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Development of Class A Surface Polyurethane LFI Composites

by
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Abstract

Recent advancements in the Polyurethane 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 while maintaining 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 layer to the 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 any 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 best 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 the PU Long Fiber Injection Technology has been the formation of defect-free surfaces, which can lead to 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 entrapment of air bubbles on or near the surface of the part. It also deposits glass fibers onto the surface, resulting in glass read-through. One way to overcome the surface defects due to both bubbles and glass 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 in increased orange peel. This is attributed to two factors: barrier coat deformation due to the 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. It involves dispensing chopped fibers and polyurethane liquid components simultaneously into an open heated mold. The polyurethane components are metered through a urethane metering machine and delivered into a specialized mixing head which chops the glass fiber to a specified and variable length (0.5 to 4 inches long) and coats it 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 a 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 LFI has extended the gel time on the heated mold to about 120 seconds, as discussed below, allowing for production of glass reinforced parts in excess of 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 70C 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 will result. Therefore, proper selection of gel time to part volume is critical.

However, lower density LFI systems present a special challenge, namely 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. Dissolved Carbon Dioxide was implemented. 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 in the parts will result. 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 at will by just 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. Additionally, Figure 2 shows un-notched Izod Impact properties made with the same system but made with different densities by simply controlling the amount of CO2 dissolved in the polyol.

Barrier Coat Technology

An attractive feature of polyurethane LFI technology is the elimination of post painting parts, as the technology allows in-mold painting commonly done on non smooth Class A surfaces such a parts with a grained surface, The demand for Class A surfaces, however, grew over the year, and until recently LFI was capable of delivering such a high quality surface only through the use of pained 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 will provide 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) as described below.

Effect of Crosslink Density on Tg

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.

AFM

The quality of the barrier layer for providing a good Class A finish was determined by (AFM). AFM, which measures the deflection of a micro scale probe brought about by forces on the surface of the specimens, and change due to chemical bonding, Van der Waals, etc, 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 deg. 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 deg. C, provides poor surfaces with a smoothness index of less than 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 of the samples. 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 that of sample D range between 16.7 and 48.6 nm.

Conclusion

Two technologies are available to produce Class A surfaces on 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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Farhad Cama for his AFM work

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.

Tables and Figures:

Figure 1

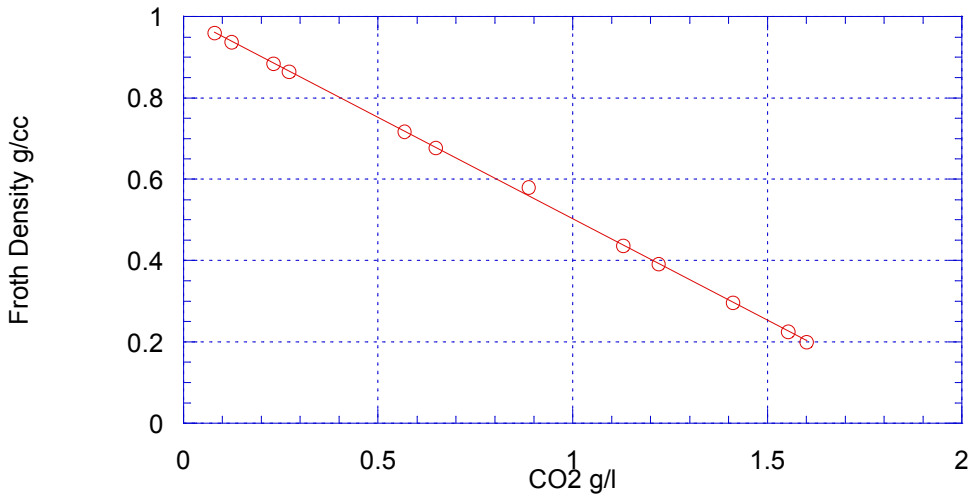


Figure 2

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

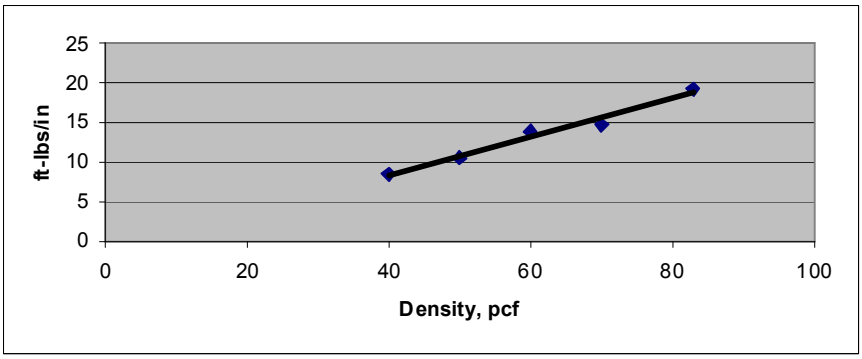


Figure 3

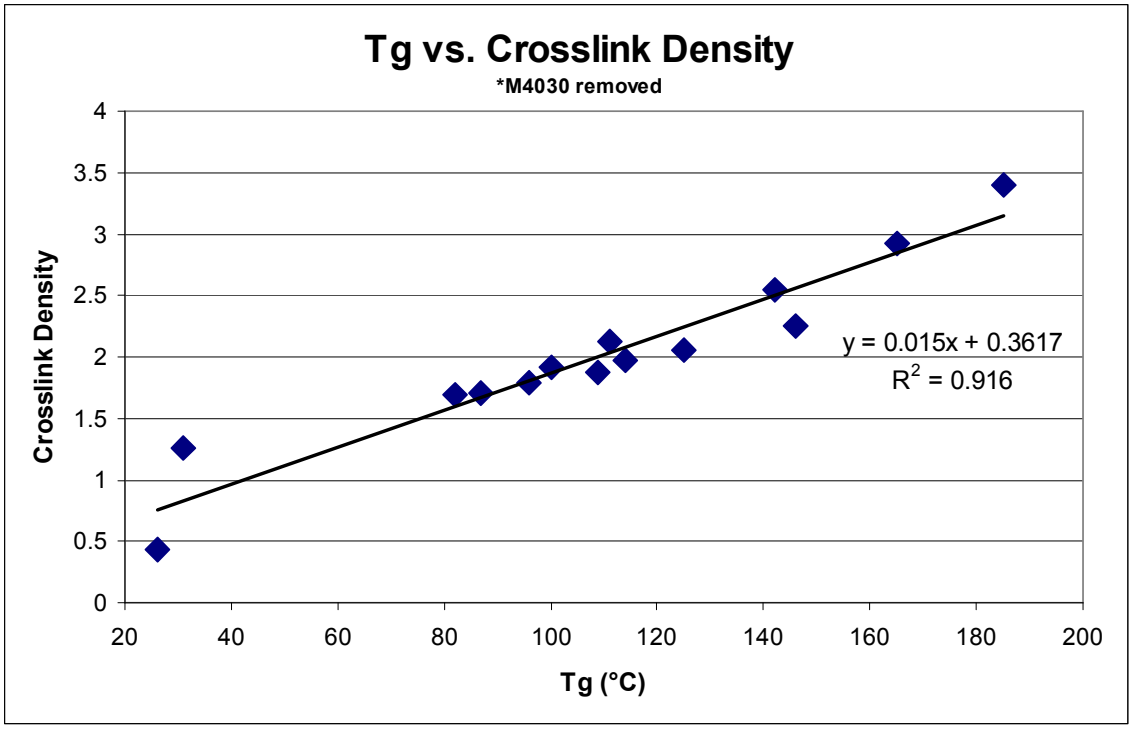
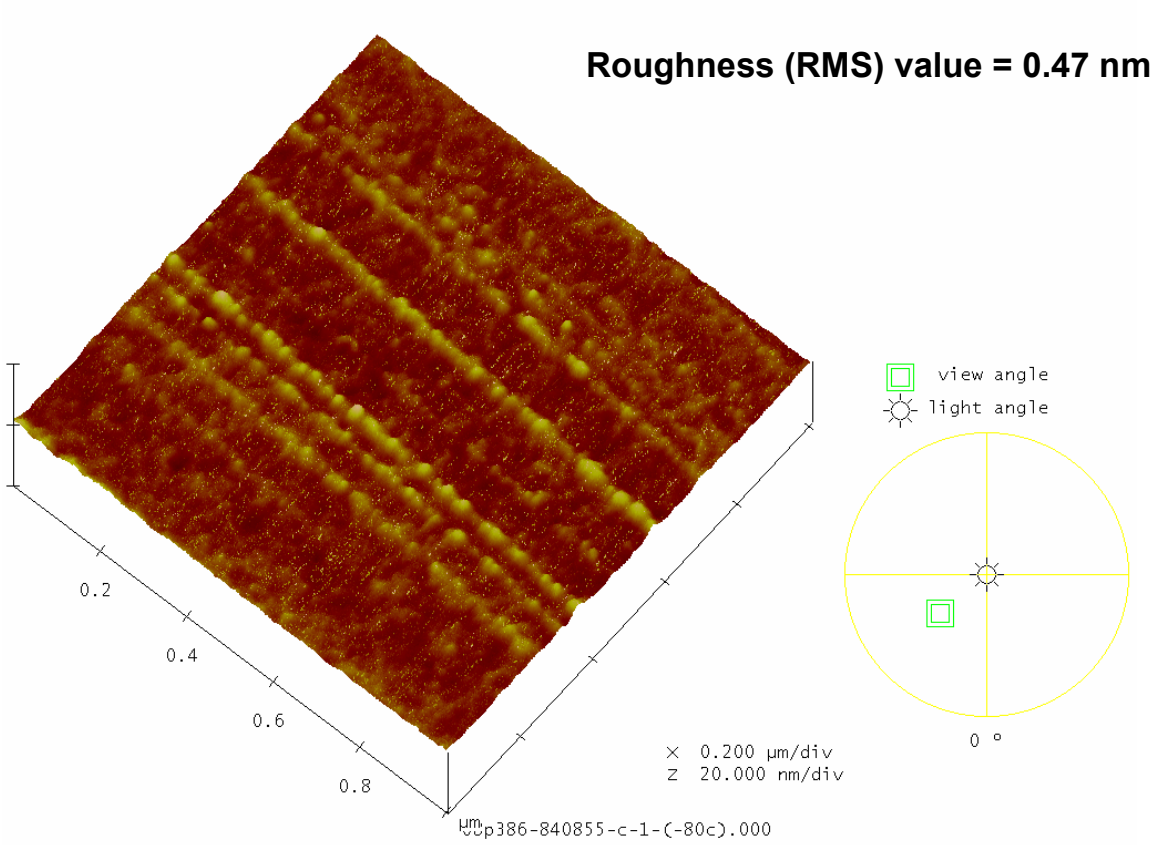
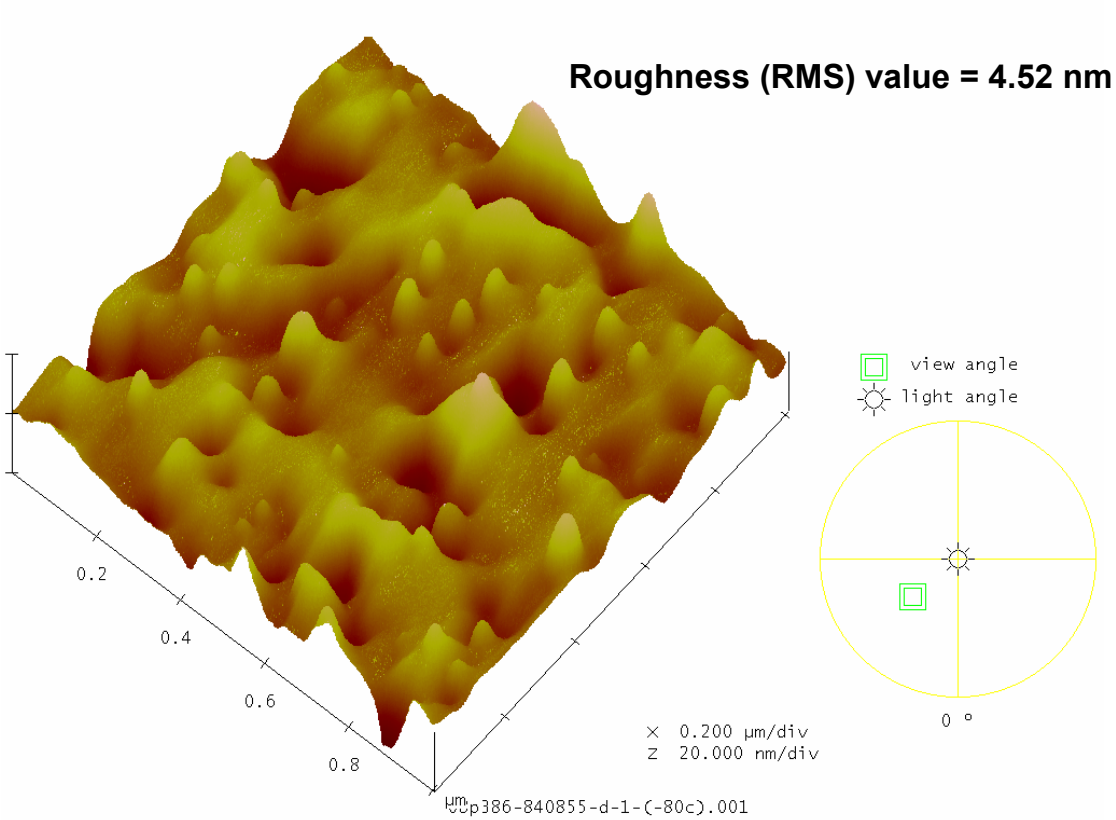

Tg vs. Crosslink Density
*M4030 removed
Crosslink Density
Tg (°C)
y = 0.015x + 0.3617
R2 = 0.916
0
0.5
1
1.5
2
2.5
3
3.5
4
20
40
60
80
100
120
140
160
180
200

Figure 4



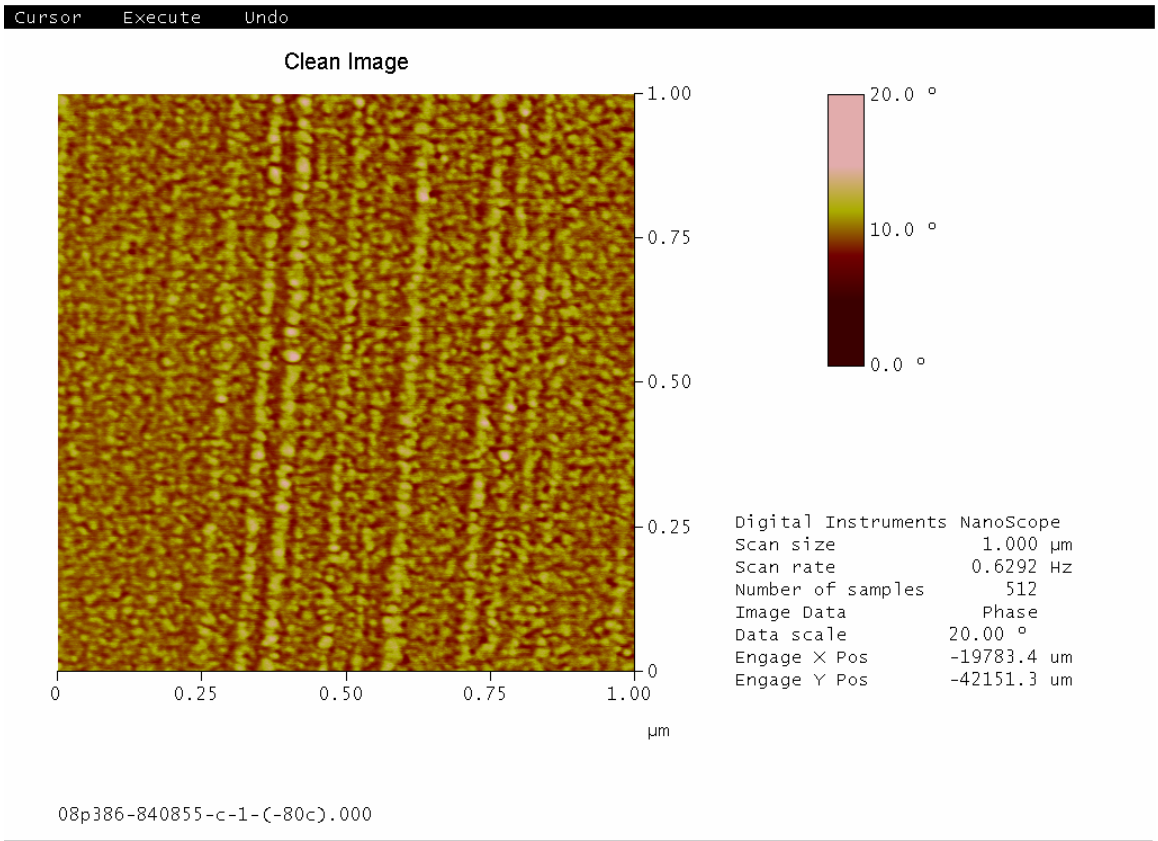
Sample 840855-C- - 3 D Height Image

Figure 5



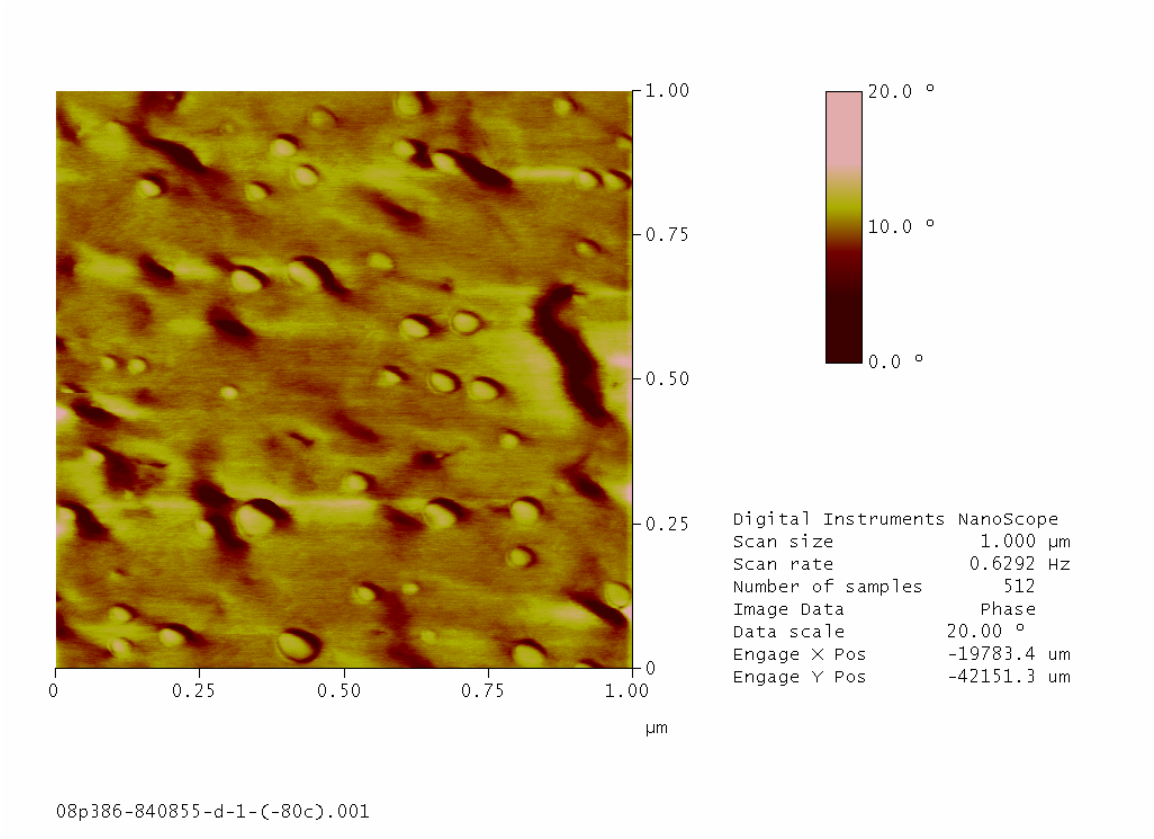
Sample 840855-D- - 3 D Height Image

Figure 6



Sample 840855-C- - 2 D Phase Image

Figure 7



Sample 840855-D- - 2 D Phase Image

Table 1

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

Table 2

[CO2] 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**