

Improving the Cleanability of Melamine-Formaldehyde-Based Decorative Laminates

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ABSTRACT: Decorative laminates based on melamine formaldehyde (MF) resin impregnated papers are used at great extent for surface finishing of engineered wood that is used for furniture, kitchen, and working surfaces, flooring and exterior cladding. In all these applications, optically flawless appearance is a major issue. The work described here is focused on enhancing the cleanability and anti-fingerprint properties of smooth, matt surface-finished melamine-coated particleboards for furniture fronts, without at the same time changing or deteriorating other important surface parameters such as hardness, roughness or gloss. In order to adjust the surface polarity of a low pressure melamine film, novel interface-active macromolecular compounds were prepared and tested for their suitability as an antifingerprint additive. Two hydroxy-functional surfactants (polydimethylsiloxane, PDMS-OH and perfluoroether, PF-OH) were oxidized under mild conditions to the corresponding aldehydes (PDMS-CHO and PF-CHO) using a pyridinium chlorochromate catalyst. With the most promising oxidized polymeric additive, PDMS-CHO, the contact angles against water, *n*-hexadecane, and squalene increased from 79.8°, 26.3° and 31.4° for the pure MF surface to 108.5°, 54.8°, and 59.3°, respectively, for the modified MF surfaces. While for the laminated MF surface based on the oxidized fluoroether the gloss values were much higher than required, for the surfaces based on oxidized polydimethylsiloxane the technological values as well as the lower gloss values were in agreement with the requirements and showed much improved surface cleanability, as was also confirmed by colorimetric measurements. © 2014 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* **2014**, *131*, 40964.

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INTRODUCTION

Melamine-formaldehyde and melamine-urea-formaldehyde resins are widely used in the impregnation of décor paper for manufacturing paper-based low-pressure (LPM) and high-pressure laminates (HPL) and overlays for outdoor and indoor applications on medium density fiberboards (MDF) and particleboard since they provide highly durable, decorative, and cost-effective surface finishes for floorings and furniture.^{1–3}

In the final consumer goods, there is a wide variety of surface textures of melamine laminates available ranging from high gloss to deep matt. While glossy melamine laminate surfaces are relatively easy to clean by simply wiping off the contaminations, matt surface finished laminates are very sensitive to stains and fingerprint marks. Hence, it is highly desirable and a very chal-

lenging task to have a technology at hand for creating a smooth matt melamine laminate surface that is resistant to staining caused by fingerprints, oil deposits, sweat, or cosmetics.

It is generally known that the surface's ability to repel contaminating fluids depends very much on its hydrophobicity.^{4,5}

To increase hydrophobicity and achieve nonwettability roughness on a nanoscale level is usually introduced to hydrophobic surfaces in order to realize Cassie-Baxter states at the interface substrate/wetting drops and additionally, the rough surfaces are usually composed of low surface energy materials. Static water contact angle is widely used to characterize hydrophobicity/hydrophilicity, wettability, and estimate surface cleanability.^{6,7} The highest water contact angles that have been achieved on smooth, low-energy surfaces are around 95–115°. ^{8–10} These methods

involve the use of chemicals such as silanes, siloxanes, fluoro compounds, and nanoparticles to achieve hydrophobic surfaces.

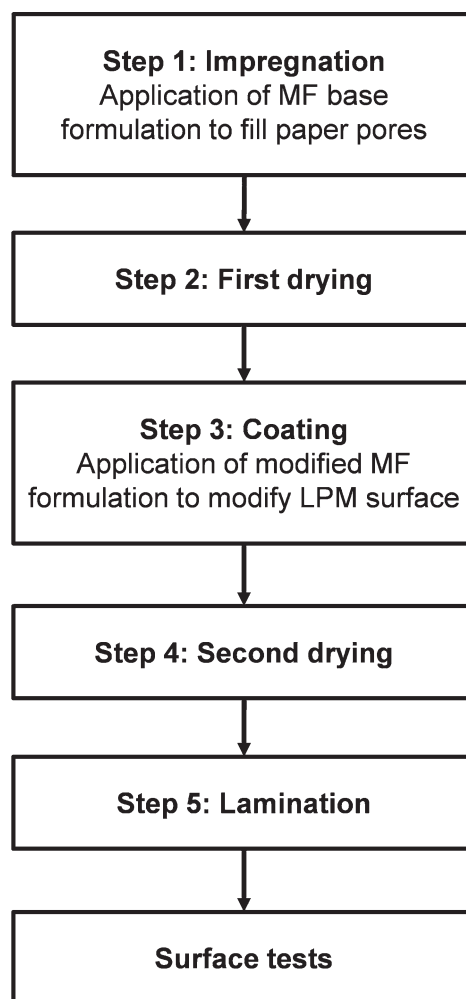
While a lot of research has been invested in creating hydrophobic surfaces and coatings, there is very little literature describing this aspect for melamine laminate surfaces. In the case of melamine surfaces, increase of hydrophobicity and improved cleanability is usually obtained by increasing surface roughness either by lamination using a textured finishing, or by using textured foils that are laminated on the surface, as an overlay.^{11,12} So far smooth, easy-to-clean melamine laminates are still not available on the market. Starting point of this work was to evaluate at which extent chemical compounds generally considered efficient for other coating types would also provide a similar effect for melamine coatings. The research was then further focused on identifying possibilities to increase hydrophobicity and cleanability of melamine laminate surfaces without increasing surface roughness or modification of technological values. To this end two macromolecular compounds based on hydroxy-terminated polydimethyl siloxane and hydroxy-terminated fluorinated polyether were chemically modified via oxidation. Hydroxy groups due to their polar nature and their ability to establish hydrogen bonds should contribute unfavorably to the overall surface interaction energy when incorporated into a melamine-formaldehyde resin surface. Hence, it was hypothesized that oxidation of the hydroxyl moieties to aldehydes should render them more suitable as antifingerprint additives for MF films. In the present contribution, both unmodified and chemically modified perfluorinated polyether and polyether-modified polydimethyl siloxane were evaluated for this purpose.

EXPERIMENTAL

Materials

Impregnation Resin. Melamine-formaldehyde resin (MF) 55 wt % in water and acid catalyst were gifts from Impress Decor Austria GmbH and used as received. Black decorative paper (80 gm⁻²) samples suitable for the preparation of deep matt LPM surfaces were a present from Technocell Dekor GmbH (Günzach, Germany).

Macromolecular Modifiers. Hydroxy-terminated polyether modified polydimethylsiloxane (Byk Silclean 3720) PDMS-OH with an average molecular weight of 7500–10,000 g mol⁻¹ according to the supplier was obtained from Byk-Chemie GmbH (Wesel, Germany). It is designed to prevent accumulation of dirt on the coatings surfaces of aqueous two-pack systems: polyurethane, alkyd-melamine, polyester-melamine, acrylic-melamine, acrylic-epoxy, and phenolic resins. Hydroxy-terminated fluorinated polyether (Polyfox PF-151N) PF-OH with an average molecular weight of around 3000 g mol⁻¹ was a gift from Omnova Solutions (Hemel Hempstead, UK). Fluoroalkylfunctional oligosiloxane (Dynasytan F8815) was a gift from Evonik Industries AG (Rheinfelden, Germany). This fluoroalkylfunctional oligosiloxane is usually used as surface modifier for hydrophobic/oleophobic treatment, for instance, in the formulation of antigraffiti and antiadhesive water-repellents and the oil-repellent antispot treatment of natural stones, wood, cellulose, leather, glass, etc. A temperature stable lipase (Lipolase 100L Type EX) was obtained from Novozymes A/S (Bagsvaerd, Denmark). Polymeric fluorosurfactant (Capstone FS-81) was obtained from Dupont (Du Pont du Nemours, Belgium) and is designed to



Scheme 1. Process steps involved in the preparation of LPM films based on impregnated paper sheets.

improve cleanability of oily dirt and other common stains on architectural waterborne coatings and latex paints. An emulsion of polydimethylsiloxane resin (Tego Protect 5100) was obtained from Evonik Tego Chemie GmbH (Essen, Germany). This modified polydimethylsiloxane resin is intended for the production of waterborne antigraffiti coatings for 2-pack water-thinnable coatings based on acrylic/isocyanate and polyester/isocyanate. It improves marker resistance and antigraffiti effect. All surfactants were used in resin formulation in a range of concentrations around their critical micelle concentration, according to supplier's recommendations.

Catalyst. Pyridinium chlorochromate and poly(4-vinylpyridinium chlorochromate) were purchased from Sigma-Aldrich Chemie GmbH (Steinheim, Germany). Cyclohexane and acetone were reagent grade and were obtained from Sigma-Aldrich Chemie GmbH (Steinheim, Germany). Ethylene glycol, diiodomethane, n-hexadecane, and squalene were also purchased from Sigma-Aldrich.

Preparation of Low Pressure Melamine (LPM) Film Samples

LPM samples were prepared from impregnated paper sheets by impregnating commercial decorative paper samples with melamine

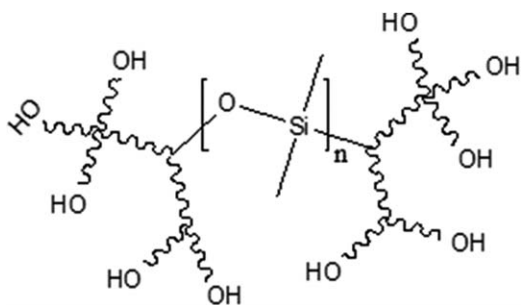


Figure 1. General chemical structures of Polyfox PF 151N and Byk Silclean 3720.

formaldehyde (MF) resin and laminating the impregnated and pre-dried papers onto particleboards as illustrated in Scheme 1.

Paper sheets of 20×30 cm were manually impregnated and coated on a laboratory scale with aqueous MF resin where the basic resin formulation was diluted with distilled water to a final solid content of 47% at application and contained no additives except for the curing catalyst (acid catalyst $< 0.1\%$). Similar to the industrially manufactured decorative paper sheets all laboratory paper samples were treated with resin in two subsequent steps with an intermediate drying phase.

In the first step, the papers were impregnated to fill the core of the paper with the basic MF resin formulation (Step 1, Scheme 1). For this, a laboratory impregnation device with accurate rollers and an electric propulsion control was used. Impregnation was performed by dipping the paper sheet into the prepared MF resin for 5 s. Then the impregnated paper was pulled through two rollers to remove the excess of resin. Thereafter, the wet papers were placed and fixed by magnets onto a drying frame and dried in a first drying phase (Step 2, Scheme 1) for 90 s at 130°C in a Mathis LTE lab Dryer (Mathis, Germany) equipped with an inline infrared sensor for measurement of the surface temperature.

After impregnation and first predrying, the paper was coated with MF in a subsequent coating step (Step 3, Scheme 1). This time, the resin was mixed with either fluorine-modified or polysiloxane-based detergent in order to establish the desired hydrophobic and antifingerprint properties. For comparison, also plain MF as used for the core impregnation was applied for the preparation of reference LPMs. To produce the second resin film on the paper surface, the impregnation procedure described above was repeated and applied to the impregnated and pre-dried paper sheets using the modified resin solutions. All papers were impregnated with a total resin load of 80 g cm^{-2} MF resin after the second drying.

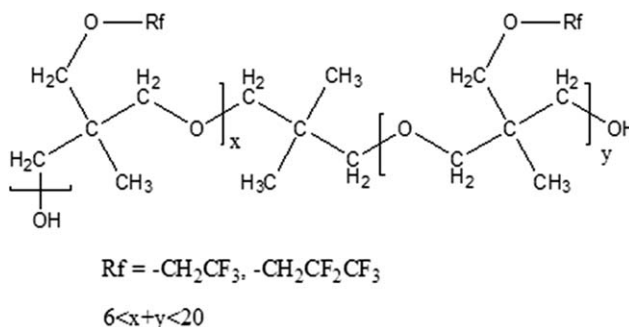


Figure 3. General chemical structures of OH-terminated fluoroether.

MF Resin Modification

Chemically modified and commercial fluorinated and siloxane-based surfactants were used to modify the MF impregnation resins and, in turn, hydrophobicity, oleophobicity, and dirt repellency of the deep-matt low pressure melamine (LPM) film surfaces. Before application of the second coating onto the pre-dried, core impregnated papers, the surfactant was added quickly and under constant stirring to the MF base formulation. The modified resin was used immediately after preparation. Plain MF surfaces were then technologically compared with modified MF surfaces.

Oxidation of PDMS-OH

The hydroxy functional chains of hydroxy-terminated polydimethylsiloxane (Figure 1) were mildly oxidized in order to modify the interfacial interaction properties of the compound.

The reaction to the corresponding aldehyde catalyzed by poly(4-vinylpyridinium chlorochromate) was performed similarly to a procedure described by Frechet et al.¹³ The reaction is schematically depicted in Figure 2.

Poly(4-vinylpyridinium chlorochromate) (30 g) was placed in a round-bottom flask containing 200 mL cyclohexane. The mixture was heated up to 75°C . To the magnetically stirring suspension 12 mL PDMS-OH in 50 mL cyclohexane was added in one portion, under stirring. The reaction was stirred at 75°C under reflux, overnight. Because of the use of polymer-bound catalyst poly(4-vinylpyridinium chlorochromate) it was possible to readily isolate the product. The filtrate was concentrated under vacuum on a rotary evaporator and the resulting product was analyzed by FTIR.

Oxidation of PF-OH

Hydroxy-terminated fluorinated polyether (Figure 3) was chemically modified in a similar way using the same reagent for mild oxidation as previously described for hydroxyl-functional PDMS chains to corresponding aldehydes.

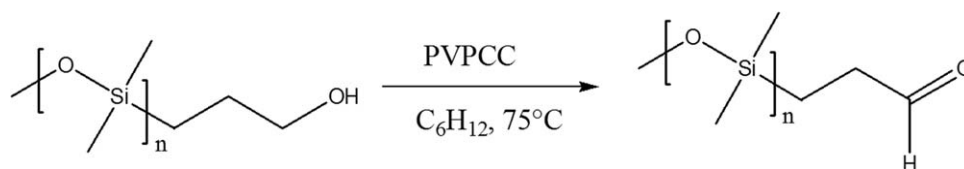


Figure 2. Schematic oxidation of OH-terminated polydimethylsiloxane.

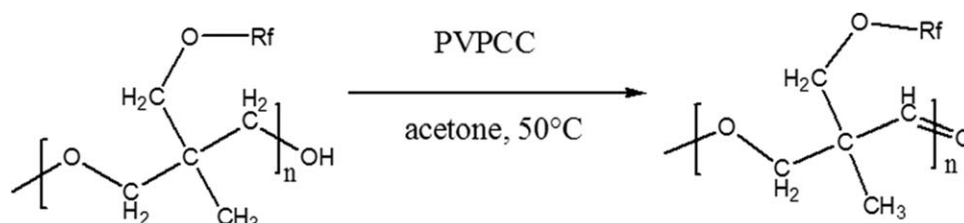


Figure 4. Schematic oxidation of OH-terminated fluoroether.

The reaction to the corresponding aldehyde catalyzed by poly(4-vinylpyridinium chlorochromate) is schematically depicted in Figure 4.

Poly(4-vinylpyridinium chlorochromate) (20 g) was placed in a round-bottom flask containing 150 mL acetone. The mixture was heated up to 50°C. To the catalyst suspension 10 mL PF-OH in 30 mL acetone was added in one portion under stirring. The reaction was further stirred at 50°C under reflux, overnight. Due to the use of polymer-bound catalyst poly(4-vinylpyridinium chlorochromate) it was possible to easily isolate the product by filtration. The filtrate was concentrated under vacuum on the rotary evaporator and the resulting product was analyzed by FTIR.

Surface Texture Measurement

Surface characterization was done using 3D-optical microscope Infinite Focus from Alicona Imaging, with 5× magnification. Average roughness of profile and average height of profile were measured for the standard matt melamine surface-finished particleboard.

Infrared Spectroscopy

Infrared absorbance spectra were recorded with a Bruker Tensor 27 FTIR spectrometer (Bruker Optik GmbH Ettlingen, Germany). The spectra were recorded with a scanning interval of 32 s in the spectral region 4000–600 cm^{-1} with a resolution of 4 cm^{-1} .

Contact Angle and Surface Energy

Contact angle measurements were performed with an OCA35 goniometer from DataPhysics with SCA20 software. The sessile

drop method was used where a 1.5 μL drop of test liquid was placed on the substrate surface and the contact angle values were recorded.

Contact angle measurements can be related to surface tensions or energies via Young's equation.¹⁴ The relation between the three forces at equilibrium present at the contact line of the liquid drop is described by Young's equation: $\gamma_{LV} \cdot \cos\theta = \gamma_{SV} - \gamma_{SL}$, where θ is the contact angle and γ is the surface energy at the liquid–vapor (LV), solid–vapor (SV), and solid–liquid (SL) interfaces. This equilibrium is the basis for the calculation of the surface tension/surface energy components and some models such as the Owens–Wendt–Rabel–Kaelble method (OWRK),^{15,16} distinguish a polar and a disperse fraction of the surface energy. The surface energy was calculated based on the contact angle values determined for water, ethylene glycol, and diiodomethane using the OWRK computation method.

Color Measurements

The efficiency of fingerprint removal was evaluated quantitatively by color measurements as follows: an area of the sample was contaminated with a fingerprint using squalene as a marker substance. The fingerprint was then removed with a cotton tissue by wiping several times and the so cleaned sample area was subjected to color measurement. For comparison, an uncontaminated region of the sample was also analyzed. Measurements were done according to the CIE $L^*a^*b^*$ system (1986), using a Color Eye XTH spectrophotometer from Gretag Macbeth, under simulated sunlight illumination (D65) at an observing angle of 10°. For evaluation of each sample, five measurements were performed and an average value was calculated.

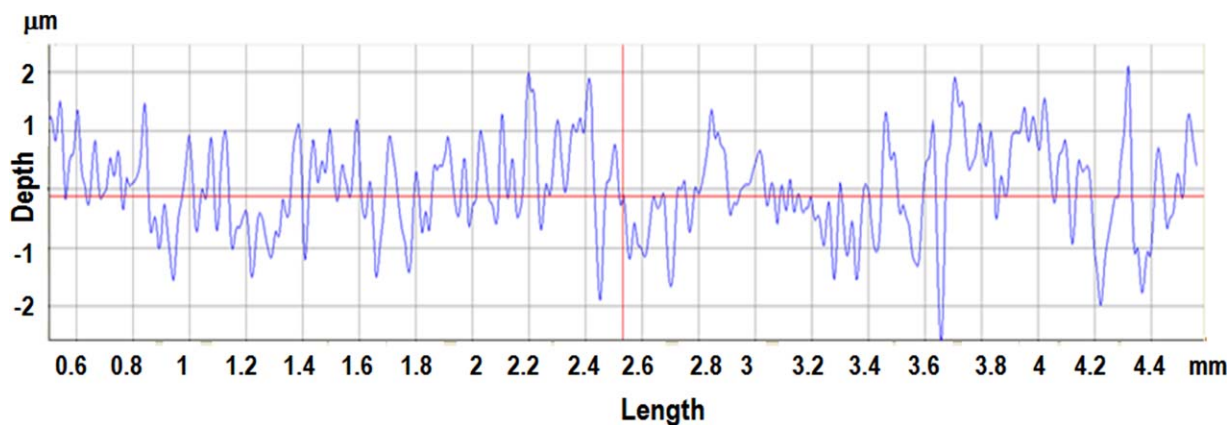


Figure 5. Roughness profile of smooth matt LPM laminated surface. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Table I. Contact Angle, Surface Energy, and Technological Values for the Laminated Surfaces Under Investigation

	Standard MF	Capstone FS81	TegoProtect 5100	Dynasylan F8815	Lipolase 100L	PF-CHO	PDMS-OH	PDMS-CHO
CA Water	79.8	84.6	96.5	79.0	87.7	27.4	92.1	108.5
(°) Ethylene glycol	59.6	58.3	76.7	58.6	66.3	47.5	68.9	87.3
Diodomethane	46.2	54.7	66.9	54.0	55.2	43.6	69.8	74.7
n-Hexadecane	26.3	35.2	39.4	37.1	38.1	44.7	41.1	54.8
Squalene	31.4	38.6	41.0	37.9	39.2	48.1	43.8	59.3
Surface energy (mN/m)	34.96	28.09	24.70	23.56	31.07	28.34	25.04	20.11
Polar	29.77	33.91	29.77	34.36	28.69	59.01	27.16	20.55
Disperse	6.86	3.66	1.14	5.67	2.73	31.84	4.94	0.27
Technol. Tests	4	4	4	4	4	4	4	4
Acid	4	4	4	4	4	4	4	4
Porosity	3-4	3-4	3-4	3-4	3-4	5	3-4	3-4
Adhesion	1	1	1	1	1	1	1	1
Gloss @85°	14.1	13.9	14.3	13.8	14	29.2	13.9	14

Surface Quality Tests

Adhesion. Cross-cut tests were done to evaluate the surface stability against mechanical damage. The degree of exterior layer delamination was assessed using the European Standard ISO 2409:2007,¹⁷ on a scale from 0 to 5. When the edges of the cut were completely smooth without any detachment of the coating, the cross-cut test scored a value of 0. For a high extent of flaking and delamination, the cross-cut test yielded a value of 5, which represents the worst rating.

Porosity. Porosity of a coated particle board gives an indication of the affinity of the surface toward dirt particles.¹⁸ Porosity was visually judged under a microscope after tinting an area of 25 cm² with soft pencil, subsequent rubbing out using a rubber and counting the remaining dark dots. The surface was classified according to an arbitrary scale from very good or “5” (no remaining stains of pencil) to very bad, or “1” (large areas of remaining pencil) in 0.5 unit intervals. Porosity values for laboratory boards above 3 indicate that crosslinking reactions are completed and a closed surface film has been formed.

Acid Value. The acid value of a coated particle board gives an indication of the chemical resistance of the surface.¹⁸ The acid value was determined by treating a defined surface spot with concentrated hydrochloric acid for 15 min. Afterwards the surface was microscopically classified according to an arbitrary scale from very good or “5” (no attack of the surface by the acid) to very bad, or “1” (surface completely destroyed) in 0.5 unit intervals. Acid values below 3 mean that the surface is hardly attacked by hydrochloric acid and the film quality is good.

Gloss. Gloss measurements were performed with a Novo Gloss Trio device from Rhopoint Instruments Limited, UK, at an angle of 20°, before and after polishing. The final gloss value was calculated as an average from five individual measurements.

RESULTS AND DISCUSSION

Surface Texture

In achieving hydrophobicity, the surface texture plays a crucial role. The work described here aims to identify possibilities to improve the cleanability of smooth, matt melamine laminates without surface texture, and roughness modifications. The studied surface (Figure 5) has a smooth texture obtained by lamination of MF-impregnated décor paper onto particleboard, using heat and pressure.

The roughness of a surface is considered as the arithmetic average deviation of its vertical irregularities: the finest peaks and valleys of surface morphology, and the planar surface.

3D microscopy measurements indicate a smooth surface, with average roughness of profile around 650 nm. Given the very low surface average roughness value, the increase in hydrophobicity is attempted chemically, without modifying surface roughness or gloss.

Reference Panels

A systematic screening of commercially available additives that are compatible with aqueous melamine formaldehyde prepolymer was first done in order to check if chemicals that have

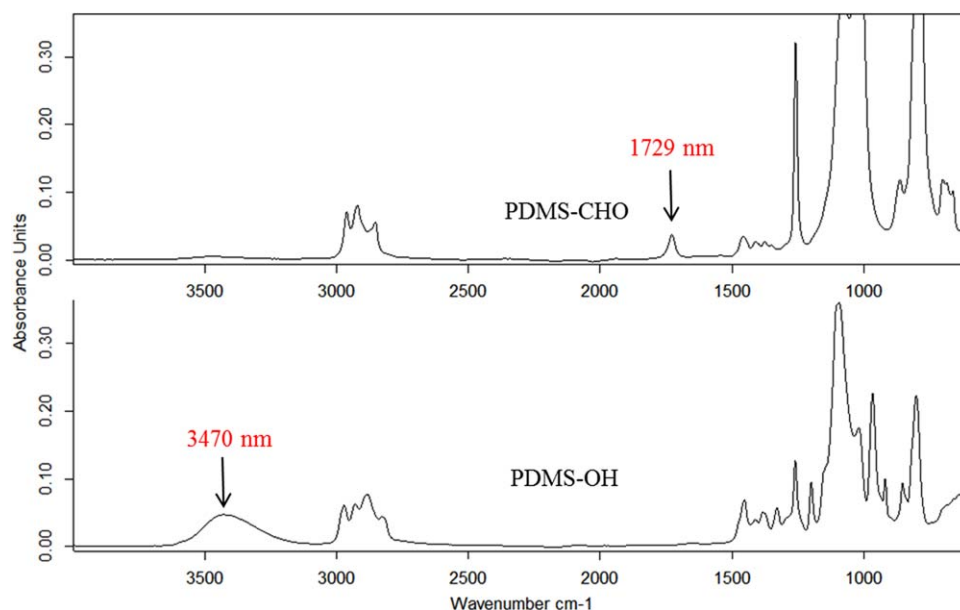


Figure 6. FTIR spectrum: oxidation of OH-terminated polydimethylsiloxane. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

proved to be increasing hydrophobicity and improving the cleanability of different water-based coatings will also have a similar effect for MF finishes. The maximum achievable effect was then used as a benchmark to assess the performance of the novel modified polymeric additives in relation to unmodified MF films and MF films modified with commercial additives.

Among the materials that are known to provide low surface energy the most commonly used is polydimethylsiloxane (PDMS).^{19–22} The water repellency of PDMS is due to the flexible —Si—O—Si—O— backbone that allows the methyl groups covalently

attached to the Si atoms to face towards the surface, thereby creating a water-repelling barrier and its low surface tension. Since the methyl group has the lowest surface tension next to the fluoromethyl group, the properties of silicone modified surfaces are often comparable to perfluorinated materials. Perfluoroalkyl polymers are known to possess surfaces of very low surface energy and not only display very good hydrophobicity but are also very repellent towards stains and oils.^{23–25} The small dipole moment of these compounds contributes to their oil and water repellency as well as to their low surface tension, low refractive index, low friction coefficient and reduced adhesion to surfaces.^{26,27}

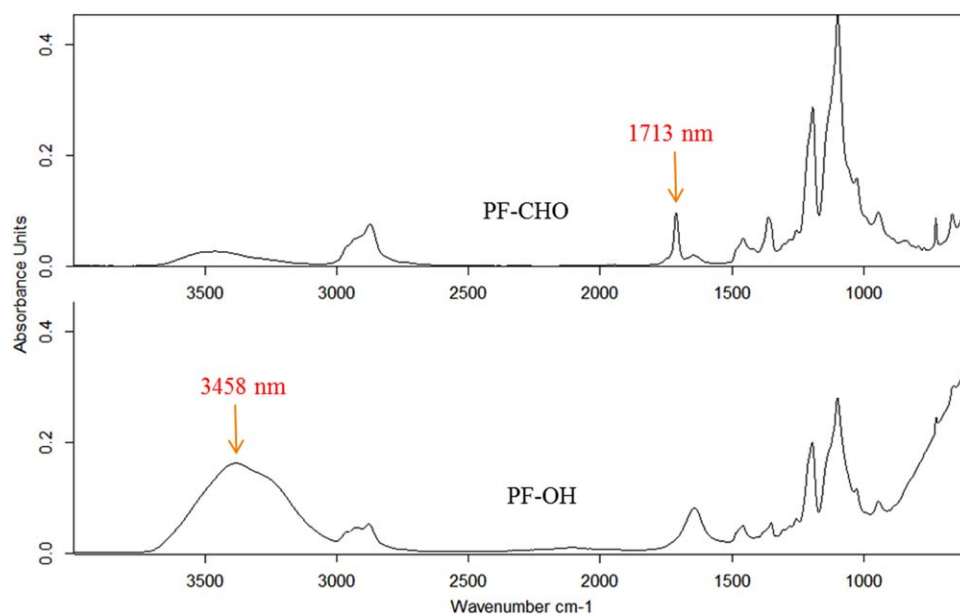


Figure 7. FTIR spectrum: oxidation of OH-terminated fluoroether. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

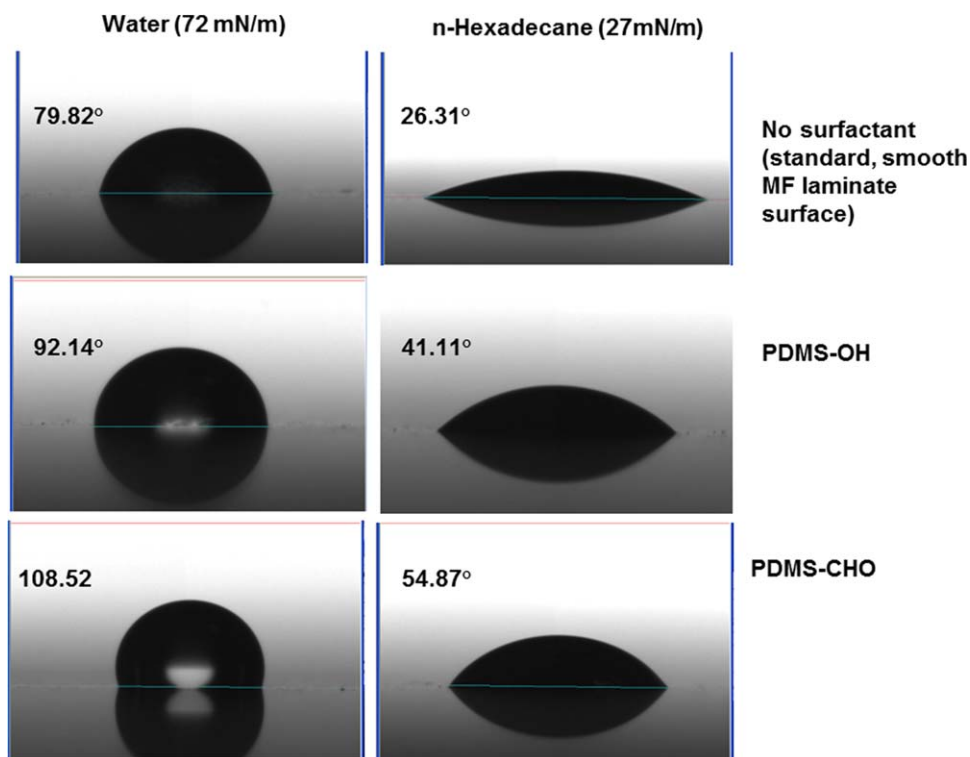


Figure 8. Goniometer contact angles photos for the MF surfaces under investigation with water and n-hexadecane. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Hydrophobic and oleophobic surfaces with low surface energies can be obtained by using silanes with polyfluoroalkyl substituents.^{28–30}

In the preliminary tests, the selected surfactants were incorporated in the MF resin formulation by hand-impregnation. Measured static contact angle values for the LPM surfaces prepared using these materials are summarized in Table I.

As compared with the contact angle (CA) values for the laminated surface containing no surfactant: CA = 79.8° for water and CA = 26.3° for n-hexadecane, the best results (highest contact angle values for water and n-hexadecane) were obtained



Figure 9. Fingerprint application and removal after 10 double-rubs Left: Matt LPM laminate with standard resin; Right: Matt LPM laminate with PDMS-CHO. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

with PDMS-OH and Tego Protect 5100. As such, the CA values measured with these surfactants were around 95° for water and around 40° for n-hexadecane. At concentrations above the critical micelle concentrations, contact angle values had either decreased, or remained constant.

Chemically Modified Surfactants and MF Resin

Oxidation of Hydroxy-Functional Surfactants. A successful hydrophobic coating must eliminate hydrogen bonding and shield polar surfaces from interaction with water by creating a nonpolar interphase. Hydroxyl groups are the most common sites for hydrogen bonding. In this approach, two highly polar hydroxy-terminated surfactants were selected for oxidation with pyridinium chlorochromate.

According to the supplier, PF-OH [Figure 3(a)] is a reactive waterborne fluorosurfactant based on poly(oxetane) polymer that is used in water-based coatings to decrease surface energy.

PDMS-OH [Figure 3(b)] is a reactive hydroxyl-terminal surfactant based on polydimethylsiloxane that orientates itself directly to the coating surface giving the coating both hydrophobic and oleophobic properties. At the same time, it reduces the polar part of the coating system's surface tension, thereby improving the cleanability of the coating.

In a first attempt the oxidation reaction to aldehyde was catalyzed by pyridinium chlorochromate, an orange powder soluble in the reaction medium. The reaction proceeded very fast at room temperature as within 5 min from addition of the alcohol to the catalyst solution the reaction changed color from orange

Table II. Colorimetric Measurements to Determine Surface Cleanability

Reference	L^*	a^*	b^*				
Reference (No Fingerprint)	28,65	-0,06	-0,73				
Sample	L^*	a^*	b^*	DL*	Da*	Db*	DE*
Reference-Fingerprint_after 10 double rubs	24,11	0,28	0,18	-4,54 D	0,34 Rö	0,91 Ge	4,64
Reference	L^*	a^*	b^*				
PDMS-CHO_(No Fingerprint)	28.12	-0,02	-0,74				
Sample	L^*	a^*	b^*	DL*	Da*	Db*	DE*
PDMS-CHO-Fingerprint_after 5 double rubs	27,79	-0,03	-0,53	-0,33 D	-0,01 Gr	0,20 Ge	0,39

to dark brown. Although the reaction was successful still the product purification proved to be very difficult and in the end traces of catalyst were still present in the product. In order to facilitate reaction work-up the polymeric derivative of pyridinium chlorochromate (an insoluble powder) was used as catalyst. Reaction with poly(4-vinylpyridinium chlorochromate) allowed for an easy reaction work-up and facilitated isolation of the pure oxidized product, that could be recovered simply by filtration.

Successful oxidation of PDMS-OH was evidenced by the decrease in intensity of the —OH broad band at 3470 cm^{-1} and the peak formation at 1729 cm^{-1} that indicates formation of the carbonyl group of the aldehyde upon mild oxidation (Figure 6).

PF-OH was oxidized using a similar procedure, in acetone, using the surfactant's terminal hydroxyl groups. Successful oxidation of PF-OH is evidenced by the significant reduction in peak intensity of the —OH band of 3458 cm^{-1} observed for the modified chain. Also, a new peak was formed at 1713 cm^{-1} indicating the formation of the carbonyl bond (Figure 7).

The oxidized polydimethylsiloxane (PDMS-CHO) and the oxidized fluoroether (PF-CHO) were used in paper impregnations. The impregnated papers were laminated on particleboards using the matt surface finishing.

Additionally, contact angle measurements were done with squalene and n-hexadecane, as an increased contact angle for oils indicates surface oleophobicity. Photographs of the recorded contact angles are presented in Figure 8 as a comparison between the standard surface prepared without surfactant, the surface formulated with PDMS-OH and the surface obtained with the oxidized polydimethylsiloxane PDMS-CHO.

Contact angles were measured for test liquids of different surface tensions: water, ethylene glycol, and diiodomethane, in order to calculate the surface energy. The contact angle values for the different surfaces are accumulated in Table I.

The water contact angle value of 108.5° obtained for the laminated surface prepared with the oxidized polydimethylsiloxane indicates a hydrophobic surface. At the same time the contact angles for oils (n-hexadecane and squalene) indicate improved

oleophobic properties for the PDMS-CHO modified chain. The low surface energy value of 20.55 mN/m and the polar part reduced to 0.27 mN/m are in agreement with the contact angle values obtained.

In literature it has been described the unusual case when static hexadecane contact angle is greater than static water contact angles as is the case with PF-CHO.^{31–34} This type of surface behavior is characteristic for self-cleaning coatings and oil resistant coatings.

Fingerprint Application and Color Measurements. To test fingerprint removal off the deep-matt melamine surface-finished laminate, fingerprints were carefully applied using minimal amounts of squalene, a component of the human sebum that can also be found in shark liver and certain plants. Color measurements were made to determine the color difference upon manual fingerprint application (Figure 9) and removal attempts. The results are commonly expressed as cleaning efficiency (cleaning index) based on lightness L^* values measured from soiled and cleaned surfaces of the sample.^{35,36}

In the case of the present MF laminate surfaces the spot where a fingerprint was applied appears darker (black) as compared with an uncontaminated spot. The color difference was measured with the spectrophotometer, using the Lightness values before and after fingerprint removal, the values are presented in Table II.

Measured color differences (DL and DE) indicate that the applied fingerprint was removed after 5–7 double-rubs on the surface prepared with PDMS-CHO, while on the standard surface (without surfactant) a darker spot still remains after fingerprint application and removal attempts, even after 10 double-rubs.

CONCLUSIONS

In preliminary experiments, typical commercial fluorinated and siloxane-based surfactants were tested as additives in low pressure melamine films for their potential to increase surface hydrophobicity and oleophobicity of the laminate. They were selected based on their compatibility with melamine and were tested in paper impregnation for the preparation of MF-coated particleboards with improved hydrophobicity and oleophobicity

related to antifingerprint and dirt release properties. Although contact angle measurements indicated a clear increase in values for water and n-hexadecane with some of the commercial surfactants, still, the improvements in removing fingerprint marks were not statistically significant.

Hydroxyl groups of PDMS-OH were oxidized in mild conditions with poly(4-vinylpyridinium chlorochromate) that allowed an easy reaction work-up and product isolation. By mild oxidation to aldehyde the chain has become more nonpolar according to IR spectrum and less involved in surface hydrogen bonding. Use of the functionalized chain in the preparation of LPM laminates resulted in surfaces with low surface energy and increased contact angles for water: 108.5°, n-hexadecane: 54.8° and squalene: 59.3°. Although the contact angle for water is not considered very high, still, the oleophobicity had an important contribution as the easy-to-clean performance was increased and the surface maintained the technological values of the laminate from before modification.

The contact angle values as well as the low surface energy calculated for this surface were supported by colorimetric results. Colorimetric lightness difference measurements showed that a fingerprint applied on the surface prepared with oxidized siloxane surfactant could be removed by 5 double-rubs with a textile cloth from the surface while from the standard surface after 10 double rubs the fingerprint mark would still be very far from being removed.

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