:

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here \( \nu_s \) is the sample Poisson's ratio, \( \nu_i \) is the Poisson's ratio of the indenter, \( E_s \) is a modulus of elasticity of the sample, \( E_i \) is an indenter elastic modulus, \( E_r \) is a resulted module.

– the contact can be modelled according to an analytical model describing the contact between a rigid indenter of a certain shape and a homogeneous isotropic elastic surface:

\[
S = \frac{2\sqrt{A}}{\pi} E_r, \tag{2}
\]

here \( S \) defines contact rigidity, \( A \) is a contact area.

This equation has been shown to work for indenters of different geometries and shapes.

The essence of the method is to obtain a load-strain relationship when a physically and geometrically certified indenter is introduced into the sample. Applied force is several millinewtons with resolution of several nanotons, strain is several nanometres (tens of nanometres) with resolution up to 0.04 nm, hence the term nanoindentation.

Additional experimental features:
- scanning - movement of the sample under load (scratch test)
- impact - oscillation of a sample under constant load

Nanoindentation is a method that allows mechanical and fatigue properties of various films, coatings and materials to be determined at the nano-scale level. Testing at very low strains and comparing the data with micro and macro experiments allow conclusions to be drawn about the relationship between the nanostructure of materials and their properties at the macro level.

In the present paper a comparison of different indentation techniques of polymer coatings on steel substrates is carried out on the measurement results. Macro tests were previously conducted for the investigated coatings to determine the bending elastic modulus of coated steel substrates [7-19]. It was shown that the coatings, despite their small thickness, have a significant influence on the elastic properties of thin steel plate specimens. In the experiments the thickness of the coatings was 0.200 mm and the thickness of the steel plates was 0.7-1.5 mm. It has been shown that the modulus of elasticity of thin plates is consistently lower under bending as compared to the modulus of elasticity of thicker plates [20-35]. This effect is confirmed theoretically within the framework of the classical model of an elastic three-layer beam with relatively soft outer layers (coating) and a rigid middle layer (steel substrate). As a result of this experimental and theoretical investigation, it was found that the elastic modulus of the epoxy-polyester coatings under study is, on the order of 3 GPa.

In the present work, the task is to verify the results obtained using the method of nanoindentation of the coating surface. This method makes it possible to determine even the bulk properties (not only surface) properties of the material quite accurately if a sufficiently high indentation force is used and if the material is homogeneous near the surface. For example, previously the elastic properties of grains in silicon carbide ceramics were measured and a Young modulus value close (within the measurement error) to the theoretically known value of the Young modulus of SiC crystals was obtained. In this work a pliable polymer coating is investigated [36-46]. It is likely that the elastic properties of this coating from indentation tests are quite difficult to estimate, due to the non-linearity of the defining relationships that are characteristic of this type of material. As a result, measurement uncertainty may arise not only due to variations in the properties of the experimental samples or due to errors in the measuring equipment, but also due to a significant increase in the error of the Oliver-Farr formula applied (1).
2 Methodology for conducting and processing the results of the experiment

The tests were carried out on 5x10 mm rectangular steel plates that were coated with AKZO NOBEL (Holland) epoxy polymer paint based on polymers. The coating was applied in a Gema chamber (Switzerland) by electrostatic spraying. The colours of the powder coatings were chosen from the international RAL catalogue. A total of 4 samples were prepared with RAL 9005 (black) coating. For experiments, a measuring complex NanoTest 600 (England) was used.

The working body of the NanoTest 600 is a pendulum, which rotates on a friction-free pivot. The pendulum is light and quite rigid at the maximum applied force (500 mN). The pendulum rod is made of ceramics, has a cylindrical shape, and is fitted with an induction coil at the end of the pendulum. Under the action of electric current, the coil moves towards the magnet, defining the law of motion of the diamond indenter towards the sample. The movement of the indenter is measured by a capacitive sensor. The depth of the diamond indenter in the sample is set at an accuracy of 0.04 nm. The experiment with the NanoTest 600 was performed according to the following procedure. The sample was attached to the substrate using adhesive and then the sample was brought to the indenter. After installing the sample in the holder of the experimental complex the surface was treated with a piezoprofilometer. This is necessary to determine the geometry of the surface where the indenter is pressed in. The results are shown in Figure 1. However, the test surface is located at an angle to the holder. This did not have an effect on the experiment because the indenter is many times smaller than the inclined surface. It can be assumed that contact occurs at the point.

The sample was indented at 10 points at 20-30 μm intervals. The load was increased at a constant rate of 0.05 mN/s until a specified maximum load of 10 mN was reached using a Berkovich indenter and up to 50 mN using a spherical indenter. This choice of load is justified by the different contact areas of the indenters. In this experiment a Berkovich indenter with

![Fig. 1. Topography of the sample coating surface.](image-url)
an apex angle of 65.3° and a radius of curvature of 200 nm was used. The radius of the spherical indenter was 10 μm. The indentation speed was set on the basis that the loading cycle should take 20 seconds.

Using experimental data, NanoTest 600 computer system automatically calculated a number of parameters: maximum penetration depth, plastic deformation, rigidity, modulus, elastic recovery, contact suppleness, plastic work, elastic work and others. For reduced modulus calculations (modulus of elasticity of the sample + indenter system), the Oliver-Farr model is used to describe the load-depth penetration part of the unloading relation. The enclosed software calculates the residual plastic strain based on the Oliver-Farr model $h_c$, rigidity $H$ and a given modulus $E_r$.

Plastic deformation $h_c$ is defined from the equation:

$$h_c = h_{max} - \varepsilon(CP_{max}). \quad (3)$$

here $C$ – is the contact pliability (equivalent to the tangent of the slope of the unloading curve at maximum load). The value of $\varepsilon$ depends on the indenter geometry, for a Berkovich indenter $\varepsilon = 0.75P_{max}$ is maximum load, $h_{max}$ – maximum penetration depth of the indenter.

Dependence function of contact area on penetration depth $A(h_c)$ is determined by calibrating the instrument on a special quartz calibration artefact.

Rigidity $H$ determined on the basis of maximum load $P_{max}$ and the contact area of the indenter with the sample $A$:

$$H = \frac{P_{max}}{A}. \quad (4)$$

To calculate the reduced modulus of elasticity of the sample, the unloading part of the curve is processed according to the relation:

$$C = \frac{dh}{dP} = \frac{\sqrt{\pi}}{2E_r\sqrt{A}} \quad (5)$$

Thus, knowing the value of $E_r$ – reduced modulus, which the instrument determines from relation (5) during the processing of experimental data, by equation (1) we can calculate the modulus of elasticity of the sample or the film on the surface of the sample [1-3]. For the calculations, we need to know the Poisson's ratio of the coating which we take to be 0.33. A change of this value within the range of 0.2-0.4, in principle, insignificantly affects the measurement results.

### 3 Measurement results

When nanoindenting paint coatings using a 10 mN Berkovich indenter, the maximum depth of penetration of the indenter into the coating was 6 μm. Using a 50 mN spherical indenter, maximum penetration was 5 μm. The obtained depth of indentation minimizes the influence of both the sample surface roughness (up to 1 μm) and the more elastic substrate (coating thickness of 200 μm) on the obtained load-deformation relation. Thus, the results of the experiment characterize only the mechanical properties of the coating material, which is also proved by the small scatter of the obtained experimental data (Table 1, Fig. 2).
Table 1. Test results of powder-coated samples (standard deviation in brackets).

<table>
<thead>
<tr>
<th>Indenter</th>
<th>$h_{\text{max}}$, nm</th>
<th>$h_c$, nm</th>
<th>$P_{\text{max}}$, mN</th>
<th>$N$, Mpa</th>
<th>$E_r$, GPa</th>
<th>$E_s$, GPa</th>
<th>$C$, nm/mN</th>
</tr>
</thead>
<tbody>
<tr>
<td>Berkovich</td>
<td>6121 (129)</td>
<td>5802 (124)</td>
<td>10 (0.0)</td>
<td>12.5 (0.5)</td>
<td>0.715 (0.028)</td>
<td>0.64 (1)</td>
<td>42.5 (1)</td>
</tr>
<tr>
<td>Spherical</td>
<td>4839 (90)</td>
<td>4509 (79)</td>
<td>50 (0.0)</td>
<td>227 (2.8)</td>
<td>6.8 (0.27)</td>
<td>6.1 (0.3)</td>
<td>8.8 (0.3)</td>
</tr>
</tbody>
</table>

Fig. 2. Loading diagram (horizontal axis - indenter movement, vertical axis - load). a: without maximum load, Berkovich indenter, (b) with maximum load 100 s, Berkovich indenter, (c) with maximum load (100 s), spherical indenter.

The nanoindentation experiment on the load-strain curve revealed that the strain...
continues to increase as the load decreases. At the same time, the load-deformation curve during unloading shows a bending characteristic of polymeric materials (Fig. 2a), which indicates the viscoelastic properties of polymers. To avoid this effect on the result of determination of the mechanical properties of the coating, it is necessary to keep the sample under maximum load for quite a long period of time. During this time, at a constant load, the strain will reach its maximum value and the relaxation processes in the polymer will occur. The unloading curve will then have a flat shape which is acceptable for the determination of elastic properties according to the Oliver-Farr method.

During the experiment, it was found that when using a Berkowitz indenter, the identifiable properties are extremely low, compared to the known macroscopic characteristics. So the value of the calculated Young's modulus of the coating turns out to be 0.64 GPa, which is five times lower than the known data from the macro-experiment (3 GPa). In the case of a Berkovich indenter, the result for the Young's modulus of coverage is overestimated and amounts to 6.1 GPa, which can be explained by the fact that the Oliver-Farr model no longer works well enough for the chosen test mode and it is probably necessary to use other approaches to identify the Young's modulus of coverage. For example, perhaps a direct numerical simulation of the indentation process, taking into account the non-linear properties of the coating and the contact parameters, could clarify the data obtained. This simulation is planned to be carried out in the course of further research.

4 Conclusions

The results of these tests show the effectiveness of the nanoindentation method for assessing the mechanical properties of paint coatings. However, the data show a significant influence of the indenter shape on the measurement results. The use of a Berkovich shaped indenter seems to be unreasonable since the pointed pyramid tip damages or cuts the coating surface, which leads to underestimated identified elastic properties. The use of a spherical indenter is more justified, as it does not damage the surface of the material. However, the elastic properties found appear to be overestimated when compared with known data from macro-experiments and typical values for the polymer class under investigation. For a more accurate identification of the elastic properties of the coating based on simulation results, it seems necessary to perform a direct numerical simulation of the nanoindentation process.

References


