Application News

No. i280

Dynamic Ultra Micro Hardness Tester

Hardness Measurement of Functional Film

Functional films are films in which new functions/value are added by processes such as surface treatment. Some examples are the application of coating or vapor deposition on a substrate film, multilayer processing to form a laminate-like structure, or printing. Functional films are used in a wide range of fields, including electrical/electronics, automotive, energy production fields, the life sciences, and packaging. Such films can be found in familiar products, including liquid crystal screens of smartphones, tablets, computers, touch panels of restaurant ordering systems and car navigation devices. Even higher added value is expected in functional films in the future.

It is necessary to evaluate the physical properties of functional films such as durability to withstand use and flexibility in forming. Until now, the pencil hardness test has been used to evaluate the susceptibility of functional films to scratching. This article introduces an example of an evaluation of a functional film by measurement of Martens hardness using a Shimadzu DUH™-211 dynamic ultra micro hardness tester.

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Pencil Hardness and Martens Hardness

Table 1 shows an outline of the pencil hardness test procedure provided in JIS K 5600-5-4: 1999 (ISO/DIS 15184: 1996), and Fig. 1 shows a schematic diagram of the test. Pencil hardness is defined as the hardness of the hardest pencil whose lead does not cause a scratch when pushed and dragged on a sample surface for a distance of at least 7 mm, and is denoted by symbols such as H (hard) and HB (hard and black).

Table 1 Outline of Procedure of Pencil Hardness Test According to JIS K 5600-5-4

Outline of procedure
- Expose 5 to 6 mm of the pencil lead, and flatten the tip of the lead.
- Place the pencil lead in contact with the paint film surface at an angle of 45°, and push the lead horizontally for a distance of at least 7 mm at a speed of 0.5 to 1 mm/s under a load of 750 g.
- Visually inspect the paint surface.
- The hardness of the hardness pencil which does not cause a scratch is defined as the pencil hardness.

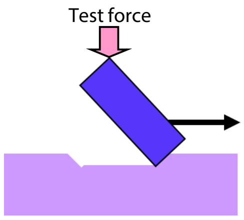

Fig. 1 Schematic Diagram of Pencil Hardness Test

Table 2 Outline of Procedure of Martens Hardness Test According to ISO 14577-1

Outline of procedure
- Using electromagnetic force, press an indenter into the sample.
- The indentation depth of the indenter into the sample is measured automatically.
- Hardness is calculated automatically from the applied test force and the indentation depth.

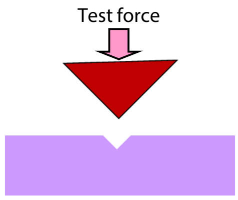

Fig. 2 Schematic Diagram of Martens Hardness Test

Table 2 shows an outline of the Martens hardness test procedure according to ISO 14577-1, and Fig. 2 shows a schematic diagram of the test. Martens hardness test is conducted by pressing a triangular pyramid shaped diamond on the sample surface under a specific load. The hardness is then automatically calculated from the indentation area (automatically calculated from the indentation depth) and the load.

Pencil hardness is widely used in hardness measurements of functional films, but measurement errors due to wear of the pencil and uncertainty due to visual judgment might occur. In this experiment, we conducted a Martens hardness test in order to evaluate the hardness of thin films. One of the advantages of the Martens hardness test compared to conventional methods is the automatic calculation of the indentation area from its depth, allowing to avoid errors and measure hardness on micro-sized regions.

Test Conditions

Table 3 and Table 4 show the sample information and measurement conditions, respectively, and Fig. 3 shows an image of the sample surface. The sample materials were three types of functional films with known pencil hardness, which consisted of a 9 µm hard coat over a PET substrate material. Measurements were conducted after fixing the samples to slide glass with an adhesive.

Table 3 Sample Information

Sample material	: 3 types of functional films
Film thickness	: Hard coat 9 µm, PET 100 µm
Pencil hardness	: ① 3H, ② H, ③ H

Table 4 Measurement Conditions

Maximum test force	: 5 levels (1,000, 500, 100, 20, 4 [mN])
Test speed	: [Maximum test force] / 10 s

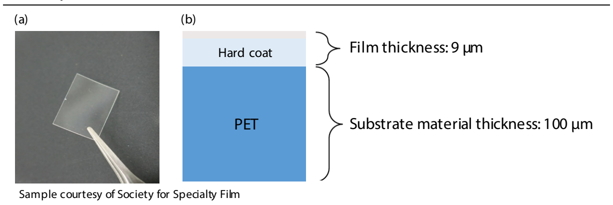

Fig. 3 Image of Sample
(a) Image of Functional Film, (b) Schematic Diagram of Cross Section

Results (1) Results of Martens Hardness Measurement

Table 5 shows the measurement results (average of 7 measurements), Fig. 4 shows the test force-depth curves, and Fig. 5 shows the average Martens hardness. Among the 5 measurement conditions, these figures show the results for the two conditions of maximum test force of 4 mN and 1,000 mN. The indentation depth in the test with the maximum test force of 4 mN was approximately 0.7 µm. Because this value is substantially smaller than the 9 µm film thickness of the hard coat, it can be inferred that the hardness evaluation was limited to the hard coat. In contrast, the indentation depth in the test with the maximum test force of 1,000 mN was approximately 14 µm, indicating that, in addition to penetrating the hard coat, the indenter also penetrated into the PET substrate material in this measurement. In this connection, since JIS K 5600-5-4 describes use of a test force of 750 gf (≈7.35 N) in the pencil hardness test, measurement that penetrates to the PET substrate material is assumed. The order of hardness under the respective conditions is as follows:

Maximum test force 4 mN : ① 3H > ② H > ③ H

Maximum test force 1,000 mN : ① 3H > ② H ≥ ③ H

With the test force of 4 mN, a difference in hardness of ② and ③ could be seen. Thus, the Martens hardness test revealed a hardness difference that could not be detected in the pencil hardness test.

Table 5 Measurement Results

Sample		①	②	③
Pencil hardness		3H	H	H
HMT115(4) *	[N/mm²]	251	207	172
HMT115(1,000) *	[N/mm²]	192	179	176
hmax(4) *	[µm]	0.62	0.69	0.78
hmax(1,000) *	[µm]	13.9	14.4	14.6

HMT115 : Martens hardness [N/mm²]
hmax : Indentation depth [µm]
* (4) and (1,000) indicate the measurements with the maximum test forces of 4 mN and 1,000 mN, respectively.

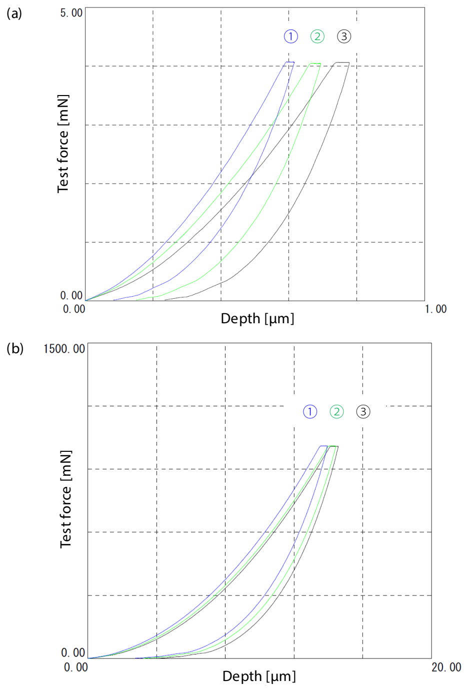

Fig. 4 Test Force-Depth Curves (Maximum Test Force: (a) 4 mN, (b) 1,000 mN)

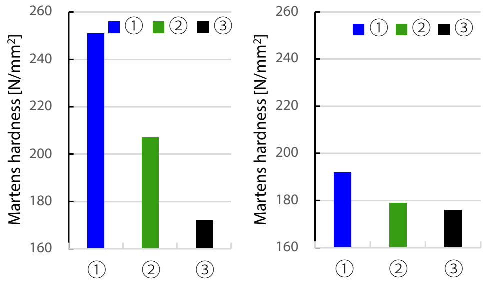

Fig. 5 Average Martens Hardness (Maximum Test Force: (a) 4 mN, (b) 1,000 mN)

Results (2) Effect of Substrate Material

Fig. 6 shows the relationship of the Martens hardness and indentation ratio, plotted for indentation ratio at test forces of 1,000, 500, 100, 20, and 4 [mN]. (Here, the "indentation ratio" means the value obtained by dividing the indentation depth by the 9 µm film thickness of the hard coat.) In the small indentation ratio region, the respective hardness values are relatively uniform, and if the indentation ratio exceeds 0.2, hardness shows a tendency to gradually approach the hardness value at the indentation ratio of 1.5. From this, it can be inferred that the results show only the hardness of the hard coat up to the indentation ratio of 0.2, but are greatly affected by the hardness of the substrate material as the indentation ratio increases beyond 0.2. It may be noted that ISO 14577-1 describes testing at an indentation ratio of no more than 0.1 in order to avoid the effect of the substrate material hardness.

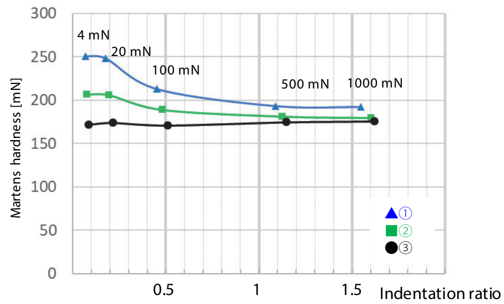

Fig. 6 Martens Hardness-Indentation Ratio Curves

Conclusion

The pencil hardness test is used in evaluations of functional films because of its simplicity. However, with increasing diversification of the applications of functional films, the difficulty of quantitative evaluation has become a concern, as judgments depend on visual inspection by the test personnel and the pencils used in the test are affected by wear. Hardness measurements by the DUH-211 ultra micro hardness tester solve these issues of human error and the coarseness of measurements, and thus enable more quantitative evaluation of hardness. The samples (①, ②, ③) used in this experiment were prepared so as to have different hardness, and differences in the samples in the assumed order of hardness were confirmed by an evaluation of Martens hardness. Although differences in the hardness of the samples ①, ②, and ③ could not be distinguished by the conventional pencil hardness test, in this experiment, quantitative measurement of the differences in sample hardness was possible by using the DUH-211.

The DUH-211 can also calculate various physical properties including the elastic modulus, creep, and indentation power in addition to Martens hardness. Thus, this testing system enables acquisition of a large amount of information by a single technique for evaluation of the physical properties of films.

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