

RECENT ADVANCES IN CLASS A POLYURETHANE LONG FIBER INJECTION (LFI) COMPOSITES

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Abstract

Recent advancements in the Polyurethane (PU) Long Fiber Composite Injection (LFI) process have resulted in a dramatic increase in its commercial interest for producing a wide range of products including PWC's, entry door skins, truck body and spa panels. One of the main reasons for this success is a development in the polyurethane chemistry of the LFI process that allows long gel times on an open hot mold yet maintains a relatively short demold time. The chemistry and processing of LFI material will be discussed, with emphasis on structure/property relationship, density reduction through dissolved CO₂, and in particular, the development of high surface quality (Class A) composites. We developed two technologies to obtain Class A surfaces on LFI parts: 1) the use of an in-mold, hybrid polyester gel coat which serves both as a barrier to glass read-through as well as the glossy surface; 2) an in-mold polyurethane paint. This technology to produce Class A composites with paint involves the use of in-mold paint, followed by a unique polyurethane barrier coat spray designed to resist both thermal and mechanical deformation, and finally the addition of the long fiber PU material. The use of the polyurethane barrier spray in conjunction with LFI serves to shorten demold time as well as improve the surface quality by preventing the glass from showing through the surface.

However, the use of a barrier spray does not guarantee a good surface, because it can easily be both thermally and mechanically deformed by the reacting LFI, which often results in surface waviness described as orange peel. In this presentation we will describe a new class of PU barrier coat which resists deformation, thus resulting in composite materials with very low orange peel, as measured by a smoothness index of 9 or greater.

Introduction

One of the major challenges to PU Long Fiber Injection Technology has been the formation of defect-free Class A surfaces. The nature of the LFI process makes it difficult to produce such surfaces because the process itself deposits a mixture of glass PU and air onto the mold surface which results in air bubbles trapped on or near the surface of the part and glass read-through. One way to overcome these surface defects is to deposit a PU barrier coat between the in-mold paint and the LFI composite. While this eliminates surface defects and the glass read-through, it creates a new problem - increased orange peel. This is attributed to two factors: barrier coat deformation due to heat generated from the LFI reaction and the difference between the coefficients of linear expansion between the various layers.

LFI Technology

LFI is a fast growing composite molding technology: chopped glass fibers and liquid PU components are dispensed simultaneously into an open heated mold. The PU components are metered into a specialized mixing head which also chops the glass fiber to specified variable lengths (0.5 to 4 inches long) and coats them with the mixed urethane liquid components. A robot then accurately and consistently positions the yet un-reacted components into the open cavity of a heated mold. After the pour is complete the mold is closed for a specified time. Later the mold is opened and the part is removed.

One of the early challenges to the advancement of LFI technology was its inability to make large parts because current mixing equipment has a maximum through put of 1 to 1.5 lbs. / sec of polyurethane. Therefore, it was up to the PU chemical design to create a longer gel time. Recent developments in polyurethane chemistry for use in the LFI process has extended the gel time on the heated mold to about 120 seconds, as discussed below, enabling the production of large glass reinforced parts weighing more than 200 lbs.

Gel Time

By controlling the chemistry we are able to extend Gel time on a hot mold, while maintaining a relatively short demold time: Table 1 shows various chemical systems developed and compares Gel time at 70°C versus its demold time. It is important to note here that the gel time determines material flow within the mold, as well as the quality of the part surface. If the material starts to gel prior to mold closing, incomplete mold fill and poor surface result. Therefore, proper selection of gel time to part volume is critical.

Table 1

Gel time, sec at 70°C	Demold , min	Demold, min with barrier coat
30	3	1.5
45	4	3
70	6	5.5
120	20	7

However, lower density LFI systems present a special challenge - since the addition of water as an environmentally friendly blowing agent also decreases the gel time of the systems, it became important to develop a blowing agent which does not impact the gel time of the polyurethanes. So, dissolved carbon dioxide (CO₂) was introduced as the blowing agent. Careful control of the amount of carbon dioxide in either the polyol or the isocyanate is key, as one must stay below the solubility limits of CO₂ in the components, if not, large bubbles will form in the parts. Figure 1 shows the froth density of the polyol at or below its solubility limits. By employing this technology, one can vary the density of the composite by adjusting the amount of CO₂ dissolved in the polyol. By doing so, none of the other process parameters need to change. Table 2 shows properties of LFI composites at various densities, made with 30 wt% glass fibers.

Figure 1

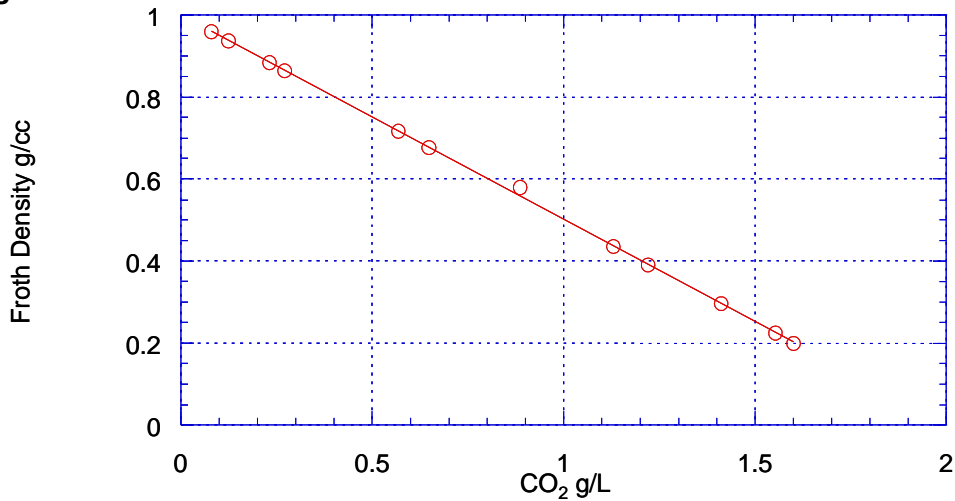
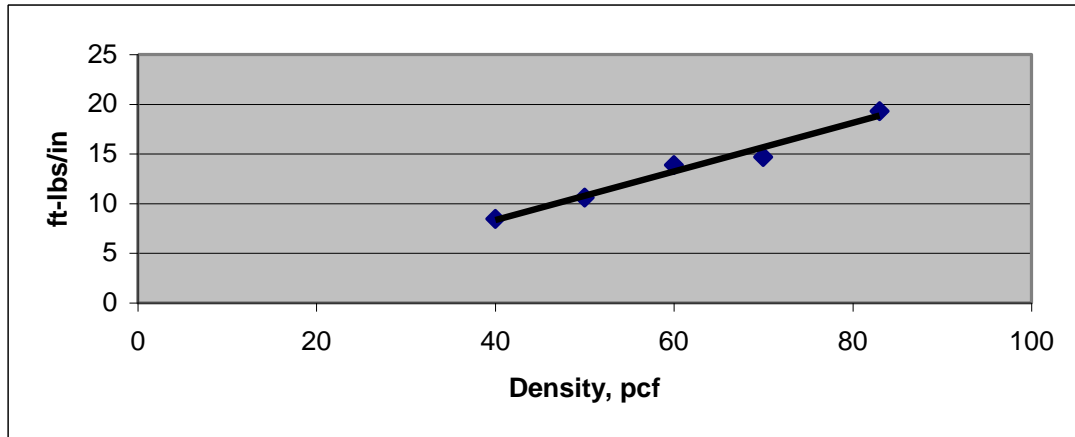


Table 2

[CO ₂] in polyol, g/l	0	0.6	0.8	1	1.2
Composite Density, g/cc	1.33	1.12	0.96	0.8	0.64
PU Density, g/cc	0.93	0.78	0.67	0.56	0.45
Inst. Dart Impact, ft-lbs	8.66	7.18	7.2	5.6	3.7
Un. Izod Impact, ft-lbs/in	19.278	14.678	13.876	10.58	8.456
Flexural Strength, psi	38,390	35,773	33,354	15,196	11,066
Flexural Modulus, psi	1,302,088	1,207,804	1,044,759	576,637	382,836

Additionally, Figure 2 shows un-notched Izod Impact properties of parts made with the same system but made with different densities by simply controlling the amount of CO₂ dissolved in the polyol.

Figure 2: Un-notched Izod of LFI at various densities made with dissolved CO₂



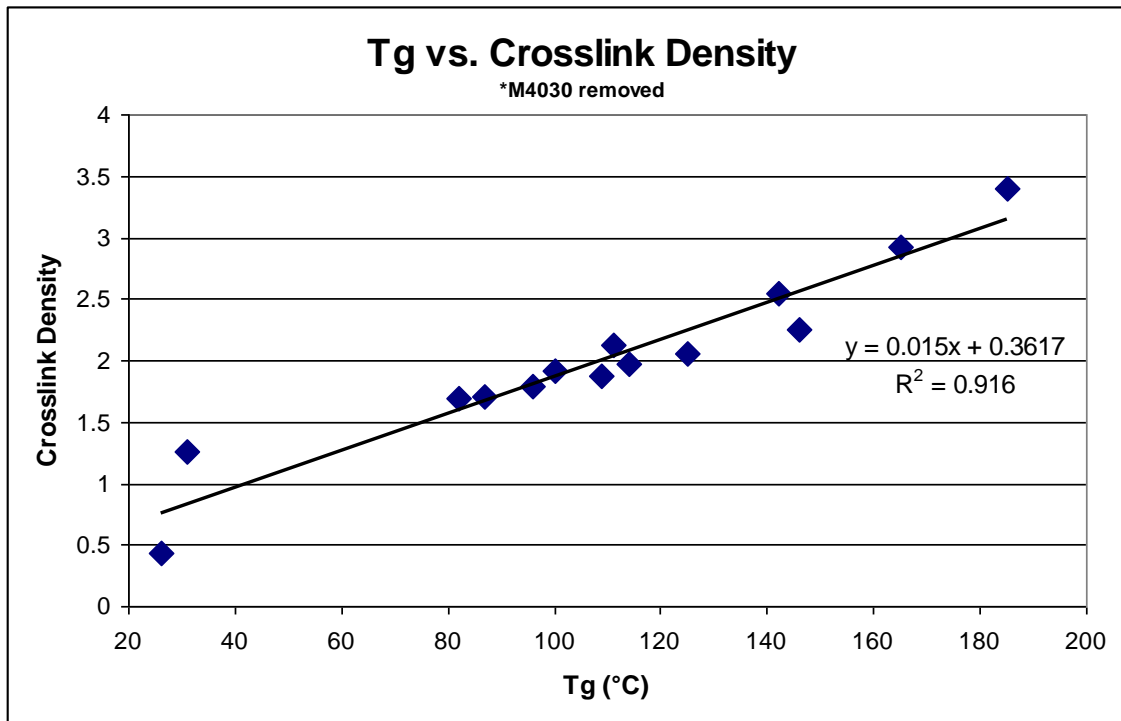
Barrier Coat Technology

An attractive feature of polyurethane LFI technology is the elimination of post painting, as the technology allows in-mold painting commonly done on non-smooth Class A surfaces, such as parts with a grained surface. The demand for Class A surfaces, however, has grown over the years, and until recently LFI was capable of delivering such a high quality surface only through the use of painted thermoplastic film. However, our development concentrated on a less costly alternative to painted film, and it involved spraying a polyurethane thermosetting film as a barrier coat between the in-mold paint and the LFI. The PU thermosetting film provides protection for the thin in-mold paint from glass read-through caused by the LFI process. The development of the proper barrier coat material is critical however, in that it can by itself cause surface defects due to deformation from the heat of the LFI reaction and the differences in the coefficient of linear expansion between it and the LFI composite. This new class of barrier coat was developed to have a high glass transition temperature and a low roughness value as determined by Atomic Force Microscopy (AFM).

Effect of Crosslink Density on T_g

There are several ways to increase the glass transition temperature of polyurethanes: a typical PU will have a low soft segment transition which is responsible for the elastomeric properties of polyurethanes such as elongation and impact, and a hard segment glass transition which is responsible for such properties as stiffness and heat. The hard segment transition can be increased by increasing the crosslink density of the system as shown in Figure 3.

Figure 3

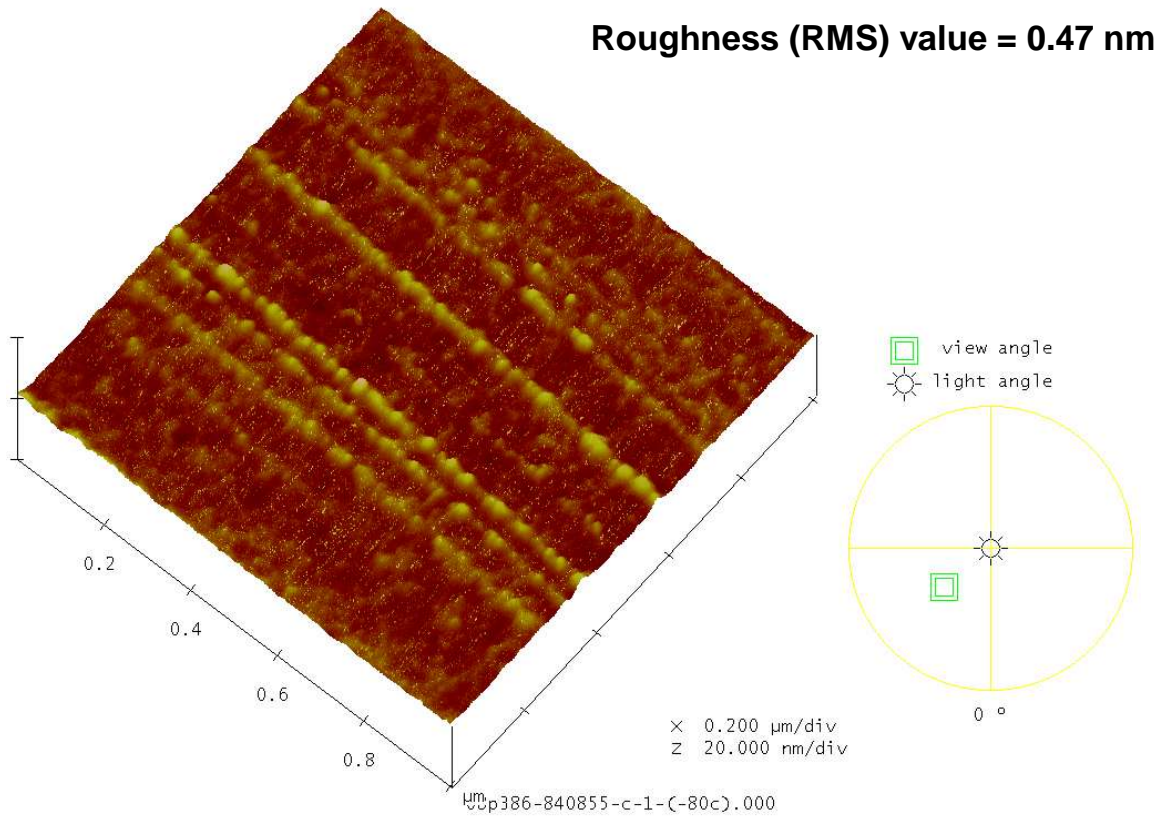


AFM

The quality of the barrier layer for providing a good Class A finish was determined by (AFM). AFM measures the deflection of a micro scale probe brought about by forces on the surface of the specimens, and change due to chemical bonding through Van der Waals forces. AFM is capable of resolutions of a fraction of a nanometer. It is superior to SEM in many aspects including its ability to produce three dimensional images, and does not need special surface treatment or high vacuum, as does SEM.

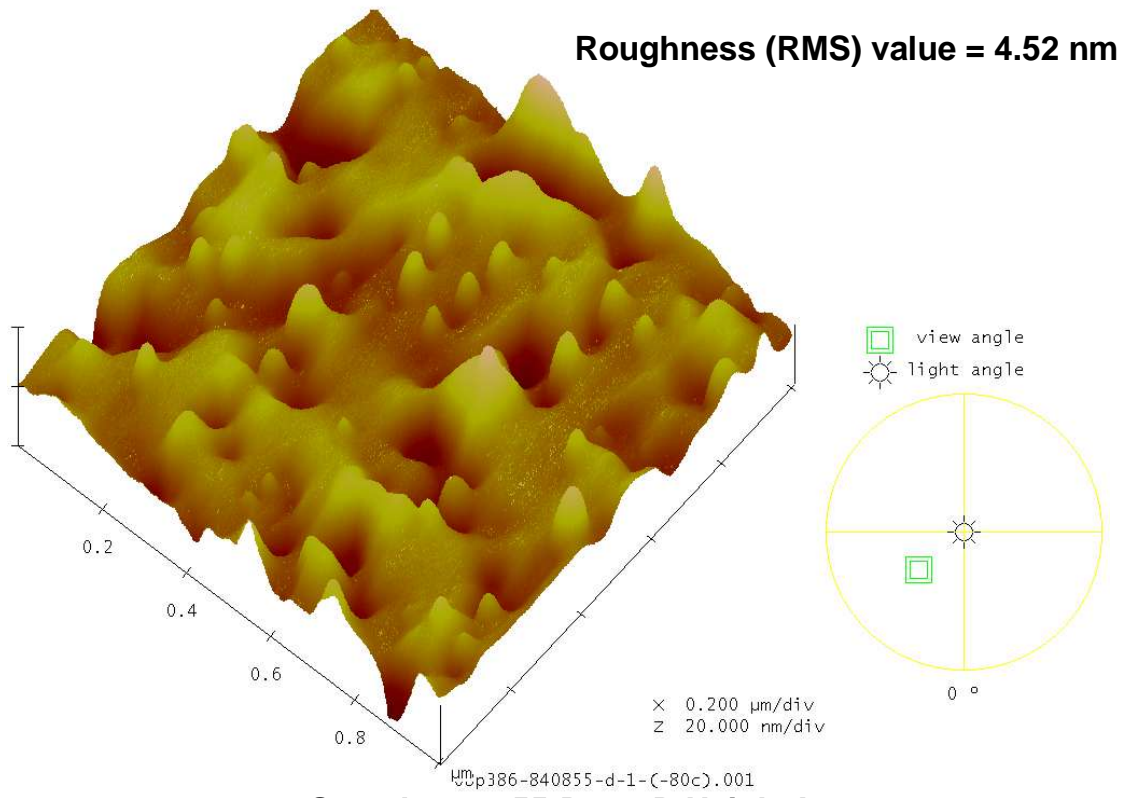
Samples C and D are two different barrier coats of different technologies. Sample C, which has a hard segment glass transition temperature of $>160^{\circ}\text{C}$ when used in the LFI process, provides excellent Class A surfaces with low orange peel as determined by a smoothness index of 9. While sample D, which exhibits a glass transition of $<100^{\circ}\text{C}$, provides poor surfaces with a smoothness index below 6. Examination of AFM 3D height data (Figures 4 and 5) shows a distinct difference in the surface roughness and is calculated to have Root Mean Square (RMS) values of 0.47 and 4.52 for samples C and D, respectively. RMS is a statistical parameter determined by the AFM software and is used as a quantitative measure of the extent of surface roughness. This parameter measures deviations of the surface heights from a reference height, namely, the average height, as a function of the surface coordinates x and y). The differences in the sample smoothness are attributed to the hard/soft segment morphology of the PU. The morphologies of the two samples are shown in Figures 6 and 7, and shows the hard segments are more uniformly distributed in the cross-section of sample C compared to sample D, (light colored areas), The hard segment sizes for sample C range between 8.7 and 16 nm, while those of sample D range between 16.7 and 48.6 nm.

Figure 4



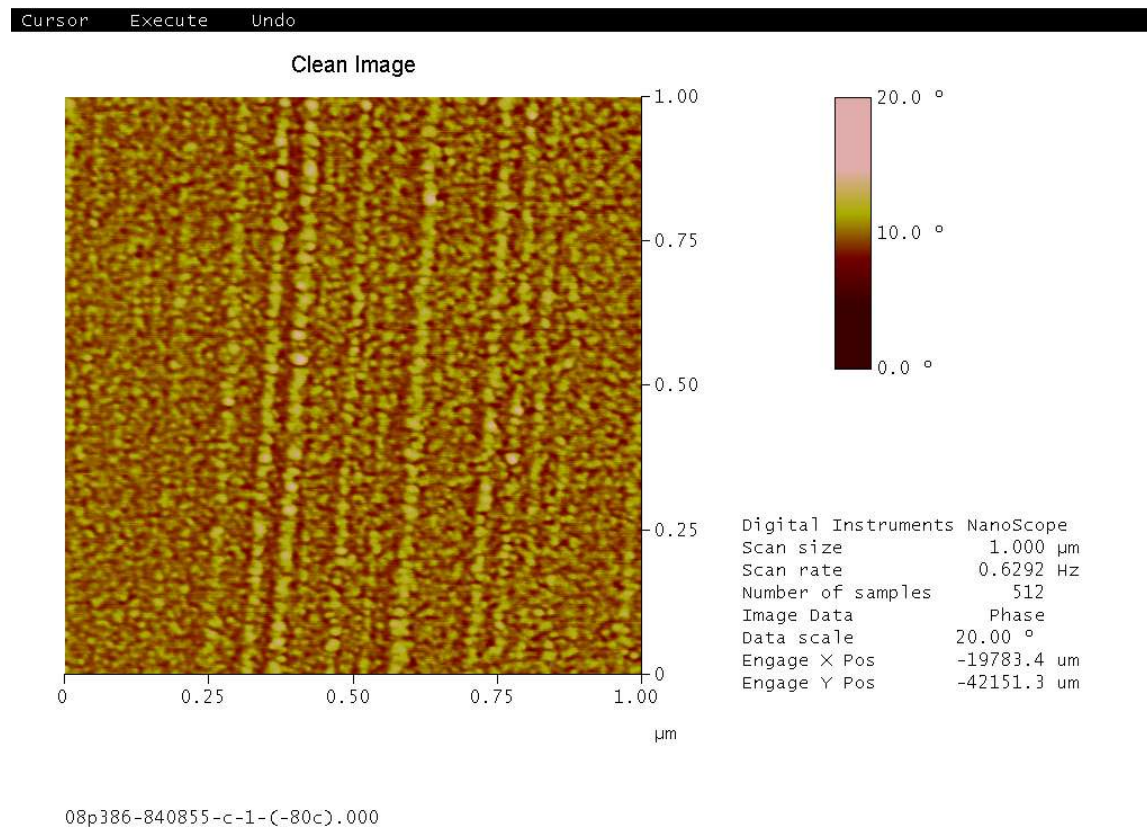
Sample 840855-C- - 3 D Height Image

Figure 5



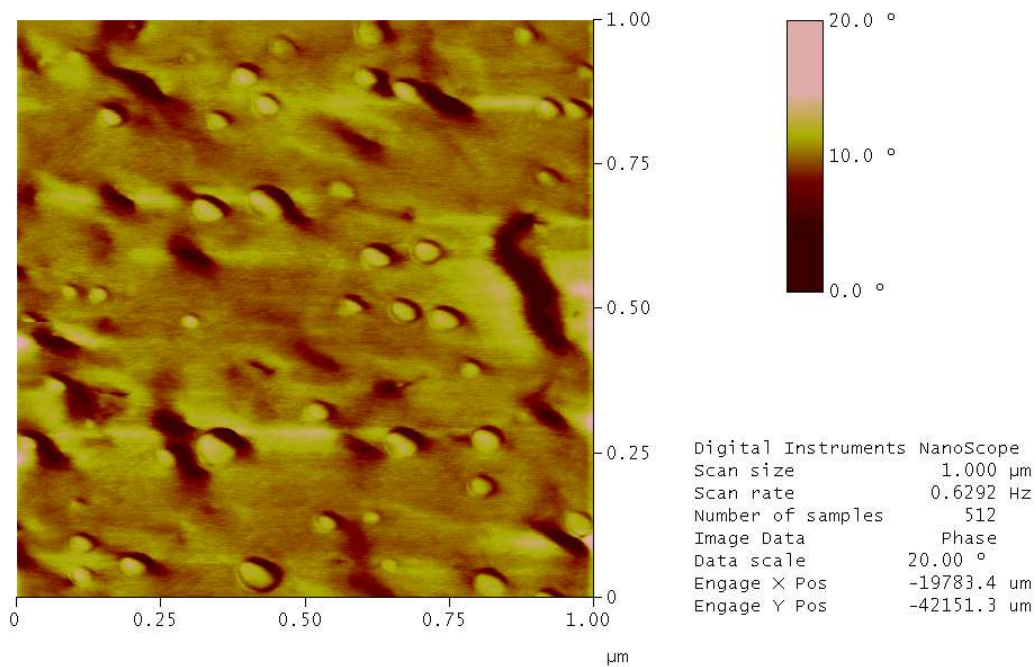
Sample 840855-D- - 3 D Height Image

Figure 6



Sample 840855-C- - 2 D Phase Image

Figure 7



Sample 840855-D- - 2 D Phase Image

Conclusion

Two technologies are available to produce Class A surfaces on large LFI composite parts: hybrid polyester gel coat, and an in-mold polyurethane paint. The hybrid polyester gel coat is specially designed to improve adhesion between the outer polyester layer and the polyurethane LFI system. Depending on its thickness, it may be used alone or with a barrier layer. The in-mold paint technology, on the other hand, must be used with a specially designed polyurethane barrier layer. This is necessary due to the very thin nature of the paint layer, which by itself is not capable of hiding the glass read-through.

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Biography

Dr. Usama Younes is a Principal Scientist in Polyurethanes at Bayer Material Science LLC. He holds a bachelor of science degree in Chemistry from Warren Wilson College, a master's degree in Inorganic Chemistry from Western Carolina University and a Ph.D. in Organic Chemistry from the University of New Orleans. After a two-year fellowship at Carnegie Mellon University, Dr. Younes worked at ARCO, Lyondell and Bayer. He's been responsible for new developments in polyurethane Long Fiber Injection technology. He holds 46 US patents and 100 foreign patents, and has authored 15 scientific publications.