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Surface analysis of matt powder coatings

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Abstract

A study of gloss reduction of powder coatings was performed using different waxes, fillers and non-compatible polymer resins (matting hardeners). Coatings with reduced surface smoothness were analysed. Scanning electron micrographs were taken to visualize the surfaces. All of the applied matting additives changed the surface profile of coating. The most interesting surface structural form is provided by wax particles. The average size of these forms was calculated by applying image analysis to some sample micrographs. The surface shape of all of the prepared coatings was analysed using surface profile measurements. Two parameters of these profiles were determined, the average roughness and the mean spacing between the surface peaks. The influence of several physical surface parameters on specular gloss characteristics is discussed.

Keywords: Powder coatings; Matting; Specular gloss; Gloss reduction; Surface analysis

1. Introduction

No measuring instrument is known to be capable of measuring the details of the appearance of a surface as seen by the human eye. Therefore, various methods have been proposed to represent the appearance of a coating and of a coated object [1,2]. The visual impression of a surface is recognized as various types of glossiness that are frequently classified as different degrees of gloss. Several criteria are used in glossiness rankings. Among these, in coatings the specular gloss (mirror-like) is the most often considered [3,4]. The specular gloss measures the intensity of mirror-type reflection, i.e. when the angle of incidence is equal to the angle of reflection. The more the light is reflected this way, the greater is the impression of gloss. Smooth and polished surfaces reflect a major part of the light in this way. On rough surfaces, the light is scattered to several directions. Therefore, the image forming quality is diminished and the reflected image is blurred.

Low-gloss coatings are popular when used for aesthetic and functional purposes. A surface with lower gloss hides surface imperfections in a way that is superior to the hiding provided by a surface of higher gloss. The application of a low-gloss coating might, therefore, be easier to achieve than that of a glossy one and be more cost effective. This is one of the reasons why matt finishes are produced.

Several techniques are known to produce coatings with lower gloss finishes. They can be divided into two basic categories, whether they act due to the presence of non-soluble particles or whether they are effective due to the addition of resinous materials that demonstrate different compatibility behaviour. Gloss reduction using non-soluble particles is widely used in liquid-based coatings. During drying processes, the loss of solvents and condensation products results in a fairly high shrinkage of the coating film. Consequently, a diffusely reflecting micro-textured surface is formed [5–8]. This matting technique is less effective in coatings that undergo little shrinkage during film formation. Such coatings include powder coatings (PC) and some types of UV curing systems where the production of matt and low-gloss finishes is not straightforward. Here, resinous materials are frequently applied that

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shows limited compatibility with the binder. This causes the formation of a coating that has an imperfectly smooth surface [9–11]. In addition, fillers with larger particle sizes are frequently applied to reduce the surface smoothness.

One of the more important properties of PC is that there is little or no volatile organic compounds (VOC) emission. Thus, PC products are considered to provide the most environmentally friendly coating system. In the past, a method for evaluating the differences in the degree of dispersion in PC has been proposed [12–14]. The method gives the average particle size and the particle size distribution. Also studied has been the influence of the input power of the extrusion equipment on the state of the pigment dispersion in PC [14]. Quantitative information was obtained using selective oxygen plasma and by evaluating the scanning electron micrograph (SEM) by image analysis [15–18]. Recently, the bonding-process efficiency and Al-flake orientation, during the curing of PC, were studied [19]. The orientation of flakes was evaluated during melting of the coating powder and was accomplished already at 100 °C. All these studies were performed on samples from a standard PC production line.

This current study was performed on the samples from standard production process in order to evaluate the various types of matting phenomena and to establish the role played by the materials used in the production of PC.

2. Experimental

2.1. Samples

The carboxy-polyester binder was used in all PC samples. Different matting additives were applied: micronised waxes, fillers and polymer resin (matting hardener). The data provided by the manufacturers are summarised in Table 1. The application of these matting additives in coating powder samples is given in Table 2. Approximately the same net concentration of matting additives was applied in all samples (9 vol%). The coating powders were prepared on a standard PC industrial production line applying the twin-screw extruder ZSK 50 with 43.2 kW of input power.

The powder samples were sprayed electrostatically onto aluminium sheets. They were cured for 10 min at 180 °C. The thickness of cured coatings was 60–70 μm. In addition, selected powder samples were sprayed over the aluminium substrate (50 cm × 50 cm) of the same thickness and cured in a gradient bar oven for 10 min. The temperature gradient was adjusted to vary nearly linearly from 80 °C at one end of the sample up to 180 °C at the other. This way, test panels with curing temperatures in the range from 80 to 180 °C were prepared.

Some samples were selectively etched to remove the topmost layer of the binder from the coating surface leaving all the other particles unchanged. The procedure was based on selective interaction of gaseous particles with coating film in a weakly ionised highly dissociated oxygen plasma [15,16].

Table 1
Description of applied matting additives (data from the producers)

Matting additive	Chemical nature	Particle size	Softening point (°C)
Wax A	Ethylene homopolymer wax		104–108
Wax B	Micronized polyolefin wax		109–117
Wax C	Micronized modified polyethylene wax	$\overline{d}$ = 8 μm, <35 μm	135
Wax D	Micronized polypropylene		154–157
Wax E	Micronized poliolefin wax		
Filler 1	$CaCO_3$	$\overline{d}$ = 5–6 μm, <20 μm	–
Filler 2	Complex mineral, consisting of mica, chlorite-containing slate and quartz	12 μm	–
Filler 3	Micronized aluminium hydroxide, $Al(OH)_3$		–
Polymer resin (hardener)	Mono-salt of a polycarboxylic acid and a cyclic amidine		210–235

All materials were used in powder form. Not all the data are available.

2.2. Measurements and calculations

Three surface properties were measured, the specular gloss, the surface profile and the topography of the coating surface.

The specular gloss is given by the ratio of the two fluxes reflected in the selected specular direction, one on the sample and the other on the standard (polished black glass with a refractive index of 1.567). The readings are expressed in GU (gloss units). The calibration was performed on the black gloss standard. A Micro-TRI-Gloss portable glossmeter measuring unit (BYK-Gardner) was used in this part of the study. All of the measurements were carried out using the 60° incidence angle.

The surface profile of the coating samples was measured using a profilometer Talysurf (Rank Taylor Hobson Series

Table 2
Matting additives used in formulations of PC samples and measurement results: the gloss, the average diameter of wax particles on a surface of a cured coating (D_{wax}), the average roughness (R_a), and the mean spacing between surface profile peaks (S)

Sample	Matting additives	Gloss (GU)	D_{wax} (μm)	R_a (μm)	S (μm)
S1	Wax A	78	2.59	0.090 ± 0.011	8.77 ± 0.54
S2	Wax B	55	9.18	0.258 ± 0.028	11.39 ± 1.00
S3	Wax A, filler 1	68	–	0.126 ± 0.004	9.63 ± 0.86
S4	Wax A, filler 1, filler 2	57	3.52	0.186 ± 0.005	11.26 ± 0.25
S5	Hardener	45	–	0.242 ± 0.031	17.8 ± 1.8
S6	Wax A, wax B	72	3.31	0.111 ± 0.015	8.75 ± 0.49
S7	Wax A, filler 2	63	5.29	0.148 ± 0.004	12.10 ± 0.35
S8	Wax C, filler 1, filler 3	66	–	0.103 ± 0.002	9.05 ± 0.88
S9	Wax D, filler 3	40	14.45	0.46 ± 0.14	19.4 ± 2.3
S10	Wax E, filler 1	56	6.36	0.234 ± 0.019	12.29 ± 0.59
S11	Wax A, wax B, filler 2	74	2.95	0.144 ± 0.022	10.76 ± 0.83

Determination of D_{wax} was not possible for samples S3 and S8.

2). This unit scans the surface mechanically with a diamond tip and transforms the data into a measured height profile of the surface, $z_m(x)$. The sampling length was set to $L = 1$ mm. The details of the surface texture on these lengths cannot be seen with the naked eye though they are responsible for the level of gloss appearing on the surface. The long-wave components of the surface profile, i.e. the so-called orange peel effect, were filtered out by high-pass filters. The filtered surface profile ($z(x)$) was characterized by the amplitude and spacing parameters. The average roughness (R_a) describes the amplitude of the profile (i.e. the average vertical deviation from the mean surface level) while the mean spacing between profile peaks (S) denotes the lateral properties of the measured surface profile [20]. The average roughness is the arithmetic mean of the absolute differences of the profile $z(x)$ from the mean line, measured within the sampling length L:

$$R_a = \frac{1}{L}\int_0^L |z(x)|\,dx \tag{1}$$

The mean spacing between profile peaks is defined by:

$$S = \frac{1}{n}\sum_{i=1}^{n}\frac{S_i}{n} \tag{2}$$

Here, S_i represents the distance between the two adjacent peaks at the mean line of the profile and n is the number of peak spacings. A profile peak is defined as the highest point of the profile between an upward and downward crossing of the mean line [20]. Three measurements of the surface profile were done on each sample.

The image of the coating surface of each sample was examined using the electron micrograph pictures. These were taken using a JEOL 5500 LV scanning electron microscope (SEM) at a 20 kV accelerating voltage. Prior to the SEM analysis, the samples were covered with a thin layer of gold. The Balzers SCD 050 sputter coater was applied for this purpose. For better resolution of the particles on the top of the coating surface, the topmost layer of the binder was removed by careful selective etching by an oxygen plasma. This process was accomplished within 20 s of exposure to plasma. The procedure was not applied to samples that did not contain fillers. The size distribution and average size of matting additives seen on the micrographs of the etched coating surfaces were determined by image analysis. Public domain software (ImageJ) was used for this purpose [21]. Transformation of the output data from ImageJ to a size distribution graph was brought about by using a separate program written in Matlab 5.3 software. It calculates also the average size of investigated particles.

3. Results and discussion

The SEM micrographs can be easily divided into groups with respect to the applied matting additives. The typical sample surfaces of the three groups: (a) matted with wax, (b) with wax and fillers, and (c) with hardener are shown in Fig. 1. The samples with fillers were etched by an oxygen plasma. The circular features were obtained for all coating surfaces in which waxes were applied as matting additives (Fig. 1a,b). The fillers appear as larger particles of irregular shapes (Fig. 1b). No typical features were observed on SEM micrograph of sample where a hardener was used (Fig. 1c).

A better view of surface topography can be seen in the micrographs obtained for the tilted samples. The structures that are responsible for the matt effect were seen on micrographs

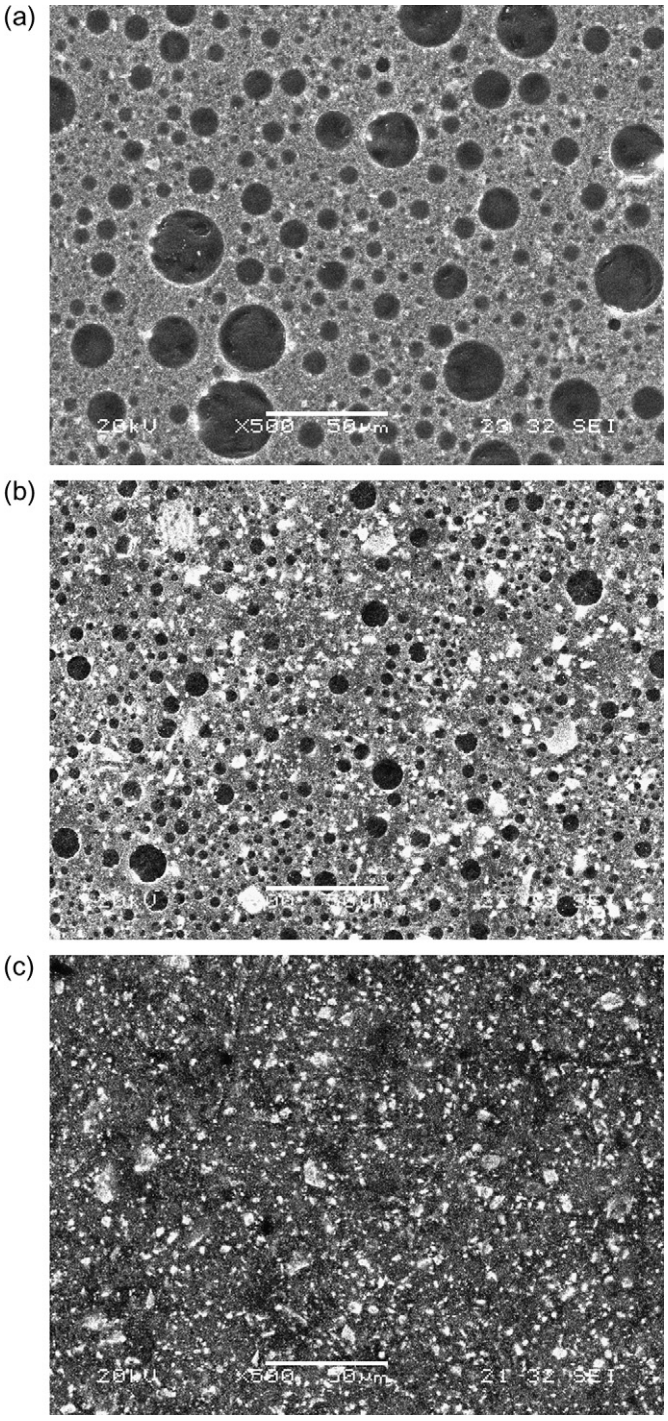

Fig. 1. SEM micrographs of matt coating surfaces: S2 (a), S4 (b) and S5 (c) (see Table 2). Samples S4 and S5 were etched by oxygen plasma. Magnification 500×.

that were scanned at an approximately 65° angle (Fig. 2). The wax particles lie on the top of the surface. Their incompatibility with the binder causes sharp edges to be clearly seen on micrographs (Fig. 2a). These diminish the surface smoothness and form a vertical surface profile. The hardener does not cause such effects and, therefore, the resulting surface of this coating is generally smooth (Fig. 2b).

The formation of wax particles on a coating surface was monitored on test panel samples which were cured in a gradient bar oven. Test panel was cut to small (1 cm × 1 cm) samples, representing coatings cured at different temperatures. These samples were used to monitor the formation of the coating surface at different curing temperatures. The wax particles of irregular shape can be seen on surfaces even at the lowest curing temperature (80 °C). They retain such a shape to the much higher temperatures where circular forms were observed (Fig. 3). This typical shape does not change with further increase in the curing temperature. The lowest curing temperature, where wax particles appear as circles on the coating surface, corresponds well to the appropriate softening temperature (see the data in Table 1).

On most of the coating surfaces it was possible to distinguish the wax particles from the other particles (fillers, pigments) by image analysis of SEM micrographs. The typical size distribution graph obtained by this analysis is shown in Fig. 4. The average sizes of wax particles, D_{wax}, were calculated from the size distribution graphs. The results are given in Table 2.

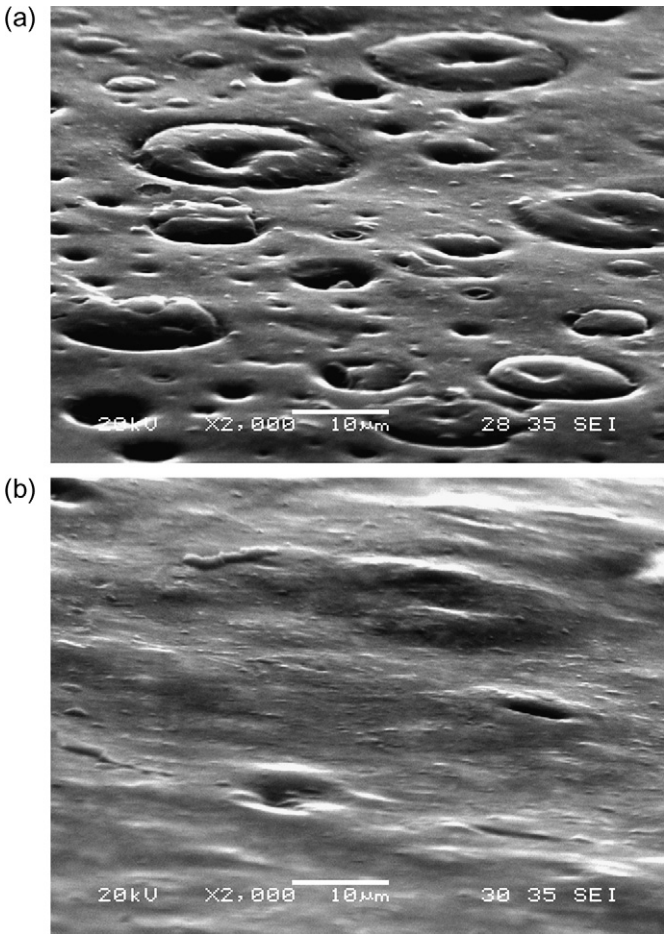

Fig. 2. SEM micrographs of tilted coating surfaces (approximately 65° angle): sample S9 (a) and sample S5 (b) (see Table 2). No etching was applied. Magnification 2000×.

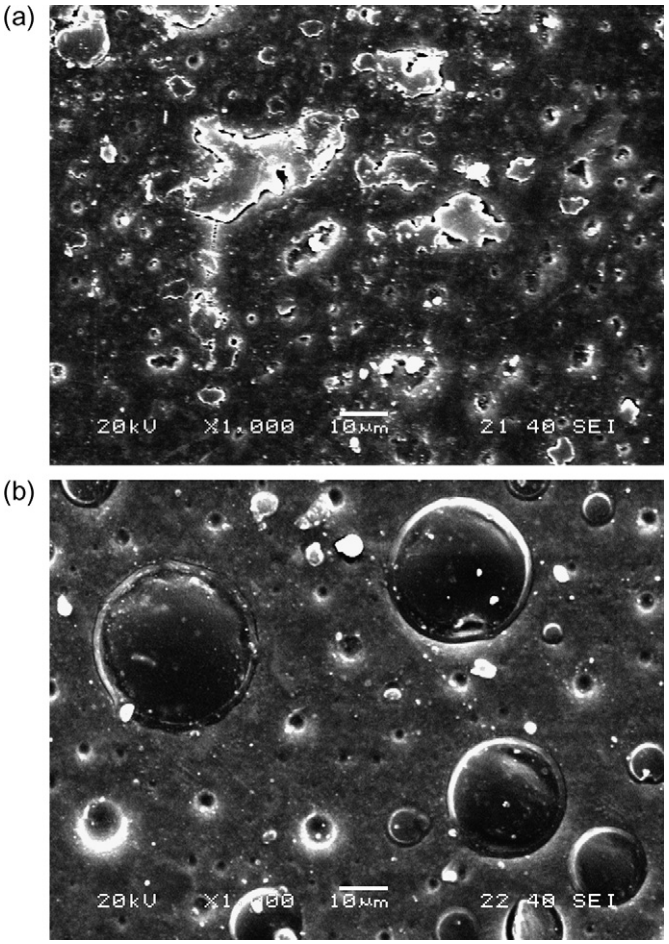

Fig. 3. Coalescence of wax particles into circular forms at elevated curing temperatures. The irregular shapes were obtained at temperatures up to 150 °C (a). The circular shapes appeared at 160 °C already and did not change at higher temperatures. Micrographs were taken of sample S9 cured in gradient bar oven (see Table 2). No etching was applied. Magnification 1000×.

The glossmeter readings (specular gloss) of all of the prepared coatings are assembled in Table 2. The surface profile parameters, i.e. the average roughness (R_a) and the mean spacing (S) were obtained by the analysis of surface profiles. The corresponding results are also given in Table 2. The mean spacing (S) is two orders of magnitude larger than the average roughness (R_a). This agrees well with results of the SEM micrographs of tilted samples (see Fig. 2). Here, the samples were considerably inclined from a horizontal position in order to obtain the impression of surface peaks. The surface profile was observed only on SEM micrographs of strongly tilted surfaces.

The dependence of specular gloss on R_a and on S is presented in Fig. 5. The dotted line shows the best fitting curve to the measured data points. A first-order exponential decay function was applied. The fitting parameters (amplitude, A;

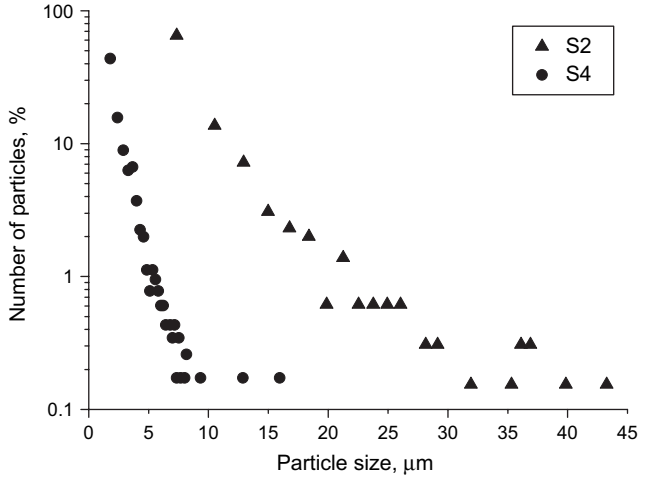

Fig. 4. Size distribution of wax particles as obtained by image analysis of corresponding micrographs for two samples (see Fig. 1 and data in Table 2).

decay constant, t; and offset, y_0) are given in the figures. The specular gloss decreases as values of both parameters of the surface profile increases. The much larger values of S compared to the R_a give considerably larger fitting parameters A and y_0. Both surface parameters influence the specular gloss in the same way. This is shown by similar shape of both fitting curves and confirmed numerically by these being practically the same decay constant t, obtained for both exponential decay functions (see fitting parameters in Fig. 5).

The average size of wax particles, D_{wax}, is a significant parameter when no fillers or hardeners are used as matting additives in the coating. This is illustrated in Fig. 6. Coatings with larger D_{wax} have a lower specular gloss. One filler does not influence this relation to a large extent. It becomes important in samples with two fillers where the deviation in the influence of D_{wax} on specular gloss is considerable. It can be concluded that the matting efficiency of waxes is larger than it is for fillers.

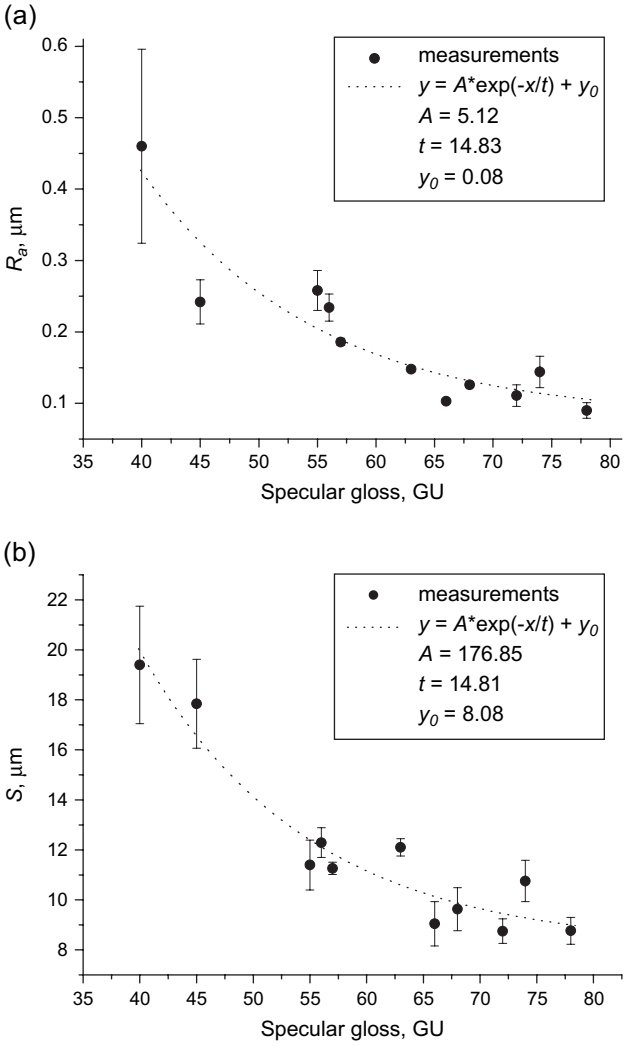

Fig. 5. The correlation of specular gloss to parameters of the surface profile: average roughness, R_a (a), and the mean spacing between surface peaks, S (b). The dotted curve represents the fitting result of experimental curve to the exponential function. The fitting parameters are given.

4. Conclusions

The matting of powder coatings with some selected matting additives was studied. The specular gloss was measured and the resulting data were analysed in terms of their dependence on selected parameters of the surfaces of several semi-gloss powder coatings.

Equal net volume concentrations of various waxes, fillers and a hardener were applied as matting additives. Characteristic circular-shaped forms of wax particles appeared on coating surfaces during curing of samples, when the temperature was above the softening temperature of waxes. No further change in their shape was observed at higher curing temperatures. The bubbles of waxes on the coating surface change the surface profile. The surface profile was also changed when other matting additives, such as fillers and a hardener, were applied.

The specular gloss is influenced by both of the parameters that related to the surface profile, namely the average

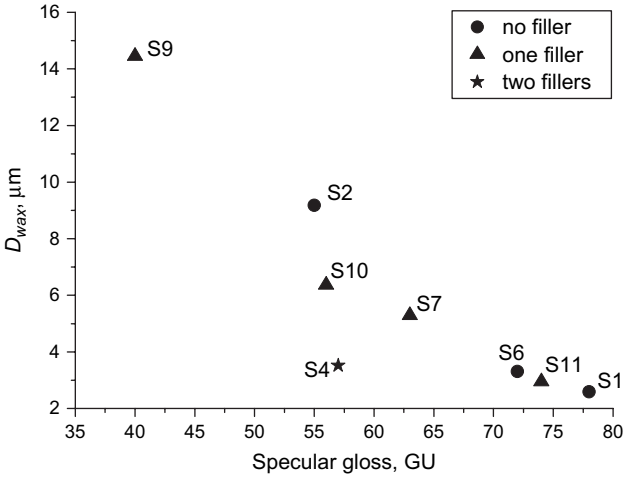

Fig. 6. The correlation of specular gloss to average size of wax particles on the coating surface, D_{wax}. The results are for samples where only waxes were applied (circles), for samples with one filler (triangles) and for that with two fillers (star). More data for samples are in Table 2.

roughness and the mean spacing between surface peaks. The influence of the variation of these parameters on specular gloss was described by the exponential function. Practically the same decay constant was obtained for both surface parameters. Therefore, the relationship between the surface height and specular gloss is similar to the relationship between the spacing and specular gloss.

Coatings with larger wax particles on the surface give a smaller specular gloss. When larger amounts of filler are applied instead of the wax matting additives, the specular gloss is influenced to a considerable extent. It is therefore very likely that the matting efficiency is larger for waxes than it is for fillers.

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