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Atomic force microscopy in evaluation of wood coating systems

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Abstract: *Atomic force microscopy in evaluation of wood coating systems.* An atomic force microscope was used for evaluation of properties of wood – coating systems and their interactions. The systems investigated were two: water based and polyurethane based. The following parameters were determined for cured coatings on glass and on wood substrates: modulus of elasticity, adhesion forces, surface deformation and surface roughness. AFM has been found as a useful tool for analyzing material properties at micro- and nano-levels. This technique was effective in detecting the heterogeneities in cured coatings and curing defects. It also confirmed interactions between the wood substrate and coating.

Keywords: AFM, modulus, adhesion force, roughness, nano-level

INTRODUCTION

Atomic force microscopy (AFM) is an effective tool for measuring force interactions between the microscope tip and material surface at micro- or nano-levels. GARDNER *et al.* (2013) presents a review of several AFM surface characteristics of polymer nanocomposites. These authors report that the AFM technique used on solid materials can determine: surface energy, adhesion (pull-off) force, surface roughness, morphology of two interacting surfaces, and elastic modulus of surface. This technique can also detect dependence of adhesion force on various factors (the tip end diameter, surface roughness, relative air humidity, surface tension, surface energy, etc.).

The AFM uses a tip oscillating over a surface affected by attractive and repulsive forces of the surface. The retraction curve expressing this dependence (Fig. 1) can serve for deriving several characteristics: reduced modulus of elasticity (based on a contact model), force of adhesion, dissipative energy and deformation of the surface due to constant force loading.

For a spherical tip end, the modulus of the surface can be fitted by Hertz model (HERTZ 1881). The adhesion force between the tip and the surface modifies that model and gives the following retraction curve used for determination of reduced modulus E* in Derjaguin-Muller-Toporovom (DMT) model (DERJAGUIN *et al.* 1975):

$$F - F_{adh} = {}^{3}/_{4} E^{*} \sqrt{R(d - d_0)^3} \tag{1}$$

where $F - F_{adh}$ is the difference between tip force and adhesion force, R is radius of the tip end and $d - d_0$ is the depth of deformation on the surface (Fig. 1).

The reduced modulus is a function of modulus E and Poisson ratio ν of the surface and the indenter (primed):

$$\frac{1}{E^{*}} = \frac{1 - \nu^2}{E} - \frac{1 - \nu'^2}{E'} \tag{2}$$

If the indenter is rigid, the reduced modulus is a good approximation of the specimen modulus (FISCHER and CRIPPS 2011).

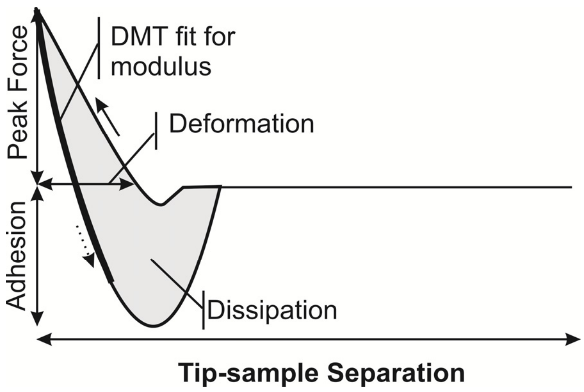


Fig. 1 Tip force vs. tip-sample separation

Wood-coating systems depend on a range of aspects needed to consider an effective system design: chemistry and morphology of the coating, and chemistry and morphology of the substrate as well as the interactions of the coating and substrate during coating process and curing (KÚDELA and LIPTÁKOVÁ 2006). The proper design of a coating system should address these properties at various levels. Atomic force microscopy can be one of the promising tools for obtaining some characteristics of coating systems at a very small scale.

The subject of this paper is atomic force microscopy used in evaluation of surface properties of wood and wood coating systems at micro- and nano-levels.

MATERIAL AND METHODS

The analysis was carried out with two coating systems polyurethane (PUR) and water-based (WB). The systems were applied on radial face of spruce wood. The wood surface was firstly sanded by a 180 grid sand paper before the coating, then the first coating layer was sanded by a 240 grid. Finally, there were applied three additional layers of the coating, without sanding. The average thickness of the PUR coating and WB systems was 152 μm and 98 μm, respectively.

These coating systems were also spread on a glassy substrate – for preparation of free films. These were carefully sliced off from the substrate after 4 days of curing. AFM was used for evaluation of the coating system properties. Prior to the measurement, a tip TAP 150 was calibrated. The deflection sensitivity of the tip was measured on hard silica (E = 70 GPa). The toughness of the cantilever was determined by Sader's method (SADER *et al.* 1999). The tip radius was assessed indirectly with a reference material of known properties (polystyrene. E = 2.7GPa). The maximum loading force was set 9 nN.

With Nanoscope AFM from Broker operating in PeakForce QMN, we obtained the following characteristics: reduced modulus of elasticity, force of adhesion and deformation of surface under the tip. The measured data were filtered based on a slope of the local surface and excluded from further consideration if the local slope was more than 30°.

The first measurements were performed on a microtomed cross section of the coated wood sample. We measured properties of each coating layer (1–4) and the wood cell walls under the first coating layer (5–6) (Fig. 2). At each position, one scan of $5 \times 1.25\ \mu m^2$ was taken.

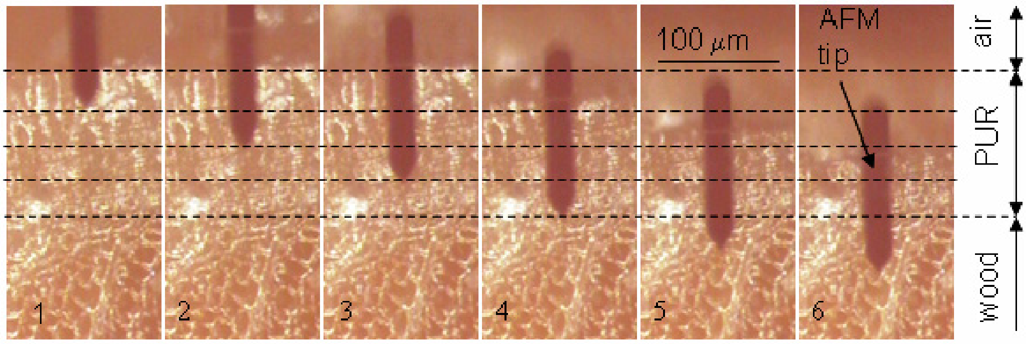


Fig. 2 Positions of the measuring AFM tip at the wood – PUR coating interface. The position 1 is within the 4th layer of the coating, position 4 is within the 1st layer of the coating, and positions 5 and 6 are the positions within the wood cell wall.

The second set of measurements consisted of tests performed on coating surfaces. An area of 10 × 10 μm was randomly selected on the surface. Three types of surfaces were tested: coated surface on wood substrate, top side and bottom side of free film. Topography, modulus of elasticity, adhesion force, surface deformation due to indentation and surface roughness were evaluated for each selected surface.

RESULTS AND DISCUSSION

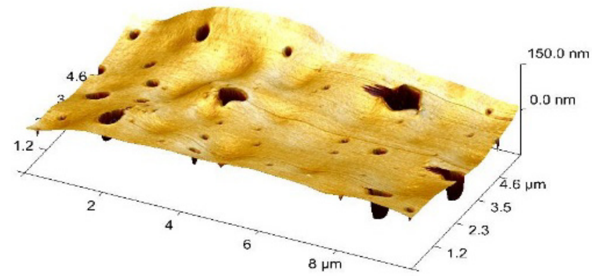
First, we tested the properties of the wood-coating system interface. The average values of each scan and their variations are in Table 1. The interaction of substrate occurred mainly in the second layer expressing the highest values of modulus of elasticity and of force of adhesion. The highest variability also implies the interaction of the first sanded layer with the second one.

Tab. 1 Experimental results of the wood-PUR coating system at various positions of the interface.

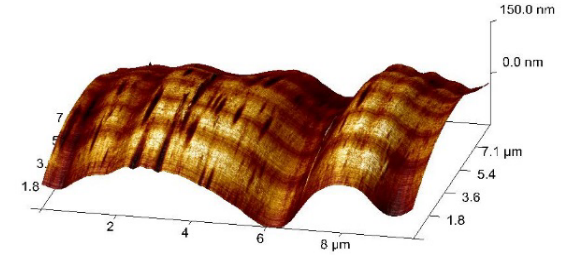
	Modulus of elasticity		**Adhesion force**		**Deformation**	
Position	$\overline{E}$ **[MPa]**	**v [%]**	$\overline{Fa}$ **[nN]**	**v [%]**	$\overline{\Delta h}$ **[nm]**	**v [%]**
4th layer	2161	18.8	14.66	6.9	2.91	14.5
3rd layer	1632	17.9	12.94	9.7	1.92	28.3
2nd layer	5318	35.7	27.16	8.7	1.37	95.4
1st layer	2849	31.5	15.49	8.3	1.75	15.7
cell wall pos.5	3877	7.4	10.82	3.9	0.22	32.3
cell wall pos.6	2307	66.5	15.87	5.5	3.79	58.4

The second set of experiments was performed on the outer surfaces of coating systems. The topography of PUR and WB coatings detected differences between the two coating systems and an effect of the substrate (Fig. 3). The PUR coating expressed more variation in topography.

a)



b)



c)

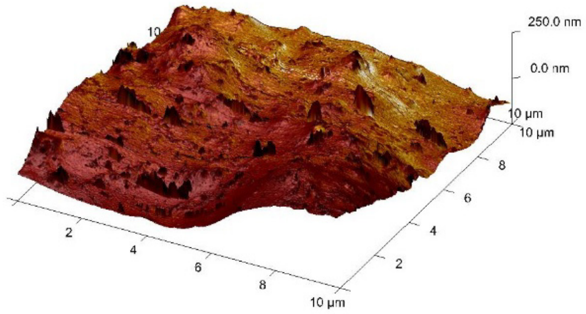
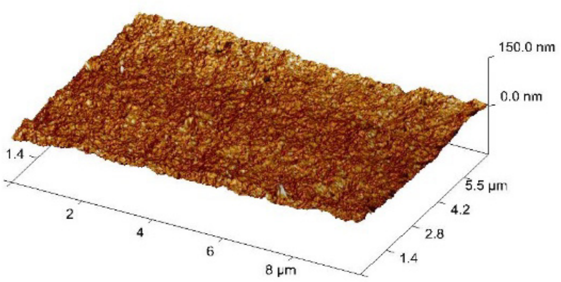


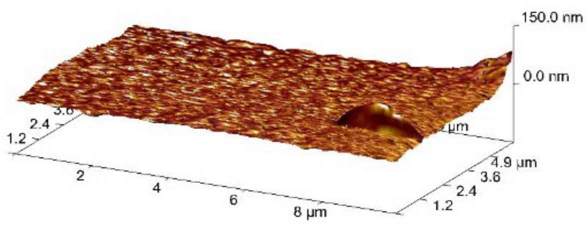
Fig. 3 Topography of the PUR coating on the glass substrate (a – PUR bottom, b – PUR top and the wood substrate (c – PUR top).
Dark colored areas exhibit lower modulus of elasticity.

Even between the top and bottom surfaces, variation is visible. The AFM scan of the bottom part of the surface showed micro bubble openings, approximately from 10 to 500 nm in diameter (Fig. 3a). The reduced modulus measured on the top surface of the free film revealed heterogeneities in the coating. The eye-shaped objects turned out to have lower modulus than their surrounding areas (Fig. 3b). The PUR surface on the wood substrate confirmed higher roughness than on the glass substrate (Fig. 3c). Unlike the PUR coatings, the WB coatings on glass were smoother, without defects (Fig. 4a, b, c).

a)



b)



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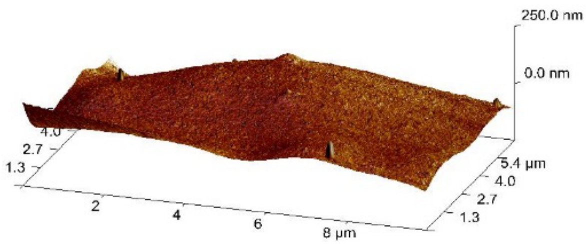

Fig. 4 Topography of the WB coating on the glass substrate (a – WB bottom, b – WB top) and the wood substrate (c – WB top). Dark colored areas exhibit lower modulus of elasticity.

These surface characteristics confirmed higher modulus and lower force of adhesion of coatings in wood surface (Table 2). The deformation of the surface varied so much that no conclusion was possible to draw. According to the expectations, the surface roughness of coating was higher for the wood substrate than for the glass substrate. This was true for both polyurethane and water-based coating systems.

Tab. 2 Characteristics of PUR and WB surfaces on wood and glass substrates.

	Modulus of elasticity		**Adhesion force**		**Deformation**		**Roughness**
	$\overline{E}$ **[MPa]**	**v [%]**	$\overline{Fa}$ **[nN]**	**v [%]**	$\overline{\Delta h}$ **[nm]**	**v [%]**	$\overline{Ra}$ **[nm]**
Sample							
PUR-1	2609	20.5	5.78	4.0	0.26	110.9	44.8
PUR-2	1938	38.0	8.91	24.6	3.94	18.5	24.0
PUR-bott	1493	3.5	9.09	2.5	1.80	28.4	11.9
PUR-top	1450	3.5	8.87	7.2	2.29	49.7	15.2
WB-1	1955	9.6	3.98	10.1	1.02	34.8	101.0
WB-2	1984	4.3	6.82	9.8	0.22	23.0	39.3
WB-bott	1378	7.2	8.40	2.4	4.33	17.7	5.2
WB-top	1292	7.8	5.24	10.6	1.89	7.9	1.8

The surface roughness affecting the adhesion force was proved, which is in accord with LAITINEN *et al.* (2013). The adhesion force value was the lowest at the maximum roughness for both coating systems.

CONCLUSION

AFM is a useful tool for analyzing material properties at micro- and nano-level. Our research results can be summarized in the following: There occurred an interaction between the coating and substrate, especially wood substrate. The modulus of elasticity of the coating depended on the substrate, with higher values observed for the coating on the wood substrate. The force of adhesion was also affected by the substrate. The wood substrate had a tendency to increase the roughness of the coating comparing to the free film. The AFM technique can be used for detecting the heterogeneity of cured coatings as well as curing defects at micro level.

LITERATURE

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Streszczenie: *Mikroskopia sił atomowych w ocenie systemów powłokowych do drewna.* Do oceny własności drewna, powłok, oraz zależności między nimi użyto mikroskopu sił atomowych. Badano dwa systemy lakiernicze, jeden na bazie wodnej a drugi na poliuretanowej. Na utwardzonych powłokach badano moduł sprężystości, siłę adhezji, deformację powierzchni oraz chropowatość powierzchni. Mikroskopia okazała się przydatna w analizie własności materiału na poziomach mikro i nanometrycznych. Technika pomiarowa wykazywała zmienności w utwardzonych powłokach, oraz same wady utwardzania, wykazywała także zależności między drewnem oraz powłokami.

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