

EFFECTS OF DUAL CURE AND SURFACE TREATMENTS ON COATING ADHESION TO DIFFERENT SMC-SUBSTRATES

Stacy M. Trey¹, Mikael Lundström,² Daniel Ståhlberg³, and Mats Johansson¹

¹ Dept. of Fiber and Polymer Technology, The Royal Institute of Technology, 10044 Stockholm, Sweden

² Becker Industrial Coatings AB, Box 2041 S-195 02 Arlandastad, Sweden

³ Scania CV AB, SE-151 87 Södertälje, Sweden

ABSTRACT

Sheet molded compound (SMC) is a highly filled, glass fiber reinforced, thermoset material used in trim and body panel automotive parts. When SMC-substrates are coated with conventional thermally cured paints, inherent porosity and entrapped volatiles of the substrate result in popping (“paint pops”) defects. UV-curable primers (UVP) provide an order of magnitude reduction of paint defects in SMC coatings, but typically have poor adhesion. The present study investigates a series of UVPs, showing the effect of resin functionality and isocyanate additive content on the adhesion of the coatings to SMC substrates. The SMC formulation is also considered regarding how variables such as surface chemistry, morphology, surface area, and degree of post mold emissions affect UVP adhesion. The present study reveals the crucial factors involved in achieving adhesion including the importance of low post-mold emissions, high surface areas, glass fiber and other oxygen moieties on the surface, and improved wetting of the surface.

1. INTRODUCTION

Sheet molded compound (SMC) is a highly filled, glass fiber reinforced, thermoset material used in trim and body panel automobile parts. It is beneficial over traditional steel in that it imparts not only lighter weight, but also improved stiffness and shatter resistance. Some problems are however associated with SMC-substrates when these are to be coated with conventional thermally cured automotive paints. As a consequence of inherent porosity and entrapped volatiles, popping paint defects (“paint pops”) appear during the curing process. The defects in the final finish require significant resources both to detect and repair them.[1] UV-curable primers (UVP) as an alternative coating provide an order of magnitude reduction of paint defects in SMC coatings while reducing floor space requirements, capital investment, and process times in comparison to molding and in-mold coating.[2] However, UV-curable coatings have poor adhesion due to the low surface free energy of polymer substrates, coating shrinkage, and reduced swelling of the coated substrate in comparison to solvent based formulations.[3]

Previous work confirms that the chemistry of dual cure UVPs affects adhesion, with the addition of solvent and isocyanate in additive quantities significantly enhancing interaction of the primer with the substrate, resulting in superior adhesion.[4] Additionally the best adhesion was observed on SMC substrates in which the surface area was increased by sanding or sanding then flaming the surface. The present work investigates not the coating, but the effect of the differences in the substrate, in this case the SMC formulation, on adhesion of UV primers.

There are many different additives that are combined with the basic SMC formulation consisting of unsaturated polyester, catalyst, glass fiber, and inorganic fillers.[5,6,7] In order to toughen and improve the impact strength of thermoset polyesters such as SMCs, liquid rubbers with reactive functional groups have been added. These liquid rubbers, such as styrene butadiene rubber, are added to the uncured resin and upon curing precipitate as particles of a few microns dispersed throughout the matrix.[8] Typically the rubber is added at 15 parts of rubber to 85 parts polyester.

Regarding low profile additives (LPA), poly(vinyl acetate) (PVAc) is commonly added to SMC systems. PVAc has been shown to delay kinetics and gel time of the polyester while inhibiting overall cure shrinkage by providing a large degree of thermal expansion in PVAc rich domains in the early stages of curing. Additionally within these domains, microvoids occur in later cure which is also effective against cure shrinkage. Similar to rubber additives, PVAc is typically added at 14 wt% and induces a phase separation upon cure, resulting in an interconnected globular morphology.[9]

Concerning mold release agents, calcium stearate is commonly added (>2 wt%) in order to ease release of the part from the mold. [10] It is theorized that the stearate becomes insoluble in the resin during cure and migrates to the surface to form a more hydrophobic layer and thus less adhesion of the part to the mold. [11]

These additives all alter the surface chemistry and post-mold emissions that result from the SMC. Thus they must be considered and evaluated when determining the impact on adhesion of UVPs to different SMC substrates.

The present study investigates a dual-cure approach to address both the popping defect problem and the poor adhesion of UV-curable primers. An initial UV-curing will seal the SMC-surface and subsequent thermal cure of isocyanate containing formulations will improve the adhesion. The effect of different pre-treatments of the SMC-substrate including sanding and flaming will be investigated. This will be performed on three different SMC formulations in order to determine how the variation in SMC formulation chemistry, amount and character of volatiles released after molding, and surface morphology and topography affect adhesion.

2. EXPERIMENTAL

2.1 Materials. The photoinitiator used was Irgacure 651 (2,2-dimethoxy-2-phenylacetophenone) from Ciba Specialty Chemicals, the flow additives BYK 333 and BYK 361N from BYK Chemie, and a 50/50 solvent mixture of Xylene/Butyl acetate from Beckers. The reactive diluents used were 1,6-Hexanediol diacrylate (HDDA) from Cytec, ethoxylated trimethylolpropane triacrylate (SR454) from Sartomer and a mixture of pentaerythritol tri- and tetra acrylate (Petia) from Cytec. Diisocyanate diacrylate Laromer[®](LR9000) from BASF, provided isocyanate moieties for thermal cure. Resins used were Ebecryl[®] 4858 and Ebecryl[®] 270, both aliphatic urethane diacrylates from Cytec, and Ebecryl[®] 1259 from Cytec and Photomer[®] 4174 from Cognis, which are both aliphatic urethane triacrylates.

2.2 UVP Formulations. Two difunctional (EB4858 and EB270) and two trifunctional resins (EB1259 and Photomer 4174) were chosen as base resins in the different UVP-formulations. Equal amounts of di (HDDA), tri (SR454), and 3.5 functional (PETIA) reactive diluents were used at 15.7 wt% each. Furthermore, two different levels of isocyanate functional monomer (L9000) were applied, 0 and 5 wt %. The base formulation contained 36.7 wt% resin, 36.7 wt% reactive diluent, 4.35 wt% irgacure 651, 0.39 wt% of the wetting agents Byk 333 and Byk 361N, 11 wt% Xylene and 11 wt% butyl acetate.

2.3 Preparation of substrates. SMC coupons of 30 x 30 x 0.25 cm dimensions were received, cut into approximately 15 x 15 cm, and washed with 2-propanol to remove surface contaminants. A general formulation for SMC plates is 9.9 wt% polyester resin, 13 wt% styrene resin, 1.5 wt% thermoplastic resin, 45.87 wt% CaCO₃, 28.0 wt% of Fiberglass 1" chop, and additive amounts of catalyst, mold release agents like zinc stearate, magnesium oxide. [12]

Three SMC formulations were evaluated; BoPreg 117 (substrate **C**) from Polytechnic AB, and formulations 646-A (substrate **A**) and 664-B (substrate **B**) from Reichhold. All formulations were molded for 2.5 minutes at 150-153°C. The differences in the base

formulations of the three are listed in Table 1. PVAc solution (sltn) and PolyLite 661-000, unsaturated polyester resin, were used in all three formulations.

Table 1: Formulation differences in the three evaluated SMC formulations.

Substrate	Polymer	Additive polymer	Release agent	Catalyst
A	PolyLite 661-000	PVAc sltn, styrene butadiene rubber (SBR)	Byk-P 9080	t-butylperoxy 2-ethylhexyl carbonate (TBEC)
B	PolyLite 661-000	PVAc sltn, saturated polyester, hydroxyethyl methacrylate (HEMA)	Byk-P 9080	t-butylperoxy 2-ethylhexyl carbonate. (TBEC)
C	PolyLite 661-000	PVAc sltn, Saturated polyester	Calcium stearate	t-butylperbenzoate (TBP)

The surfaces were subjected to various surface treatments to enhance adhesion properties. Flaming was performed with a flame torch with a mixture of 50 % butane and 50 % propane. The blue flame was about 1 – 2 cm from the substrate and passed rapidly twice (approximately 1 m/s). The sanding was done manually using sandpaper with roughness number 600. The different surfaces are hereafter denoted with an (F) for flamed, (S) for sanded, (S/F) for sanded and flamed, and (NT) for no surface treatment.

2.4 Film formation. All formulations were applied on the SMC substrates using a rod-applicator of 24 mils, giving a dry film thickness of 30 microns. The films were then left for a flash-off period for 5 minutes at 65 °C before they were UV-cured with a dose of approximately 1.35 J/cm² using Fusion electrodeless D-bulbs. The thermal post-curing of isocyanate containing formulations was performed in convection ovens at 90 °C for 30 minutes after UV-curing.

3. INSTRUMENTATION

3.1 Contact angle. Static contact angle measurements were performed for the SMC surface modified sheets using a KSV contact angle meter, CAM 200 (Helsinki, Finland). The values reported were taken after the contact angle had reached a stable value, usually 2 s after deposition of the droplet. The average of 10 measurements is reported.

3.2 Confocal scanning laser microscopy (CSLM). An Olympus OLS3000 confocal microscope equipped with topography software was used. Images were also recorded in the non-confocal mode (conventional dark-field and bright-field light microscopy).

3.3 X-ray photoelectron spectroscopic analysis (XPS). XPS surface analysis was carried out on a Physical Electronics Quantum 2000, using a monochromatic Al X-ray source ($h\nu=1486.86$ eV). An initial survey spectrum was recorded and then for surface analysis of oxygen and carbon a 45° angle monochromatic Al K α X-ray source operated at 25.3 W and a pass energy of 58.7 eV was used. Although SMC samples of approximately 2.5 x 2.5 cm were introduced into the spectrometer, the area of the specimens sampled by the analyzer electron optics was 100 μ m x 100 μ m. The energy scale was calibrated by setting the CH_n carbon 1s binding energy at 285.0 eV and the oxygen 1s binding energy to 531.5 eV. Relative peak intensities were measured and the averages of triplicate measurements are reported.

3.4 High pressure water jet adhesion test (HPA). Adhesion of the primers to the SMC surfaces was also determined by the water spray under high-pressure test according to Volvo Car Corporation STD 1029,5471. An X is made on the film and 50°C water at 150 bar, 100 mm from the sample for 1 minute at 1 sweep per second. The reported value is % flaking of the primer.

3.5 Headspace gas chromatography-mass spectrometry (GC-MS). Vials containing 1 cm³ SMC cubes and 2 μ L of para-methylstyrene standard were thermostated for 30 min

at 90 °C in a Perkin-Elmer 101 headspace device. The air from the vial was then injected into a Perkin-Elmer 8500 model GC coupled to an ion trap detector (ITD) mass spectrometer to separate and identify volatile products. The column used was a DB-225 (50%-cyanopropylphenyl)-methylpolysiloxane, 30_0.32 mm) from J&W scientific (Folsom, CA). The column temperature was held 8 min at 40 °C and then programmed to 200 °C at 5 °C=min.

3.6 Cross-cut test. Adhesion testing of the primers on SMC surfaces was achieved by cross-cut test equipment according to Volvo Car Corporation STD 1029.5472 which conforms to ISO 2409-1992. Excellent adhesion in which no coating is removed is assigned a 0 and a 5 is assigned if more than 65% of the coating is removed.

3.7 Determination of solvent and resin uptake. The solvent and resin uptake was determined gravimetrically by weighing samples before and after immersion in the tested solution. Immersion time was 1 hour and the subsequent weight was recorded. At least three specimens of each sample type were tested. A top-loaded Mettler AE 100 balance with resolution 10⁻⁵g was used.

4. RESULTS AND DISCUSSION

4.1 Effect of UVP-formulation and surface pretreatments on adhesion.

The UV cure formulations based on the 4 different resins and 0 wt % isocyanate content, were coated on the three SMC formulations with 4 different substrate treatments and then cured. The adhesion of these primers were tested by crosshatch adhesion and almost all non treated (NT) and flamed (F) SMC surfaces yield values of 5, with very poor adhesion. The exception to this is Eb270 based primer on SMC A-NT and A-F, with a value of 4 and Photomer 4174 based primer on A-NT with a value of 3. The sanded (S) and sanded/flamed (S/F) surfaces result in improved adhesion of UVPs. (Figure 1a.) Overall there is better adhesion on surface A in comparison to B and C. This is especially apparent for Eb 4858 and Eb 1259 based resins.

With the addition of 5 wt% isocyanate moiety to the UVP formulations, there is an overall enhanced adhesion of the formulations to the SMC surfaces regardless of the surface treatment. (Figure 1b.) Similarly, the adhesion improves on substrates A and B in comparison to C. Surface treatment still plays a significant role in adhesion, as seen by the better adhesion of UVP on all SMC formulations with S and S/F surfaces in comparison to NT and F.

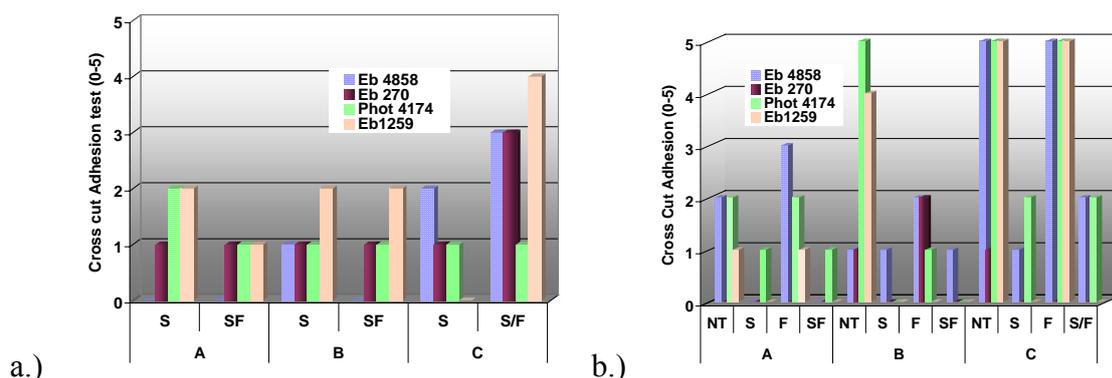


Figure 1: Cross cut adhesion test of a.) UVP's on S and S/F SMC surfaces, 0 wt% LR9000 b.) UVP's containing 5 wt% LR9000.

The adhesion of the UVP containing 0 wt% isocyanate on different SMC surfaces measured with the water jet high pressure adhesion test yields similar results as the cross hatch adhesion tests. (Figure 2a.) NT and F SMC surfaces all give values of 100% flaking with the exception of Eb 4858 on substrate B-NT in which there is only 80% flaking. There is a difference between the adhesion of Eb1259 UVP on surface A, with 100 % flaking compared to surfaces B and C in which less than 5 % flaking was seen.

Conversely, Eb 4858 UVP gave flaking of <85% on S/F **B** and **C** composites and 0 flaking on **A**-S/F. The reasons for this could be attributed to differences in surface chemistry or differences in post mold emissions of the SMC since the surface roughness is analogous.

With the addition of 5 wt% LR9000 to the UVP formulation, there is an overall increased adhesion. (Figure 2b.) The adhesion of UVP on **C**-NT and **C**-F substrates is the weakest and shows improvement on **B**-NT and **B**-F with the best adhesion on **A**-NT and **A**-F surfaces. This correlates to the post mold emissions of the SMC's which is further discussed later. S and S/F surfaces still display the best adhesion due to the enhanced surface roughness. An interesting point is that there seems to be no correlation of functionality or equivalent weight of the UVP resin to the adhesion. This indicates that cure shrinkage does not play a significant role in adhesion as measured with cross cut and HPA detection methods.

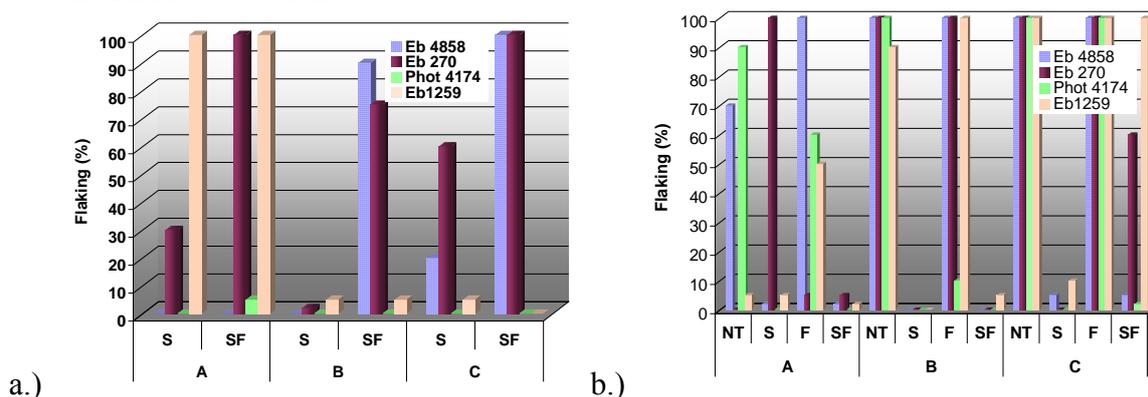


Figure 2: (a.) High pressure adhesion (HPA) test with only sanded and flamed SMC substrates, 0 wt% L9000 b.) HPA test with 5 wt% L9000.

4.2 Effect of surface properties of the SMC-substrates.

XPS-analyses were performed on the different substrates to further examine if the SMC additives and surface treatments substantially affect the chemistry of the substrates and thus the adhesion of UVP. (Figure 3.) With surface treatments involving sanding and flaming, oxidation is expected as denoted by an increase in the peak intensity at 531.8 eV and an increase in the peak at 288 eV signifying the presence of carbonyls. This increase does occur in all treated surfaces of **A** and **B** substrates in comparison to the NT. Similarly, the carbon signal for **A** and **B** decreases in all treated samples indicating that the presence of polymer at the surface is either oxidized or displaced to expose fillers and glass. This is most likely due to exposure of fillers including glass.

It is worth mentioning that **C** does not have as sizable drop in the carbon signal as the **A** and **B** substrates. It is possible that the surface of **C** is not as efficiently oxidized or that the filler on the surface due to calcium carbonate is constant regardless of the surface treatment. Additionally, **B**-NT does not show a significant increased amount of oxygen on the surface from the HEMA. This suggests that HEMA is not enriched at the surface to any great extent.

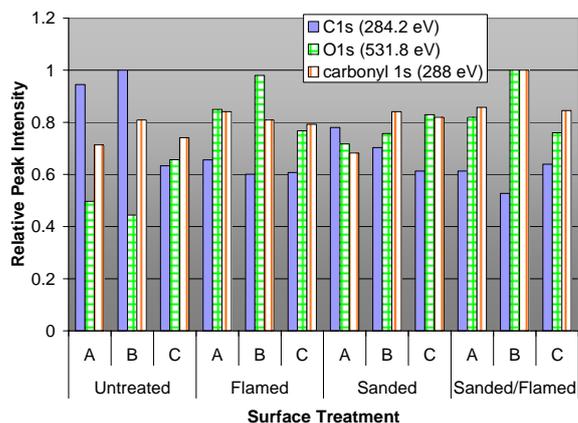


Figure 3: XPS of the three SMC surfaces with different surface treatments.

Contact angle studies were performed in order to extrapolate more about the surface chemistry of the three different SMC substrates, Since the SMC is of very heterogeneous composition on the micron scale, and the difference in surface roughness is considerable from sample to sample, it is impossible to base any confidence on surface free energy calculations. Therefore, the wettings of the different SMC substrates were compared using the two solvents and two reactive diluents. (Figure 4.) It is apparent that the **A** and **B** substrates give better wetting of the solvents with xylene having the best wetting indicating more hydrophobic surfaces. Petia overall gave the least amount of wetting, possibly due to the higher viscosity. Petia contains a hydroxyl group per molecule indicating that the SMC surfaces increase in hydrophobicity from **A** to **B** to **C**. Surface roughness may also play a role. The enhanced wetting of all solvents and resins on **A** over **B** and **C** formulations directly correlates to better adhesion of UVPs.

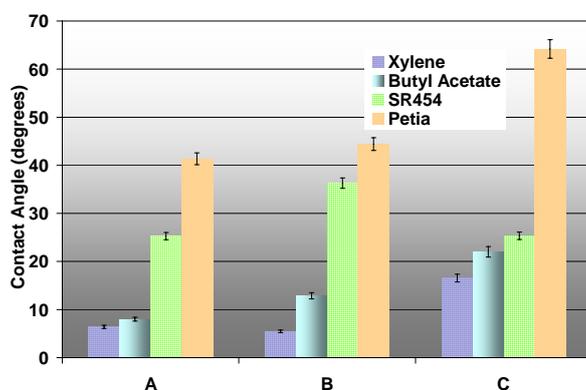


Figure 4: Degree of wetting of solvents and reactive diluents on the three SMC formulations.

4.3 Effect of emission from the different SMC-substrates

The quantification of emission of volatiles from cured SMC molded plates has been a point of interest in the past 20 years. Furthermore, there has always been an effort to reduce these volatiles in order to reduce paint defects that could result. Since there is a difference in the SMC formulations, it is important to understand how this affects the post mold emissions and if there is a correlation to the adhesion of UVPs. It was seen from the headspace GC results that **A** has the least amount of styrene emissions in comparison to **B** which is lower than **C**. (Table 2.) The lower values of **A** and **B** may be due to the change in initiator and also the mold release agent. **A** uses SBR and **B** uses HEMA with saturated polyester additives. There needs to be further studies as to why formulation **A** has much lower emissions in comparison to **B**. It is clear that with the change in initiator and mold release agent in **A** and **B** that the emissions are much lower

in comparison to **C**. Additionally, there is a parallel between lower emission SMC formulations and better adhesion of UVP.

Table 2: Emissions from the three SMC substrates in this study.

Sample	Run 1	Run 2	Avg styrene ($\mu\text{l/g}$)
A	0.01	0.01	0.01
B	0.56	0.72	0.64
C	1.48	1.80	1.65

The lower emissions of **A** and **B** in comparison to **C** may also be the result of the change in catalyst. TBP has less efficient initiating sites and has shown to create benzene based small molecules that volatilize from the SMC in post molding. TBEP, is a more active initiator with a higher initiating efficiency. (Figure 5.)

With more efficient initiating sites, there is an increased chance that fragments of the initiator will tie into the growing chains instead of volatilizing from the material after post-molding. Higher conversion of the styrene is achieved and thus a reduction in the residual styrene content. Additionally in comparison to benzene based initiators, there is no formation of benzene.¹³ This may also contribute to the lower emissions of **A** and **B** formulations compared to **C**.

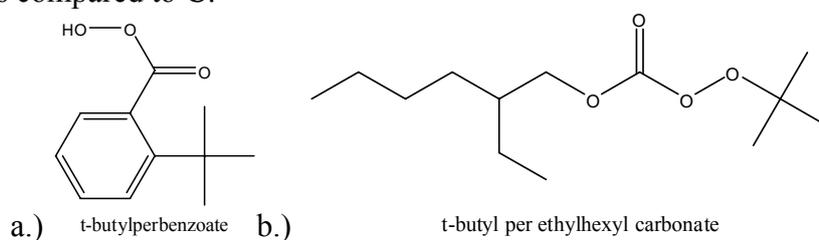


Figure 5: Initiators used in the SMC formulations studied in this study. a.) t-butylperbenzoate b.) t-butyl per ethylhexyl carbonate.

4.4 Effect of surface morphology and surface area of the SMC-substrates.

In order to determine if the morphology of the SMC's surface has a large effect on the adhesion of UVPs, confocal imaging was used to determine the surface area, composition, and morphology. As seen in Figure 6, SMC **A**-NT (a) and **B**-NT (b) both show homogeneous and relatively flat surfaces with the exception of pores indicating styrene release during the curing/molding process. This is not apparent in SMC **C**-NT (c) and is ascribed to why there are more post-emissions of styrene from SMC **C** since there is no evidence of styrene volatiles escaping during molding. Also the surface of **C**-NT is much more heterogeneous with filler appearing at the surface which was confirmed by the high intensity of the carbon peak in the XPS measurement. It is difficult to correlate these morphologies to adhesion of UVPs since all NT surfaces resulted in equally poor adhesion of UVP.

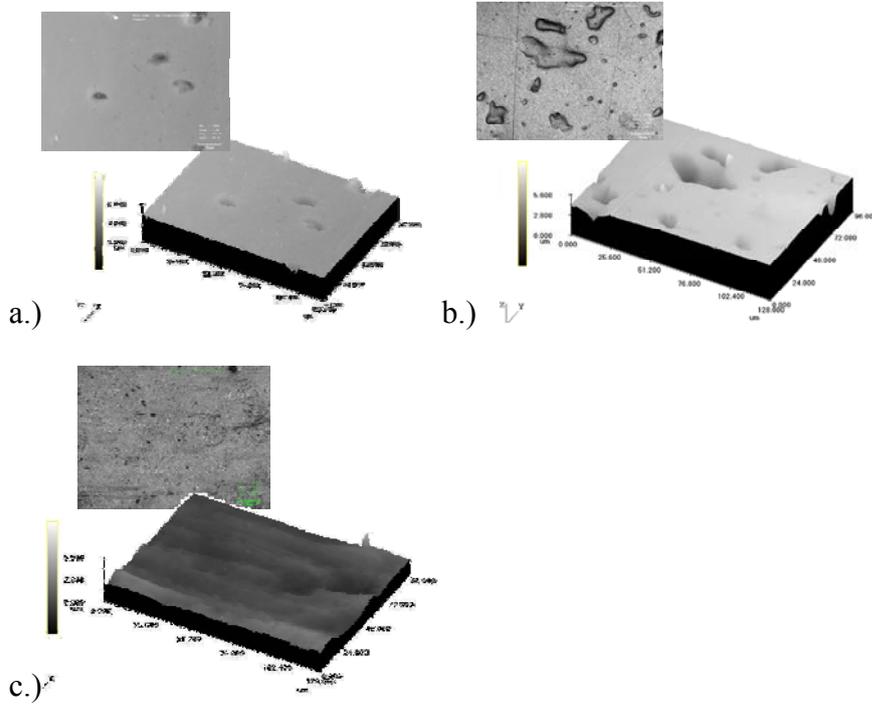


Figure 6: Untreated SMC substrates (a.) **A** (b.) **B** and (c.) **C**.

The flamed surfaces for all SMC formulations show very flat surfaces devoid of any morphology. They also had equally poor adhesion of UVPs which result from the lower surface area.

The sanded surfaces however exhibit a totally different surface structure. SMC **A-S** (Figure 7a) shows the appearance of filler and glass fibers and an increased surface area. This is also the case with **A-S/F** (Figure 7b) but the flaming exposes the glass fibers more as the polymer is removed. Both of these surfaces show better adhesion than the NT and F surfaces.

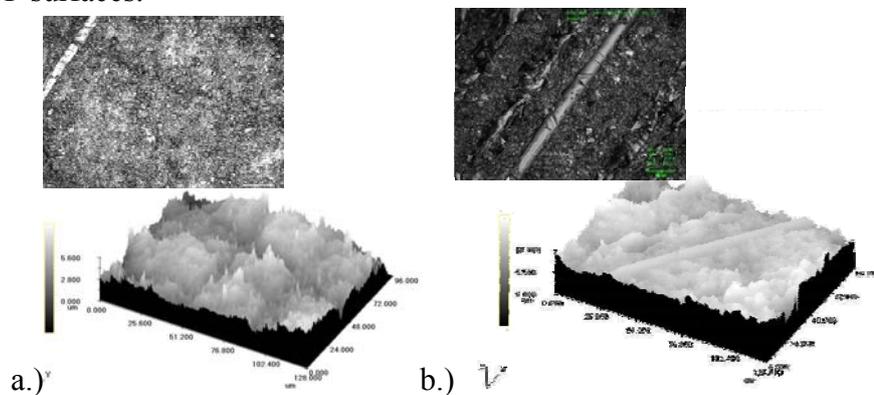


Figure 7: SMC **A** a.) sanded and b.) sanded and flamed. (128 x 96 μm)

The surfaces of **B-S** appears to have more surface area than **A** and the same trend is seen with glass fibers exposed more in **B-S/F** surfaces than in **B-S**. (Figure 8) Additionally **A** and **B**, S and S/F surfaces give similar adhesion behavior of UVPs meaning that a large factor in improved UVP adhesion is the enhanced surface area and morphology of the substrate.

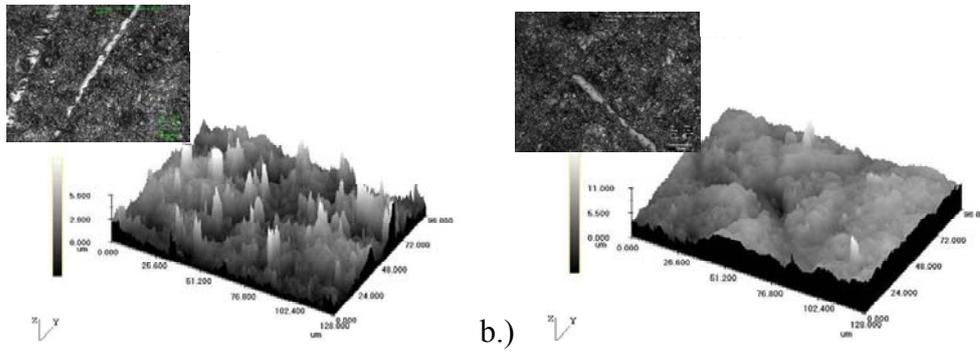


Figure 8: SMC **B** a.) sanded and b.) sanded and flamed. (128 x 96 μm).

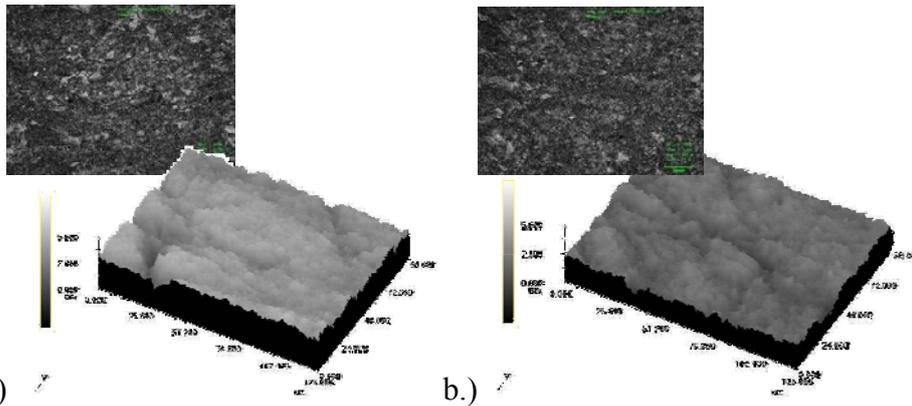


Figure 9: SMC **C** (a.) sanded and (b.) sanded and flamed. (128 x 96 μm).

Conversely to surfaces **A** and **B** SMCs, glass fibers are not uncovered in the **C-S** and **C-S/F** surfaces, with fillers at the interface, but not as much of a height difference in peaks and valleys as observed by confocal imaging. (Figure 9 a and b) This coincides with poor adhesion of UVPs to substrate **C** in comparison to **A** and **B**. The topography also demonstrates the effect of no HEMA or SBR additive which results in a flatter morphology.

Substrate ratio of surface area to projected area values were calculated from the 128 x 96 micron surfaces. (Table 3.) The higher surface areas of the S and S/F surfaces compared to NT and F correlates to greater adhesion of UVPs to these substrates. However, worse adhesion of UVPs to **C**, although having a higher surface ratio, indicates that the also chemical makeup of the surface plays a role in adhesion with no glass fiber revealed at the surface and peak to valley ratio being much lower than **A** and **B**.

Table 3: Ratio of surface area to projected area calculations($S (\mu\text{m}^2)/A (\mu\text{m}^2) \pm 0.005$)

Substrate ratio of surface area to projected area	No Treatment	Flamed	Sanded	Sanded/Flamed
A	1.016	1.002	1.201	1.243
B	1.098	1.020	1.305	1.250
C	1.078	1.134	2.168	2.085

CONCLUSIONS

This research concludes that changing the SMC formulation does influence the degree of adhesion of UVPs. Better adhesion of UVPs were those containing 5 wt% isocyanate functional monomer, SMC formulations containing the catalyst TBEC over TBP, and those having lower post mold emissions.

Additionally regarding surface morphology, those substrates with greater peak to valley height ratio and not necessarily total surface area were important factors in ensuring better adhesion performance of UVPs. Moreover, substrate **C** showed no visible fibers

which may have been contributing factors to the improved adhesion of UVPs to surfaces **A** and **B** over **C**.

Although this research has answered many questions about different SMC formulations and their effect on UVP adhesion, there are many questions that have arisen and would be of interest to investigate in the future. Topics include the effect of the mold release agent and how this changes the surface properties and subsequent UVP adhesion. Additionally of interest would be to investigate what the mechanism of post-mold emissions from the SMC is in terms of disruption of cure of the UVP and how this disrupts coating adhesion.

ACKNOWLEDGMENTS

Authors would like to thank the following suppliers for providing materials and for assistance with conducting experiments: Beckers IC, Sartomer, Cytec, BYK, Cognis, BASF and Ciba, and Polytec Composites Sweden AB. Also Dan Jacobsson and his help in use of Kimab's confocal laser imaging instrument and Björn Atthoff for his expertise in XPS. VINNOVA/PPF, grant #2005-01757 and the KAMI Research Foundation are appreciatively acknowledged for their financial support. Sonny Jönsson is gratefully acknowledged for his valuable discussions on the project topic.

REFERENCES

- 1- Abrams L.M. and Castro J.M., "Powder Coating of Sheet Molding Compound (SMC) Body Panels". *Polymer Composites*, 2001; 22: 702-709.
- 2- Brandl, C., "Radiation Curing for the Automotive Market" *SAE Technical Paper Series*, 1996; 960916.
- 3- Villeneuve S., Wolf J-P., et al. "New Priming Technology Adhesion Performance of UV-Curable Coatings on Plastic." *JCT Coatings Tech*, 2004; May.
- 4- Trey, S., Sidenvall, P., Alavi, K., Ståhlberg, D., Johansson, M., "Effects of Dual Cure And surface treatments on coating Adhesion to SMC Substrates" submitted to *Progress in Organic Coatings*, January 2008.
- 5- Rodrigues, J. A., Marques, A. T., "The influence of flame retardant agents in the fire performance of SMC" *Material Science Forum*, 2004; 455-456: 849-852.
- 6- Atkins, K.E. "SMC: Thinner — Smoother — Tougher a New Generation of Low Profile Additives" *Journal of Elastomers and Plastics*, 1982; 14: 117-135.
- 7- Smith, C. L.; Fisher, D. H. "Dimer acid derivatives as enhancers" Sept 9, 2003; US patent 6617394, Ashland Inc.
- 8- Rodriguez, E. L. "Effect of a reactive styrene-butadiene block copolymer on some mechanical properties of fiberglass reinforced composites" *Journal of Materials Science Letters*, 1990; 9: 1362-1364.
- 9- Bulliard, X.; Michard, V.; Månson, J. A., "Low-profile mechanisms in polyester/PVAc blends" *Polymer Engineering and Science*, 2006; 46: 303-313.
- 10- Serre, C.; Vayer, M; Erre, R., "Behavior of internal mold release agent during BMC thermosets composites cure and aging" *Journal of Materials Science Letters*, 2001; 20: 1989-1991.
- 11- Karbhari, V.M., "Effect of Internal Mold Release Agent on the Cure and Property Variation in Resin Transfer Molding Composites" *Journal of Materials Science Letters*, 1998; 17: 2061.
- 12- Dillard, J. G., Burtoff, C., Buhler, T, "Surface Chemical Study of Sheet Molded Composite (SMC) as Related to Adhesion" *Journal of Adhesion*, 1988; 25: 203-227.
- 13- <http://www.arkema-inc.com/literature/pdf/299.pdf> "Luperox® JWEB50: An initiator for higher molecular weight PS and improved productivity" accessed March 20, 2008, posted by Tim McKinney, March 2005 by Arkema Inc.