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## A STUDY OF PROPERTIES OF POSS-MODIFIED VARNISH COATINGS UV-CURED ON A WOOD SURFACE

*Research was carried out in a new topic area related to the quality of lacquer finishes on wood surfaces, such as furniture or floor elements. Selected results are presented relating to basic mechanical properties of composite varnish coatings modified with a selected commercial POSS compound, photo-cured on the surface of a chosen wood species. The test results obtained for two groups of varnish coatings differing in the varnish binder used (oligoether or oligoester) pointed to various effects of POSS modification of the varnish compositions and UV-cured coatings. These effects were dependent on the functional property considered as well as the content of POSS nanofiller in the varnish composition. In general, the presence of selected POSS molecules in the UV coating structure improved its abrasion and linear scratching resistance, but did not improve – or even slightly reduced – the adhesion of the coating to the wood surface.*

**Keywords:** POSS nanofiller, varnish composition, polymer nanocomposite, composite coating, reference coating, coating properties

### Introduction

Over the last decade or more, interest in the application potential of organo-inorganic nanohybrid polymers has significantly increased, particularly among research centers in the United States, Europe and China. Nanohybrid polymers belong to the group known as molecular composites, which means that their heterogeneity is revealed only in the nanodimensional range. The molecular heterogeneity of nanohybrid polymers is expressed in the fact that their macromolecules are composed of both organic fragments (carbon-carbon, carbon-oxygen chemical bonds) and inorganic ones (e.g. silicon-oxygen or metal-oxygen chemical bonds). The result of suitable curing of the polymers themselves or their precursors is composite materials with a mixed structure that uniquely combine physical properties which do not occur simultaneously for polymeric networks of exclusively organic construction. The presence in the hybrid polymer network of a composite, e.g. specific inorganic structures, gives

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it characteristic properties, as for glasses or ceramics, such as increased hardness and resistance to scratching and chemical agents [Bizet et al. 2006]. At the same time, due to the presence in the polymer network of the composite of organic structural fragments, the cured polymer composite can combine the aforementioned properties with favorable elasticity or adhesion to the substrate.

Mixed organic-inorganic structures of polymer networks are characteristic of the so-called functional coatings, which are a new type of protective coatings [Kurek 2004; Hu and Shea 2011; Constantin et al. 2013]. One of the methods for obtaining mixed-structured nanocomposites is to incorporate inorganic structural fragments into chains of organic oligomers. This can be achieved, *inter alia*, using polyhedral oligomeric silsesquioxanes, i.e. POSS compounds, which are substances of mixed organic-inorganic chemical structure [Guirong 2007; Janowski and Pielichowski 2008; Marciniak 2010; Ayandele et al. 2012]. POSS compounds have the general formula  $(RSiO_{1.5})_n$ , in which R may be a hydrogen atom or an organic substituent, and  $n$  is the number of silsesquioxane structural units from which the molecule of the POSS compound is built. Usually this number is 8, but less often it may be 10 or 12.

POSS molecules are symmetrical chemical objects with well-defined shapes and with sizes in the range 1-3 nm. Because of these molecular sizes, POSS compounds are among the reactive spherical nanofillers that can be incorporated into an organic polymer matrix. The first successful syntheses of compounds from the POSS group were carried out and described by Scott [1946]. Research on this group of compounds was renewed in the 1990s, particularly in the United States by the Feher group at California-Irvine University and the Lichtenhan group at the Air Force Research Laboratory. The first of these research groups made a significant contribution to the development of multiple methods of synthesis and chemical modification of POSS compounds, while the second group made pioneering achievements related to the use of POSS compounds in the synthesis of new composite polymeric materials [Lichtenhan et al. 1993; Lichtenhan et al. 1995; Haddad and Lichtenhan 1996; Lee and Lichtenhan 1999]. Suitably functionalized molecules of POSS compounds are able to react with selected organic precursors [Kopesky et al. 2006; Amerio et al. 2008; Cordes et al. 2010; Andrzejewska et al. 2011]. Owing to this property, nanohybrid polymers containing POSS structures have been obtained, which are included in the group of polymer nanocomposites [Liu and Zheng 2005; Janowski and Pielichowski 2008; Wang et al. 2011; Pilch-Pitera 2013].

POSS-containing polymer nanocomposites are new-generation materials that represent an alternative in various fields to the use of polymeric materials with homogeneous organic structure only [Philips et al. 2004; Pielichowski et al. 2006]. The results of a number of studies show that polymer nanocomposites made with POSS molecules containing different (reactive and chemically passive) functional groups in their structure generally have superior some mechanical properties, a higher glass transition temperature ( $T_g$ ), and greater

hydrophobicity and thermal stability [Dutkiewicz et al. 2014] in comparison to corresponding organic polymers not containing those molecules [Li et al. 2001; Liu and Zheng 2005; Kopesky et al. 2006; Qin et al. 2010; Wojtas et al. 2010; Andrzejewska et al. 2011; Prządka et al. 2016].

The aim of this study was to compare the functional properties of varnish coatings UV-cured on a wood surface as organo-inorganic polymer composites, with reference coatings made exclusively with the use of appropriate organic precursors, depending on the total content of the selected POSS nanofiller and the type of organic precursors used in the varnish composition.

## Materials and methods

The wood substrate used for all varnish coatings was MDF board covered on both sides with beech veneer (*Fagus sylvatica* L.), of quality class A. Beech veneer of 0.6 mm thickness was used as a direct substrate material. MDF boards with dimensions (1050 × 650 × 16) mm were covered with the beech veneer by attaching the veneer strips in a direction parallel to the long side of the panel. Before the coating process, the veneer surface was sanded using a Homag sanding machine, where pre-sanding was performed with P150 abrasive paper and final sanding with P180 abrasive paper.

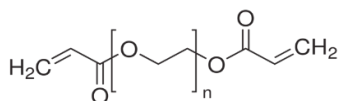
Transparent UV-curable varnishes prepared in the laboratory were applied. Two groups of varnish compositions were prepared, differing in the type of film-forming oligomer used (oligoetherol acrylated as binder – formula A; or oligoesterol acrylated as binder – product sample from Sartomer- -Arkema; Table 1) and the types of applied acrylic monomers, which included tetra(ethylene glycol) diacrylate (formula B), as well as tri( $\alpha$ -propylene glycol) diacrylate (formula C1) and tri( $\beta$ -propylene glycol) diacrylate (formula C2) used as a commercial mixture of isomers. The same POSS nanofiller purchased from Hybrid Plastics Inc. as mixture of POSS compounds for  $n = 8, 10$  and  $12$  (formula D for  $n = 8$ ), was used in the varnish compositions of both groups. Within each of these groups, one varnish composition not containing POSS molecules (reference composition) and two compositions with 4% and 8% m/m contents of POSS modifier were prepared (table 1). In all prepared varnish compositions (1-6), phenylbis(2,4,6-trimethylbenzoyl) phosphine oxide (formula E) was used as the UV initiator of free-radical polymerization.

**Table 1. Basic characteristics of UV-curable varnish compositions used in the study**

Code of varnish composition	Ingredients of varnish composition	Content of ingredients [% m/m]	Dynamic viscosity coefficient <sup>1)</sup> [mPa·s] ( <i>Temperature of measurement</i> )
<i>Varnish compositions – Group I</i>			
1	Poly(ethylene glycol) diacrylate (PEGDA)	100.0	59 (23°C)
	Tetra(ethylene glycol) diacrylate (TTEGDA)		
	Phenylbis (2,4,6-trimethylbenzoyl) phosphine oxide (BAPO)		
2	Poly(ethylene glycol) diacrylate (PEGDA)	96.0	62 (23°C)
	Tetra(ethylene glycol) diacrylate (TTEGDA)		
	Phenylbis (2,4,6-trimethylbenzoyl) phosphine oxide (BAPO)		
3	Nanofiller Acrylo POSS <sup>®</sup> Cage Mixture (Ac-POSS)	4.0	75 (23°C)
	Poly(ethylene glycol) diacrylate (PEGDA)	92.0	
	Tetra(ethylene glycol) diacrylate (TTEGDA)		
	Phenylbis (2,4,6-trimethylbenzoyl) phosphine oxide (BAPO)		
	Nanofiller Acrylo POSS <sup>®</sup> Cage Mixture (Ac-POSS)	8.0	
<i>Varnish compositions – Group II</i>			
4	Tetraacrylate of oligoesterol (PETTA) <sup>2)</sup>	100.0	111 (23°C)
	Tri( $\alpha$ -propylene glycol) diacrylate (T $\alpha$ -PGDA)		
	Tri( $\beta$ -propylene glycol) diacrylate (T $\beta$ -PGDA)		
	Phenylbis (2,4,6-trimethylbenzoyl) phosphine oxide (BAPO)		
5	Tetraacrylate of oligoesterol (PETTA) <sup>2)</sup>	96.0	103 (23°C)
	Tri( $\alpha$ -propylene glycol) diacrylate (T $\alpha$ -PGDA)		
	Tri( $\beta$ -propylene glycol) diacrylate (T $\beta$ -PGDA)		
	Phenylbis (2,4,6-trimethylbenzoyl) phosphine oxide (BAPO)		
	Nanofiller Acrylo POSS <sup>®</sup> Cage Mixture (Ac-POSS)	4.0	
6	Tetraacrylate of oligoesterol (PETTA) <sup>2)</sup>	92.0	158 (23°C)
	Tri( $\alpha$ -propylene glycol) diacrylate (T $\alpha$ -PGDA)		
	Tri( $\beta$ -propylene glycol) diacrylate (T $\beta$ -PGDA)		
	Phenylbis (2,4,6-trimethylbenzoyl) phosphine oxide (BAPO)		
	Nanofiller Acrylo POSS <sup>®</sup> Cage Mixture (Ac-POSS)	8.0	

<sup>1)</sup> The given values of the dynamic viscosity coefficient were measured at an L2 spindle rotation speed of 200 rpm ( RC02 rotational viscometer was used as the measuring device).

<sup>2)</sup> Tetraacrylate of oligoesterol based on adipic acid and 1,2,3-propanetriol structures (Sartomer-Arkema product supplied free of charge in the form of product samples for research).

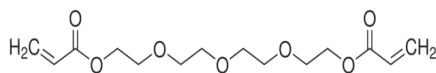


$$n = 9 \div 11$$

(A)

Poly(ethylene glycol) diacrylate (PEGDA)  
(Sigma-Aldrich)

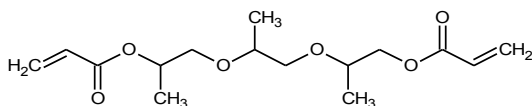
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(B)

Tetra(ethylene glycol) diacrylate (TTEGDA)  
(Sigma-Aldrich)

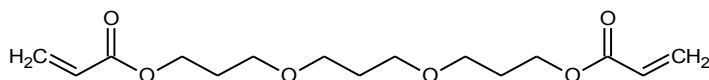
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(C1)

Tri( $\alpha$ -propylene glycol) diacrylate ( $T\alpha$ -PGDA)  
(Sigma-Aldrich)

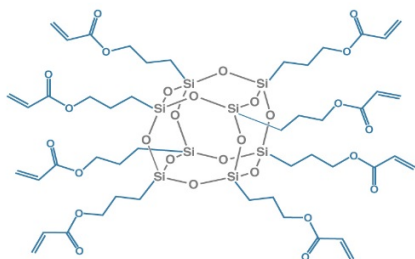
+



(C2)

Tri( $\beta$ -propylene glycol) diacrylate ( $T\beta$ -PGDA)  
(Sigma-Aldrich)

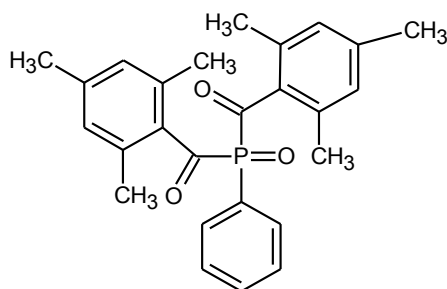
Commercial mixture of isomers



(D)

Octakis(3-acryloyloxypropyl) POSS  
(Ac-POSS)

(Hybrid Plastics Inc.)



(E)

Phenylbis(2,4,6-trimethylbenzoyl)  
phosphine oxide (BAPO)

(Sigma-Aldrich)

Experimental varnish coatings for further tests were formed one-sidedly on the surfaces of the beech-veneered MDF elements, using the previously prepared varnish compositions. Individual varnish compositions were applied to the surfaces using Erichsen spiral applicators (80 and 60  $\mu\text{m}$ ). Compositions 1-3 were applied in three layers, and compositions 4-6 in two layers. Curing of the

layers of individual varnish composition applied to the veneer surface was carried out in an industrial UV tunnel at the Bürkle Process Technologies coating segment in the Sherwin-Williams Technical Center, Poland. UV-curing was performed using gallium (120 W/cm) and mercury (120 W/cm) radiators in one section (three curing cycles for each polyether-based coating layer, and four curing cycles for each polyester-based coating layer). The tested varnish coatings applied to beech-veneered MDF boards were labeled with the numerical codes 1-6, corresponding to the codes of the varnish compositions from which the coatings were made.

Conditioning of the varnish coatings produced on the surface of beech-veneered MDF elements was carried out in ITD laboratory under standard conditions ( $23 \pm 2^\circ\text{C}$ ,  $50 \pm 5\%$  RH) for a period of 7 days. The tests of physical and functional properties described below were carried out in the laboratory under the conditions  $23 \pm 2^\circ\text{C}$  and  $50 \pm 5\%$  RH, according to the requirements of the methodological standards cited.

The thickness of all experimental varnish coatings was measured using the acoustic method according to [PN-EN ISO 2808: 2008 p. 5.8]. Only one test sample, with dimensions (320 × 220) mm, was used for thickness measurement of a given type of varnish coating. The final result of the measurements made for a given varnish coating was the average value of 10 unit thickness measurements made in randomly chosen test areas on the coating surface. A QuintSonic PRO ultrasonic thickness gauge (manufactured by ElektroPhysik) was used to measure the thickness of each varnish coating. The gloss of the varnish coatings was measured using the method described in [PN-EN 13722: 2006]. Only one test sample, with dimensions (320 × 220) mm, was used for gloss measurements of a given type of coating. The gloss measurements of the tested coatings on beech-veneered MDF boards were made at a light incidence angle of  $60^\circ$  along the wood fiber direction, in five different test areas on the sample. The final result of measurements for the coating variant was the average value. The measurements were performed for each type of varnish coating using a REFO 3 multi-angle glossmeter (Dr. Lange).

The resistance of the coatings on beech-veneered MDF boards to linear scratching was tested using method A described in [PN-EN 15186: 2012] [Banecki 2011]. According to this method, three test samples with dimensions (100 × 100) mm were used for testing of a given type of varnish coating. The following equipment was applied in the tests of linear scratch resistance:

- a scratch hardness tester model 239/II (Erichsen GmbH & Co KG), equipped with an electric drive, ensuring linear movement of the scratching blade at a speed of  $20 \pm 10$  mm/s with loading in the range 1–20 N;
- a workshop measuring microscope (PZO) with 20-fold magnification, enabling the measurement of scratch width with uncertainty  $\pm 0.01$  mm;
- a conical scratching blade made of diamond, with radius of the spherical part  $R = 0.30 \pm 0.01$  mm and opening angle of the cone  $\alpha = 60 \pm 1^\circ$ .

The impact resistance of varnish coatings on beech-veneered MDF board was tested using the method described in [PN-ISO 4211-4: 1999]. According to that standard, only one test sample, with dimensions (210 × 290) mm, was tested for a given type of varnish coating. The degree of damage to the varnish coating was visually evaluated for five test areas corresponding to one impact energy value and distributed according to the standard over the surface of the coating. As a complementary evaluation parameter, the average value of diameters of the residual indentations, formed in the same five test areas after striking of the tested coating using the specified energy, was applied. In this test, six impact energy values (ranging from 49.3 to 1972.7 mJ) were used, corresponding to the free falls of a normalized weight from six different heights between 10 and 400 mm. A device constructed according to the description given in the standard, with a steel ball of 14 mm diameter and a hardness of 60-66 HRC, was used to perform the impact resistance tests. A measuring magnifier of ±0.05 mm uncertainty was used to take measurements of the diameters of residual indentations formed in the tested varnish coatings.

The abrasion resistance of the experimental varnish coatings was tested using the method given in [PN-EN 15185: 2011]. Three test samples with dimensions (100 × 100) mm were used for testing of a given type of varnish coating. In addition, as a measure of the abrasion resistance of each tested coating, the value of the abrasion resistance index defined by equation (1) was adopted for comparative testing purposes:

$$W_{ABR} = \frac{IP}{TH_{av}} \quad (1)$$

where:  $W_{ABR}$  is the abrasion resistance index (rev./μm);  
 $IP$  is the average value of the initial wear point determined using the corrected IP values calculated for three test samples, rounded to the nearest 10 revolutions (rev.);  
 $TH_{av}$  is the average thickness of the varnish coating (μm).

The above-defined index was used to compare objectively the abrasion resistance of individual experimental coatings on beech veneer surfaces differing in thickness. During the study, the initial wear point ( $IP$ ) was considered to correspond to the first clearly recognizable wear through the tested varnish coat to the veneer surface in four quadrants of the sample area. To perform the tests of abrasion resistance of the varnish coatings, the following apparatus and materials were used:

- Taber Abraser model 5151 (Taber Industries Co.);
- abrasive paper (Taber S-42), zinc plates (Taber S-34), Taber CS-0 disks;
- red waterproof ink, to identify the initial wear point ( $IP$ ) of the varnish coating on beech-veneered MDF board; excess ink was removed from non-abraded coating using 96% ethanol.

Adhesion of the prepared varnish coatings to the substrate (beech veneer on MDF board) was tested and evaluated using the method described in [PN-EN ISO 4624: 2004]. Adhesion of the varnish coating was assessed by determining the strength of the coating against peeling off the wood surface and estimating the percentage shares of the types of tearing of the sample in the strength test. The tests were carried out for six individual samples of each type of varnish coating on beech-veneered MDF board. The tests and assessment were performed using:

- steel measuring stamps with a face area of 1000 mm<sup>2</sup>;
- fast-drying glue based on cyanoacrylates;
- a round cutter adapted to the size of the measuring stamp;
- a measuring magnifier of  $\pm 0.05$  mm uncertainty.

Measurements of the tearing force were carried out in ITD strength laboratory using an Instron machine (model 33R4204), equipped with a measuring head for loads up to 50 kN, with the feed speed of the measuring head set at 8 mm/min.

## Results and discussion

### Physical properties of coatings

Table 2 gives descriptions of the individual varnish coatings produced for testing purposes, i.e. composite coatings containing Ac-POSS molecules and reference coatings which did not contain Ac-POSS molecules. The table also contains selected physical properties of the coatings.

### Functional mechanical resistance of POSS-modified composite coatings compared with reference organic coatings on a wood surface

Figure 1 illustrates the results of linear scratch resistance tests of individual varnish coatings on a wood surface. The results indicate that the addition of 4% or 8% m/m Ac-POSS (in composite coatings 2 and 3 respectively) resulted in a significant increase in the resistance of those coatings to linear scratching (by approx. 17%) compared with the reference organic coating (no. 1). At the same time, in the case of composite coatings 5 and 6, which were based on polyester binder and contained structures of acrylic monomers (T $\alpha$ -PGDA and T $\beta$ -PGDA), neither the lower (4% m/m) nor the higher content (8% m/m) of Ac-POSS in the UV-cured coating material caused any change in the coating's resistance to scratching compared with the reference organic coating (no. 4).

The results show that varnish coatings based on polyether binder with a content of tetraethylene glycol diacrylate (TTEGDA) are more resistant to scratching than varnish coatings based on polyester binder with a mixture of acrylic monomers (T $\alpha$ -PGDA + T $\beta$ -PGDA). This may suggest an increase in the

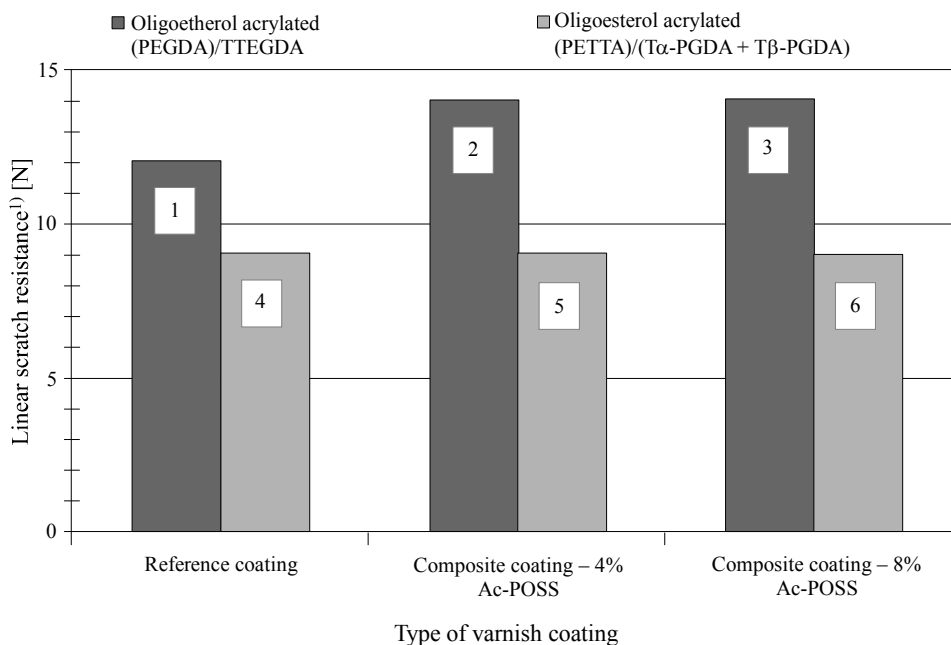


**Table 2. Characteristics of the layer structure and selected physical properties of coatings made of varnish compositions applied and UV-cured on the surface of beech-veneered MDF elements**

Code of varnish coating	Type of organic binder/ acrylic monomer in varnish composition	General description of varnish coating	Coating thickness <sup>1)</sup>		Coating gloss <sup>2)</sup>	
			Average value [μm]	v [%]	Average value	v
			[%]		[%]	
1		3-layer varnish coating of organic structure only (reference coating)	188	7.4	80.5	1.5
2	Oligoetherol acrylated (PEGDA) /TTEGDA	3-layer varnish coating – polymer composite of organic-inorganic structure (4% m/m Ac-POSS)	189	9.5	85.1	0.7
3		3-layer varnish coating – polymer composite of organic-inorganic structure (8% m/m Ac-POSS)	196	4.1	83.7	2.4
4		2-layer varnish coating of organic structure only (reference coating)	81	3.7	85.0	1.2
5	Oligoesterol acrylated (PETTA) / (Tα-PGDA+Tβ-PGDA	2-layer varnish coating – polymer composite of organic-inorganic structure (4% m/m Ac-POSS)	77	15.6	86.1	0.2
6		2-layer varnish coating – polymer composite of organic-inorganic structure (8% m/m Ac-POSS)	81	7.4	85.8	0.6

<sup>1)</sup> Values calculated from 10 thickness measurements performed for each type of varnish coating.

<sup>2)</sup> Values calculated from 5 measurements of coating gloss performed along the grain at a light incidence angle of 60°. v – variability coefficient.



**Fig. 1. Linear scratch resistance of varnish coatings coded 1-6, UV-cured on surface of beech-veneered MDF boards, depending on Ac-POSS content and type of organic precursors in varnish composition**

<sup>1)</sup> The value presented on the chart is the average of the values of intermediate scores determined for three individual samples of each type of varnish coating, rounded to the nearest whole number acc. to PN-EN 15186:2012

hardness of composite coatings 2 and 3 compared with the reference coating (no. 1), while the elasticity of those coatings remained similar to that of the reference coating, despite their modification with a 4% or 8% addition of Ac-POSS. In the case of composite polyester coatings 5 and 6, the results of the tests and the assessment of scratching traces showed that the Ac-POSS molecules in those coatings produced no improvement in their resistance relative to the reference coating (no. 4). The more irregular edges of scratches observed for coatings 5 and 6 during microscope measurements of scratches' widths indicate that these coatings were more prone to crumble as a result of transverse stress caused by the diamond scratching blade under its suitable loading.

Table 3 presents an evaluation of the degree of damage to the tested varnish coatings caused by impacts using defined energy values in the range 49.3-1972.7 mJ. Analysis of the final assessments indicates that the varnish coatings based on polyether or polyester structure demonstrated different reactions to medium and high values of impact energy (246.6-1972.7 mJ). It was also found that an increase in the content of Ac-POSS nanofiller in the composite coatings

(no. 2 → 3 and no. 5 → 6) caused changes in those coatings' susceptibility to cracking, which was different from that observed for the relevant reference organic coatings (nos. 1 and 4). Coating 2, based on polyether binder with a 4% m/m content of Ac-POSS, demonstrated increased susceptibility to minor and medium cracks compared with the reference organic coating (no. 1). This was accompanied by an increase in the diameter of the residual indentations. Nevertheless, the results indicate that increasing the content of Ac-POSS nanofiller to 8% m/m (in varnish coating 3) resulted in the absence of any cracks in that coating (grade "4") and in decreased diameters of indentations for the majority of impact energies used. An exception was the result obtained for the highest energy of impact, which in the case of coating 3 created indentations with larger diameters, and hence also greater depths, than in the case of coating 2 and reference coating 1, although no cracks occurred in coating 3. This demonstrates the enhanced plastic strain ability of coating 3 (without the occurrence of any cracks) compared with the reference coating 1. It should also be noted that in the case of low impact energy (49.3 and 123.3 mJ) the 4% or 8% m/m addition of Ac-POSS nanofiller did not cause any changes in the degree of damage to composite coatings 2 and 3 in comparison to coating 1 (table 3). Tests of coating 5, based on polyester binder with 4% m/m Ac-POSS nanofiller, showed that it was able to absorb medium impact energy (246.6 or 493.2 mJ), which resulted in plastic strain of the coating without the occurrence of cracks.

On the other hand, increasing the content of Ac-POSS to 8% m/m resulted in the considerable susceptibility of coating 6 to cracking (grade "3"), while the diameters of residual indentations decreased. This may suggest the increased rigidity of coating 6 compared with coating 5, which contained half the quantity of Ac-POSS nanofiller (tables 2 and 3). In the case of high impact energy (986.4 and 1972.7 mJ) the Ac-POSS content in composite coatings 5 and 6 had no significant influence on the degree of damage. Both varnish composite coatings demonstrated susceptibility to minor and medium cracks (grade "3") and to major cracks going beyond the area of indentation (grade "1"), corresponding to the susceptibility to cracking observed for the reference organic coating (no. 4), for impact heights of 200 and 400 mm respectively.

When low values of impact energy were considered, a 4% or 8% m/m content of Ac-POSS in the polyester-based composite coatings did not cause any differences in their susceptibility to cracking compared with the reference coating (no. 4). It should be noted that for lower values of impact energy (49.3-246.6 mJ) the average diameter of residual indentations, and hence their depth, gradually decreased when proceeding from the reference organic coating (no. 4) to composite coatings containing 4% or 8% Ac-POSS nanofiller (coatings 5 and 6). This may suggest that the hardness of the composite coatings increased, compared with the reference, as the content of Ac-POSS increased.

**Table 3. Impact resistance of tested coatings made of varnish compositions applied and UV-cured on the surface of beech- veneered MDF board**

Code of varnish coating acc. to Table 2	Impact height [mm]					
	10	25	50	100	200	400
	Impact energy [mJ]					
	49.3	123.3	246.6	493.2	986.4	1972.7
Final assessment of degree of damage to varnish coating using standard rating scale from 5 to 1						
<i>(Diameter of residual indentation in varnish coating<sup>1)</sup> – mm)</i>						
<i>{Variability of diameter of residual indentation in varnish coating<sup>2)</sup> – %}</i>						
	4	4	4	4	4	4
1	(2.60) {4.7}	(3.02) {6.8}	(3.50) {0.0}	(4.08) {5.3}	(5.00) {1.4}	(5.78) {0.8}
	4	4	3	3	3	3
2	(2.56) {3.5}	(2.88) {1.6}	(3.58) {3.6}	(4.16) {1.3}	(5.62) {3.6}	(6.12) {2.1}
	4	4	4	4	4	4
3	(2.38) {1.9}	(3.14) {2.8}	(3.40) {2.1}	(4.08) {7.4}	(5.10) {2.4}	(6.36) {1.4}
	4	4	4	3	3	1
4	(2.68) {3.1}	(3.16) {1.7}	(3.72) {1.2}	(4.02) {1.1}	(4.98) {4.4}	(5.96) {0.9}
	4	4	4	4	3	1
5	(2.56) {8.1}	(3.02) {8.2}	(3.56) {1.5}	(4.68) {1.8}	(5.24) {2.2}	(6.30) {0.0}
	4	4	3	3	3	1
6	(2.52) {1.8}	(3.12) {7.6}	(3.46) {2.6}	(4.26) {4.6}	(5.16) {2.2}	(6.24) {0.9}

<sup>1)</sup> Presented value is an average value of the diameters of residual indentations measured in five test areas on the tested coating, calculated for a defined impact energy value.

<sup>2)</sup> Presented value is the variability coefficient of diameters of residual indentations.

Coating 6 (containing 8% m/m Ac-POSS nanofiller) demonstrated plastic strain ability without cracking, but only in the case of low values of impact energy. Medium and high values of impact energy resulted in medium-sized cracks in this coating, and even larger cracks for the highest impact energy (1972.7 mJ).

In summary, of the two reference coatings, varnish coating 1 (based on polyether binder containing TTEGDA as a reactive acrylic monomer)

proved to be less susceptible to damage (cracking) within the standard range of impact heights (10-400 mm, corresponding to impact energies of 49.3-1972.7 mJ). Coating 3, based on the same organic precursors and containing 8% m/m Ac-POSS nanofiller, was found to be the least susceptible to cracking, within a broad range of impact energy values, among the tested composite coatings.

Table 4 presents detailed results of the abrasion resistance tests of the individual varnish coatings. Analysis of the calculated values of the  $W_{ABR}$  index indicates that both for coatings based on polyether binder and for those based on polyester structure, the abrasion resistance of the coating increased as the content of Ac-POSS modifier increased. The  $W_{ABR}$  index values calculated for composite coatings 2 and 3, containing 4% and 8% m/m Ac-POSS nanofiller, were respectively 5.0% and 15.8% higher than the value obtained for the organic

**Table 4. Abrasion resistance of tested coatings made of varnish compositions applied and UV-cured on the surface of beech-veneered MDF board**

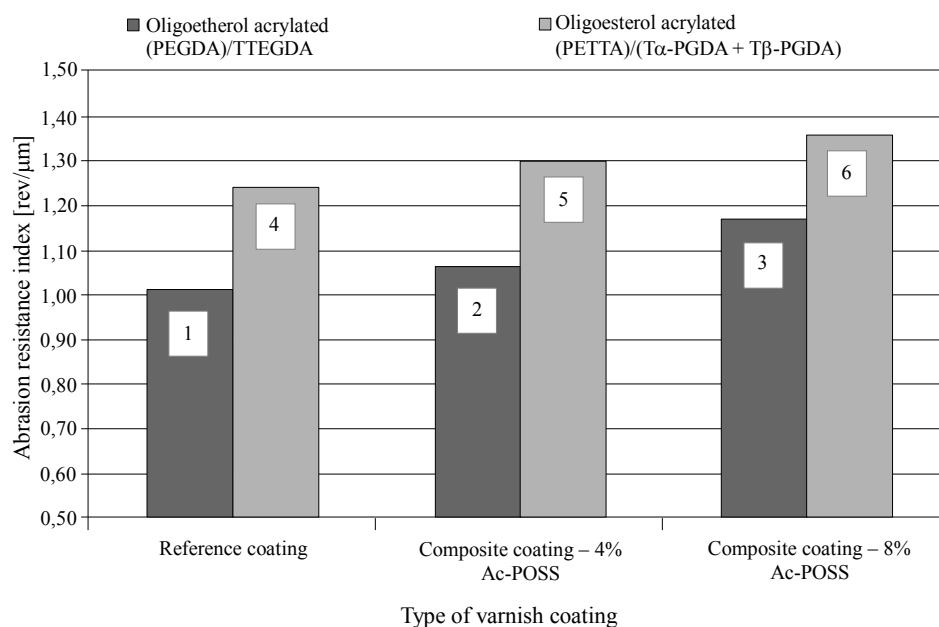
Code of varnish coating acc. to Table 2	IP <sub>cor</sub> <sup>1)</sup> [rev]			Final assessment IP <sup>2)</sup> [rev] (Average coating thickness [ $\mu$ m])	Abrasion resistance index $W_{ABR}$ [rev/ $\mu$ m]
	Test sample no. 1	Test sample no. 2	Test sample no. 3		
1	174	192	192	190 (188)	1.01
2	206	206	197	200 (189)	1.06
3	268	219	197	230 (196)	1.17
4	107	98	107	100 (81)	1.24
5	98	107	107	100 (77)	1.30
6	107	98	116	110 (81)	1.36

<sup>1)</sup> Value of IP parameter corrected taking into account the correction factor  $f=0.894$  calculated for the batch of abrasive paper used for abrasion tests of all varnish coatings

<sup>2)</sup> Average value of corrected IP calculated for three test samples, rounded to the nearest 10 revolutions

reference coating 1. Similarly, the  $W_{ABR}$  index values calculated for the polyester-based composite coatings 5 and 6 (containing 4% and 8% m/m Ac-POSS nanofiller) were respectively 4.8% and 9.7% higher than the value obtained for the reference coating (no. 4). The  $W_{ABR}$  index values calculated for coatings based on polyester binder containing acrylic monomers (T $\alpha$ -PGDA and T $\beta$ -PGDA) were on average approximately 20% higher than the index values calculated for coatings based on polyether binder (nos. 1, 2 and 3).

Figure 2 illustrates the differences in the values of the  $W_{ABR}$  index observed for composite coatings modified with Ac-POSS additives in comparison to the relevant reference coatings, as well as the differences in abrasion resistance between both groups of tested varnish coatings (polyether- and polyester-based).



**Fig. 2.** Abrasion resistance index values assigned to varnish coatings coded 1–6, UV-cured on surface of beech-veneered MDF boards, depending on Ac-POSS content and type of organic precursors in varnish composition

It may be noted that the trend described above occurred for both types of organic binders in the tested varnish coatings, while the intensity of the increase in the coating's abrasion resistance, observed for the same increase in the content of Ac-POSS modifier, was higher in the case of polyether-based coatings. On the other hand, varnish coatings based on polyester binder proved to be more resistant to abrasion, while the increase in the content of Ac-POSS modifier in those coatings resulted in a smaller growth in abrasion resistance.

Table 5 presents detailed results of evaluation of the adhesion of the tested varnish coatings to the surface of the beech veneer. Analysis of the mean values of tearing resistance calculated for varnish coatings 1, 2 and 3 did not indicate any clear relation between the content of Ac-POSS nanofiller in the coating's structure and the coating's adhesion to the beech veneer surface. However, as the content of Ac-POSS nanofiller in composite coatings of that group (i.e. in nos. 2 and 3) increased, changes were observed in the manner of tearing of unit samples of the tested coatings. In the case of samples of reference coating 1, the dominant manner of tearing, in percentage terms, was adhesive detachment at the veneer/varnish coating boundary (A/B). Only for one of the six tested samples of that coating a significant proportion of cohesive detachment (A) in the base MDF was observed. In the case of composite coating 2, containing 4% m/m Ac-POSS nanofiller, the dominant (in percentage terms) manner of tearing of samples from the beech-veneered MDF board was still adhesive delamination at the veneer/coating boundary. However, for at least one tested unit sample of that coating, greater detachment at the varnish coating/glue joint boundary (-/Y) was also observed. This manner of tearing also occurred on a much greater scale (10-75%) for samples of composite coating 3, containing 8% m/m Ac-POSS nanofiller.

Examining the test results obtained for polyester-based coatings on beech-veneered MDF boards (nos. 4, 5 and 6), it is found that in the case of both coating 4 (with solely organic structure) and composite coating 5, the dominant manners of delamination were cohesive tearing in the beech veneer layer (A) and adhesive detachment at the veneer/coating boundary (A/B). In the case of coating 6, containing 8% m/m Ac-POSS, it was observed that, distinct from varnish coatings 4 and 5, samples of coating 6 on the beech-veneered MDF board were delaminated almost exclusively through adhesive detachment at the veneer/coating boundary (A/B). This means that the adhesion of coating 6 decreased compared with the reference coating (no. 4), if mean values of tearing resistance for those coatings are considered. The analysis provides evidence that, of the two tested groups of varnish coatings, the polyester-based coatings exhibited better adhesion to the surface of beech veneer, and in their case increasing the content of Ac-POSS modifier resulted in a change in the manner of delamination following the strength test.

Table 5. Adhesion of tested UV-varnish coatings to the surface of beech veneer on MDF board

Code of varnish coating acc. to Table 2	Tearing resistance [MPa] [Description of delamination type] <sup>1)</sup>						Average value	Variability coefficient [%]
	No. 1	No. 2	No. 3	No. 4	No. 5	No. 6		
1	1.193 [A5%,A/B80%, -/Y10%,Y/Z5%]	1.168 [A3%,A/B93%, -/Y3%,Y/Z1%]	1.244 [A2%,A/B87%, -/Y10%,Y/Z1%]	1.405 [A5%,A/B90%, -/Y5%]	1.176 [A30%,A/B64%, -/Y5%,Y/Z1%]	1.2614 [A2%,A/B97%, -/Y1%]	1.241	7.17
2	1.214 [A2%,A/B92%, -/Y5%,Y/Z1%]	1.142 [A/B95%,-/Y5%]	1.236 [A/B95%,Y/Z5%]	1.440 [A5%,A/B92%, -/Y3%]	1.358 [A5%,A/B80%, -/Y10%,Y/Z5%]	1.259 [A/B85%, -/Y15%]	1.275	8.39
3	1.284 [A5%,A/B75%, -/Y20%]	1.184 [A3%,A/B87%, -/Y10%]	1.138 [A/B40%, -/Y60%]	1.120 [A/B35%, -/Y65%]	1.100 [A/B25%, -/Y75%]	1.190 [A5%,A/B85%, -/Y10%]	1.169	5.6
4	1.400 [A40%,A/B60%]	1.361 [A75%,A/B25%]	1.459 [A90%,A/B10%]	1.35 [A5%,A/B95%]	1.311 [A5%,A/B95%]	1.400 [A5%,A/B95%]	1.381	3.69
5	1.264 [A95%,A/B5%]	1.149 [A98%,-/Y2%]	1.259 [A5%,A/B95%]	1.266 [A5%,A/B95%]	1.206 [A5%,A/B95%]	1.267 [A95%,A/B5%]	1.235	3.89
6	1.214 [A2%,A/B96%, -/Y2%]	1.451 [A2%,A/B96%, -/Y2%]	1.363 [A5%,A/B95%]	1.348 [A5%,A/B95%]	1.11 [A50%,A/B48%, -/Y2%]	1.337 [A5%,A/B95%]	1.371	7.44

<sup>1)</sup> Delamination types denoted with the literal symbols defined in PN-EN ISO 4624:2004.



## Conclusions

The results of the study showed that 4% or 8% m/m additions of Acrylo POSS<sup>®</sup> nanofiller in varnish compositions based on oligoether binder resulted in a distinct increase in the linear scratching resistance of the respective composite coatings UV-cured on beech veneer on MDF board, in comparison with the reference coating. On the other hand, changes in the susceptibility to cracking of the composite coatings, resulting from the use of two different contents of the POSS nanofiller, were manifested at medium and high values of impact energy for polyether-based coatings, and already at medium values of impact energy for polyester-based coatings. Both for coatings based on polyether structures and those based on polyester binder, the results proved that the resistance of the varnish coating to abrasion increased as the content of Acrylo POSS<sup>®</sup> nanofiller in the original varnish composition increased. Of the two tested groups of varnish coatings, the polyester-based coatings demonstrated better adhesion to the surface of the beech veneer, while composite coatings from that group containing 4% or 8% m/m Acrylo POSS<sup>®</sup> nanofiller demonstrated an average adhesion to the veneer surface that was worse than or comparable to that of the organic reference coating. The results obtained have been used as a basis for the planning of further applied research on new ways to enhance the functional properties of UV varnish coatings applied on wood surfaces.

## References

- Amerio E., Sangermano M., Colucci G., Malucelli G., Messori M., Taurino R., Fabbri P.** [2008]: UV curing of organic-inorganic hybrid coatings containing polyhedral oligomeric silsesquioxane blocks. *Macromolecular Materials and Engineering* 293: 700-707
- Andrzejewska E., Marcinkowska A., Wegner K.** [2011]: Nanocomposites obtained by photopolymerization of (methacrylate monomer)/(methacrylate functionalized polyhedral oligomeric silsesquioxane) system. *Polimery* 56 [1]: 63-66
- Ayandele E., Sarkar B., Alexandridis P.** [2012]: Polyhedral oligomeric silsesquioxane (POSS)-containing polymer nanocomposites. *Nanomaterials* [2]: 445-475
- Banecki J.** [2011]: Comparative studies of furniture lacquer coatings' resistance to linear scratching acc. to the method described in TS 15186:2005. *Drewno* 54 [185]: 61-80
- Bizet S., Galy J., Gerard J.-F.** [2006]: Structure-property relationships in organic-inorganic nanomaterials based on Methacryl-POSS and dimethacrylate networks. *Macromolecules* 39: 2574-2583
- Constantin F., Gârea S.A., Iovu H.** [2013]: The influence of organic substituents of polyhedral oligomeric silsesquioxane on the properties of epoxy-based hybrid nanomaterials. *Composites Part B* 44: 558-564
- Cordes D.B., Lickiss P.D., Rataboul F.** [2010]: Recent developments in the chemistry of cubic polyhedral oligosilsesquioxanes. *Chemical Reviews* 110: 2081-2173
- Dutkiewicz M., Maciejewski H., Marciniak B., Szolyga M.** [2014]: Thiirane functional spherosilicate as epoxy resin modifier: Synthesis and thermal stability. *Journal of Thermal Analysis and Calorimetry* 117 [1]: 259-264

- Guirong P.** [2007]: Polyhedral oligomeric silsesquioxane (POSS). Physical properties of polymer handbook, chapter 34: 577-584
- Haddad T.S., Lichtenhan J.D.** [1996]: Hybrid organic-inorganic thermoplastics: Styryl-based polyhedral oligomeric silsesquioxane polymers. *Macromolecules* 29: 7302-7304
- Hu L.-C., Shea K.J.** [2011]: Organo-silica hybrid functional nanomaterials: how do organic bridging groups and silsesquioxane moieties work hand-in-hand? *Chemical Society Reviews* 40: 688-695
- Janowski B., Pielichowski K.** [2008]: Polimery nanohybrydowe zawierające poliedryczne oligosilseskwioxany. *Polimery* 53 [2]: 87-98
- Kopesky E.T., McKinley G.H., Cohen R.E.** [2006]: Toughened poly(methyl methacrylate) nanocomposites by incorporating polyhedral oligomeric silsesquioxanes. *Polymer* 47: 299-309
- Kurek J.** [2004]: Powłoki funkcyjne. *Lakiernictwo Przemysłowe* [4] 30: 20-21
- Lee A., Lichtenhan J.D.** [1999]: Thermal and viscoelastic property of epoxy-clay and hybrid inorganic-organic epoxy nanocomposites. *Journal of Applied Polymer Science* 73: 1993-2001
- Li G.Z., Wang L., Toghiani H., Daulton T.L., Koyama K., Pittman Jr C.U.** [2001]: Viscoelastic and mechanical properties of epoxy/multifunctional polyhedral oligomeric silsesquioxane nanocomposites and epoxy/ladderlike polyphenylsilsesquioxane blends. *Macromolecules* 34: 8686-8693
- Lichtenhan J.D., Otonari Y.A., Carr M.J.** [1995]: Linear hybrid polymer building blocks: methacrylate-functionalized polyhedral oligomeric silsesquioxane monomers and polymers. *Macromolecules* 28: 8435-8437
- Lichtenhan J.D., Vu N.Q., Carter J.A., Gilman J.W., Feher F.J.** [1993]: Silsesquioxane-siloxane copolymers from polyhedral silsesquioxanes. *Macromolecules* 26: 2141-2142
- Liu H., Zheng S.** [2005]: Polyurethane networks nanoreinforced by polyhedral oligomeric silsesquioxane. *Macromolecular Rapid Communications* 26: 196-200
- Marciniak B.** [2010]: Funkcjonalizowane oktasilseskwioxany klatkowe (T8) jako podstawa hybrydowych nanokompozytów polimerowych. *Przemysł Chemiczny* 89 [9]: 1184-1187
- Phillips S.H., Haddad T.S., Tomczak S.J.** [2004]: Developments in nanoscience: polyhedral oligomeric silsesquioxane (POSS)-polymers. *Current Opinion in Solid State and Materials Science* [8]: 21-29
- Pielichowski K., Njuguna J., Janowski B., Pielichowski J.** [2006]: Polyhedral oligomeric silsesquioxanes (POSS)-containing nanohybrid polymers. *Advances in Polymer Science* 201: 225-296
- Pilch-Pitera B.** [2013]: Blocked polyisocyanates containing monofunctional polyhedral oligomeric silsesquioxane (POSS) as crosslinking agents for polyurethane powder coatings. *Progress in Organic Coatings* 76: 33-41
- Prządka D., Marcinkowska A., Andrzejewska E.** [2016]: POSS-modified UV-curable coatings with improved scratch hardness and hydrophobicity. *Progress in Organic Coatings* 100: 165-172
- Qin Y., Bi Y., Ren H., Zhu F., Luo M., Zhang L.** [2010]: Poly(methylmethacrylate)/Methacryl-POSS nanocomposites with excellent thermal properties. *Chinese Journal of Chemistry* 28: 2527-2532
- Scott D.W.** [1946]: Thermal rearrangement of branched-chain methylpolysiloxanes. *Journal of the American Chemical Society* 68: 356-358
- Wang X., Hu Y., Son L., Xing W., Lu H., Lv P., Jie G.** [2011]: UV-curable waterborne polyurethane acrylate modified with octavinyl POSS for weatherable coating applications. *Journal of Polymer Research* 18: 721-729

**Wojtas A., Zaborski M., Kosmalska A.** [2010]: Wpływ dodatku oligosilsekwioxanów klatkowych T<sub>8</sub> na właściwości mechaniczne kauczuku silikonowego. *Polimery* 55 [3]: 208-214

### List of standards

- PN-EN ISO 4624:2004** Farby i lakiery – Próba odrywania do oceny przyczepności (Paints and varnishes – Pull-off test for adhesion)
- PN-EN ISO 2808:2008** Farby i lakiery – Oznaczanie grubości powłoki (Paints and varnishes – Determination of film thickness)
- PN-EN 13722:2006** Meble – Ocena połysku powierzchni (Furniture – Assessment of the surface gloss)
- PN-EN 15185:2011** Meble – Ocena odporności powierzchni na ścieranie (Furniture – Assessment of the surface resistance to abrasion)
- PN-EN 15186:2012** Meble – Ocena odporności powierzchni na zarysowanie (Furniture – Assessment of the surface resistance to scratching)
- PN-ISO 4211-4:1999** Meble – Badanie powierzchni – Ocena odporności na uderzenie (Furniture – Tests for surfaces – Part 4: Assessment of resistance to impact)

### Acknowledgements

The research was carried out under statutory project no. ST-2-BBP/2012/N, financed by the Ministry of Science and Higher Education as part of the subsidy for statutory activities. Acknowledgments are given to the members of the research teams of ITD Surface Testing and Wood Investigation Departments for active participation in the implementation of mechanical tests. The authors are extremely grateful to representatives of Sherwin-Williams Poland Sp. z o.o. for providing access to the equipment used to form the tested varnish coatings, and to sales representatives of Sartomer-Arkema Group for the free provision of product samples for the research work.

*Submission date: 15.10.2018*

*Online publication date: 15.11.2019*