FACTS: A "FLOW ANALYSIS CURE TIME SYSTEM" FOR FIBER REINFORCED THERMOSET PLASTICS

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Abstract

The continuing development of the "new" type of spiral flow tool for evaluation of reinforced thermoset resin systems has led to the use of an improved sensor for determining gel and cure times. The use of this sensor, which monitors the impedance values during the cure cycle, gives us a better understanding of the reactions that are occurring during the cure. This understanding will aid us in quantifying the dynamic reactions and interactions of the components of the composite materials during the compression molding process.

The "new" spiral flow tool is designed as a compression mold, equipped with a real-time data collection system for the dielectric (impedance) values during cure. Temperature and pressure data is also acquired from the mold in two locations during the cure cycle. The temperature and pressure sensors are located at the charge area and along the flow channel. The collected data provides an insight into the complex behavior of the material during molding, allowing one to compare and contrast different materials.

The development of additional software to analyze and display the data collected makes it easier to understand the data and the data easier to use to compare formulation changes. The utilization of the new sensor, which is already being used in production molds, gives a good correlate to the cure on the production floor. Real time collection of the pressure, temperature, and cure data of the composite material as it flows through the mold makes this laboratory tool an industry standard for development and quality control of compression molding compounds.

Historical Background

Originally, the spiral flow test was developed for the injection molding industry which uses homogeneous materials. The old spiral flow mold consisted of a spiral channel 0.250" wide x 0.125" deep x 48" long. Material was moved through the channel from a central, cylindrical area by pressure exerted from a hydraulic piston[1]. The material was moved through the channel which has a constant cross sectional area at a uniform rate dependent upon the pressure of the hydraulic ram. (figure 1) The current use for this tool is with Fiber Reinforced Plastics (FRP), which include SMC, BMC, and TMC.

FRP is a filled, thermosetting polymer system with fibrous reinforcement. This composite material is widely used in the automotive, industrial, consumer, and marine industries. FRP"s ability to flow and fill complex designs, superior strength-to-weight ratio, and corrosion resistance at a low cost, makes it favorable over steel in many applications.

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[1] *"SHEET MOLDING COMPOUND CHARACTERIZATION UTILIZING SPIRAL FLOW" by Leach, Rabinovich, and Castro*

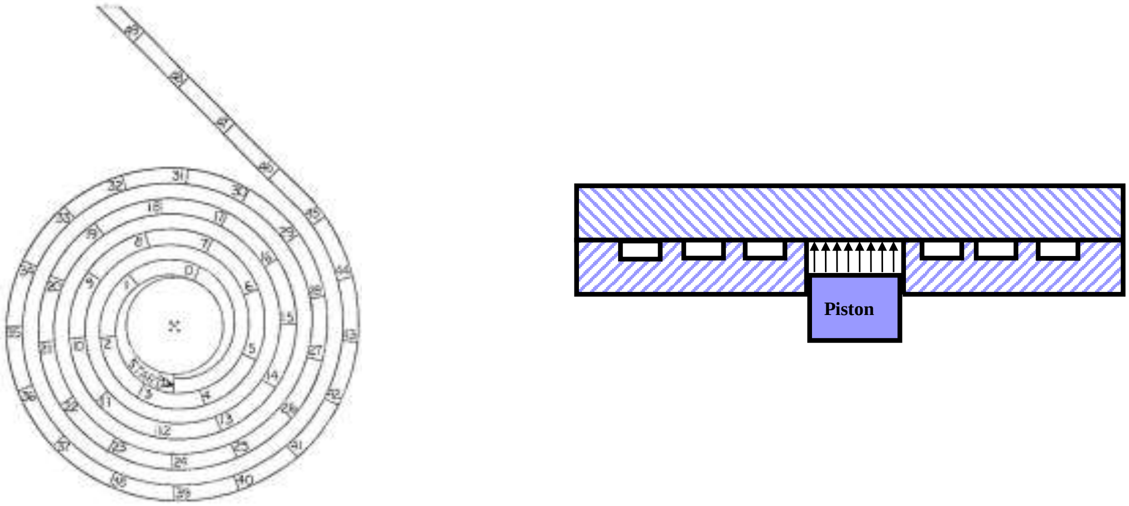


Figure 1: Original Spiral Flow Tool Design – Top and Side Views

To measure the flow using the old tool, long fiber reinforced materials had to be cut into 1/8" square pieces to reduce the fiber length of the reinforcement to allow the material to move through the small channel. Having to cut the FRP into such small pieces was a major limitation of this old design and misrepresented the behavior of material with fiber reinforcement longer than 1/8". Another very significant limitation of the old spiral flow design is the misrepresentation of the nature of compression molding as the compression molding process does not have a cavity of constant thickness during the flowing of the FRP.

New Spiral Flow Tool

The new spiral flow tool was built to address the above limitations. The mold has a 6" square loading area and a 2" wide channel that is 48" long for a relative flow measurement (figure 2). It is a compression mold with shear edges and can mold plaques up to 0.75" thick. Molding pressure can be varied to control flow in the part.

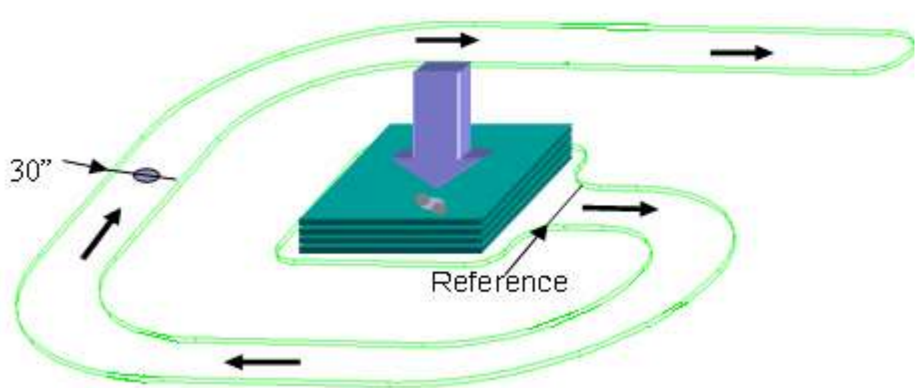


Figure 2: Modern Spiral Flow Tool

During the compression molding process the cavity through which the materials flows is ever decreasing in cross sectional area until one of the following three events occur:

1 The cavity is completely filled by the material.

2 The material gels, stopping it from flowing further.

3 The mold reaches the stops, after which the cross sectional area no longer decreases.

New Analysis Sensors and Software

The purpose in using a new sensor and developing new software was to make the system more reliable and easier to use as a quality control and development tool. The new spiral flow tool was fitted with a Signature Control Systems dielectric cure sensor and data acquisition system. As an option one can have two (2) combination „temperature / pressure‟ sensors added to the mold. These sensors would be located at 0” and 30” along the path of the 2” wide channel to record pressure and temperature changes as the FRP flows through the mold and cures. The data from all the sensors is acquired and recorded at 0.3-second intervals during the press cure cycle.

The Signature Control Systems dielectric cure sensor is the same sensor available to FRP production plants. The use of this sensor gives the lab system the ability to correlate more closely with Signature Control production systems already in use. With this system one can evaluate the effects of catalyst, inhibitor, temperature, pressure, reinforcement loading, reinforcement type, and part thickness on the cure behavior of the FRP. The temperature / pressure sensors located at 0” and 30” will yield additional data on the differences in cure under the charge pattern and after flowing 30” in a hot mold.

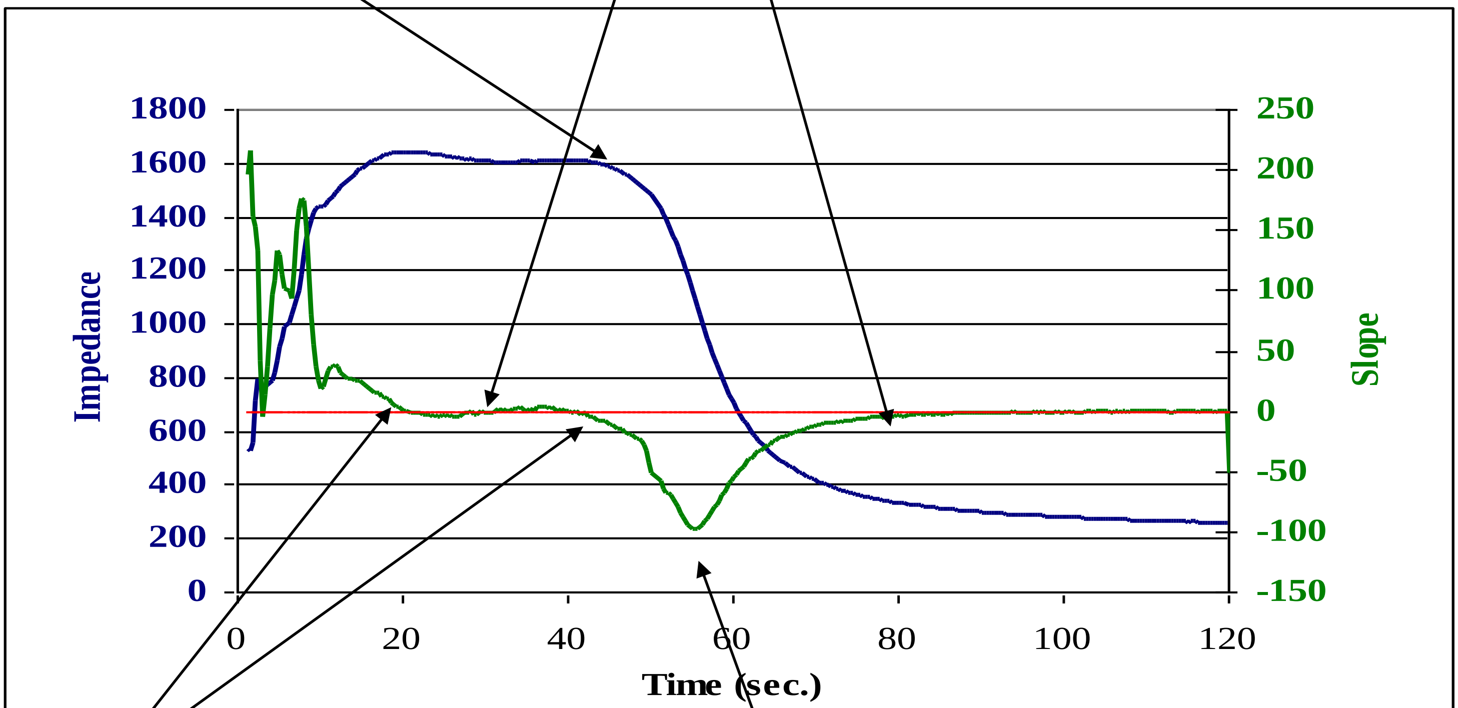
New software has been developed to analyze the data collected by the acquisition equipment. It will produce a graph of the impedance values, the derivative of that data, and calculates the times for critical points on the curve. The critical points of interest are the “Gel Time”, the “Cure Time”, the “End of Gel Time”, the “Mid Plateau Time”, and the “Plateau Width” in seconds.

The “Gel Time”, “Cure Time”, “End of Gel Time”, “Mid Plateau Time”, and “Plateau Width” are all determined from the impedance curve generated while the Spiral Flow mold is being run. The impedance values are acquired and saved during the molding cycle. An increase in the impedance value is associated with a reduction in the viscosity and/or an increase in molecular mobility of the compound being molded. The slope derivative of the impedance curve is calculated and used to isolate the desired points. The “Gel Time” is defined as the time at which the impedance value starts to rapidly decrease from the area of its highest point. This is the point on the curve at which the reduction of the viscosity caused by the heating of the compound from being in the mold is less than the increase in viscosity being caused by the cross linking of the polymer due to the catalytic reaction. The “End of Gel Time” is determined by examining the derivative of the impedance curve to find the point where the rate of reaction starts to slow down. The lowest point on the derivative curve defines the inflection point, the time at which the rate of increase in viscosity starts to slow down or the rate of the reaction is decreasing. While the viscosity of the material is still increasing, the rate at which it is increasing is slowing. The “Cure Time” is the time at which the rate of increase in viscosity is approaching zero. The cure time is determined by the approach of the slope derivative to the zero line. At this point in time the value of the impedance is still decreasing but the rate of the decrease is approaching zero. A value of “–3” on the derivative curve has been found to have good correlation with the visual analysis of the curve for cure time and at this point the part is sufficiently cured to open the press and have a fully cured part. See figure 3 for the details.

Gel time is defined as the time when the increase in viscosity due to the cure is greater than the reduction due to the increase in temperature.

Mid-Plateau time is defined as the time at the center point of the plateau, and is based on the derivative crossing the 0 slope line.

Cure time is defined as the time at which the slope of the ` impedance curve approaches 0. .



Plateau Width is defined as the time between the beginning and the end of the plateau. It is based on proximity of the derivative to the 0 slope line.

End of Gel time is defined as the time when the rate of the increase in viscosity begins to slow the down.

Figure 3

With different materials the gel peak can have a plateau as seen in figure 3, a "normal" bell curve as seen in figure 4, or even a double peak as in figure 5 in the area of the highest impedance values. For plateau and double peak materials we also look at the mid-point of the plateau and the plateau width as further indicators of what is happening during the cure.

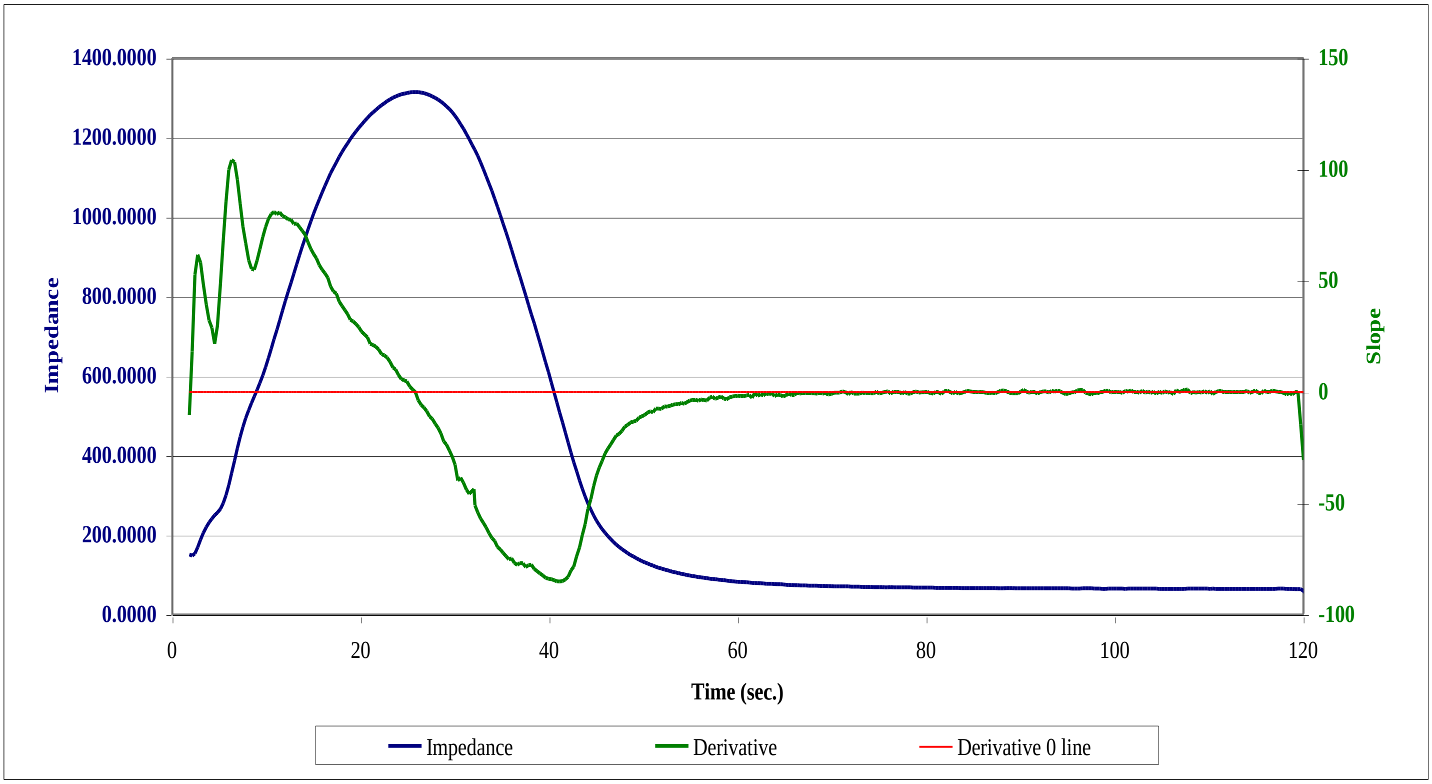


Figure 4

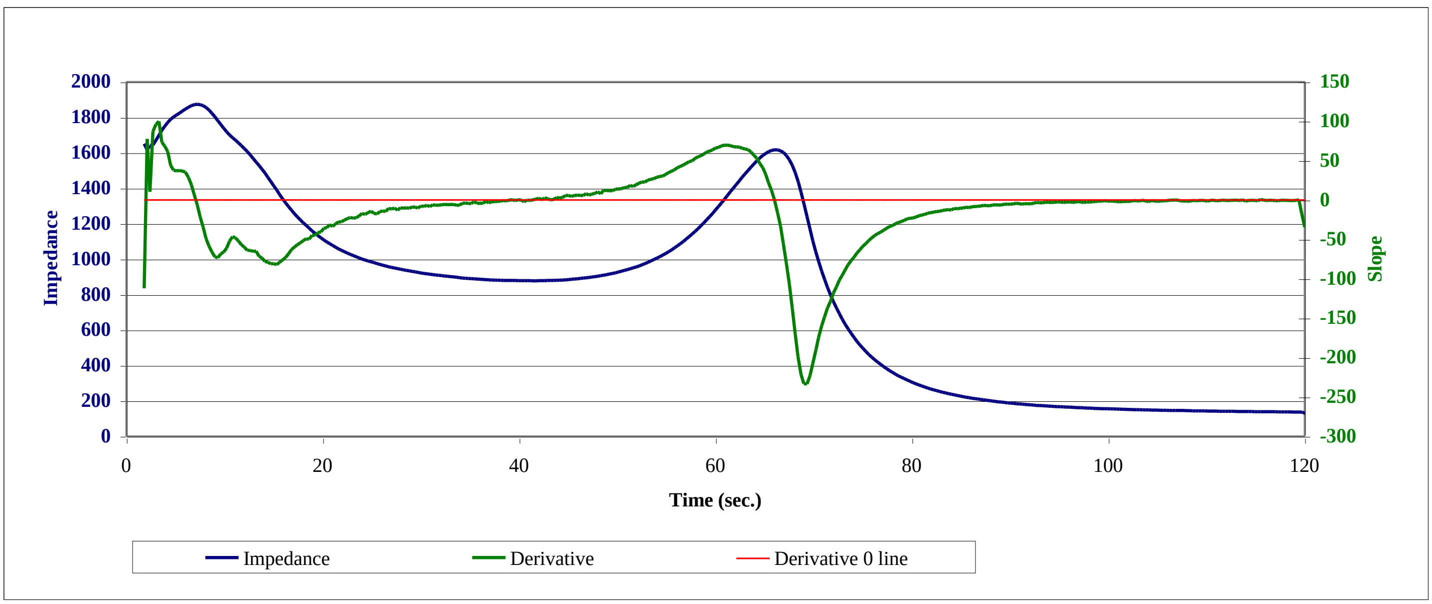


Figure 5

The software for generating the curve and determining the times is easy to use, as all functions are accessible by clicking “buttons”. From this main screen you can import files for analysis; print graphs of the data; create, average, and print a summary sheet of the times and set-up data; and “clear” the form by clicking the appropriate buttons. See figure 6 for a screen shot of the data analysis page.

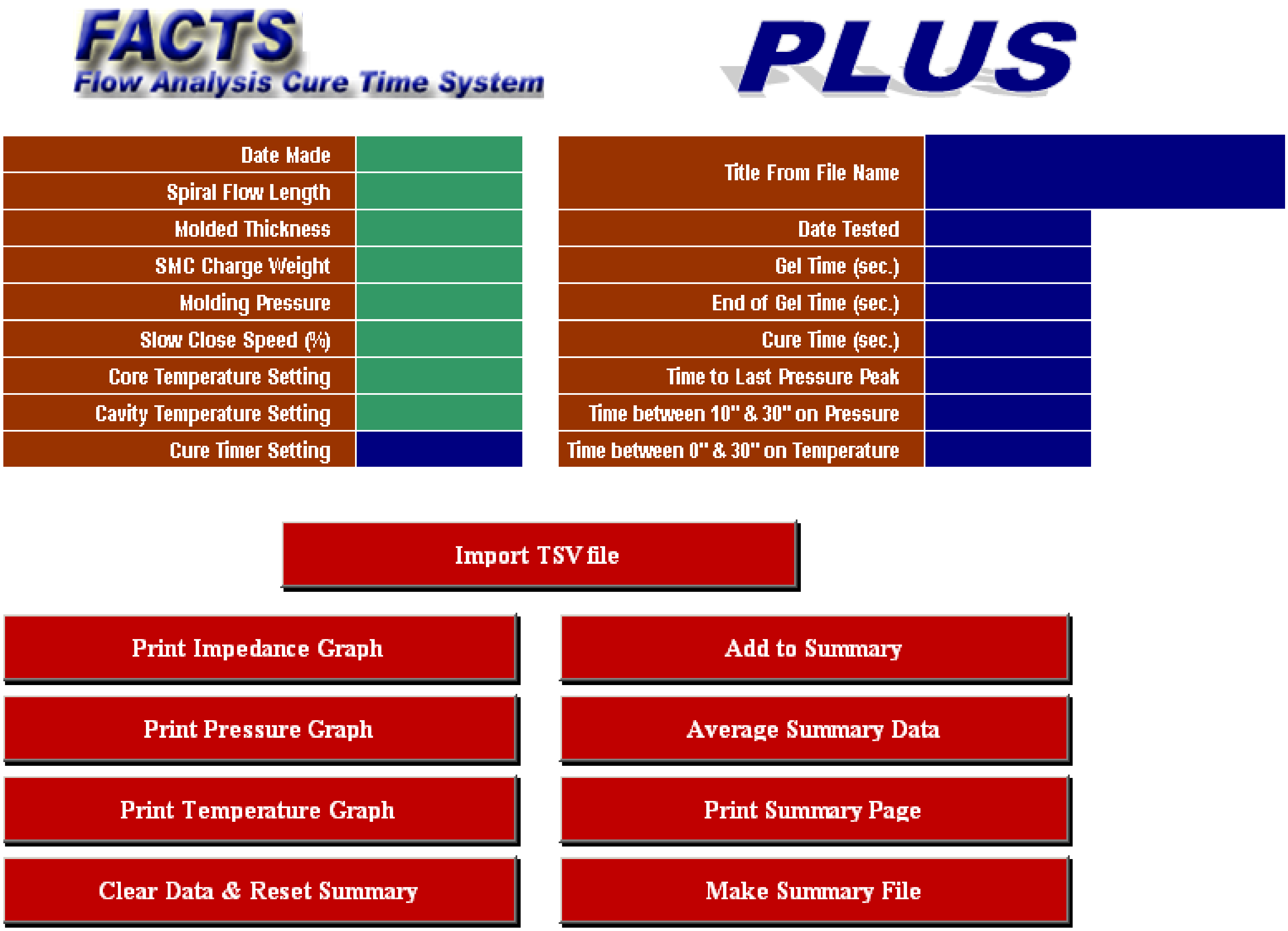


Figure 6

The summary sheet can contain the following information: Sample ID, Cycle No., Date Made, Date Tested, Gel Time, Cure Time, Spiral Flow Length, Mid Plateau Time, Plateau Width, Molded Thickness, and End of Gel Time. After entering data from several runs clicking a button will average the data (figure 7).

"FACTS" Summary Sheet

Sample ID	Cycle No.	Date Made	Date Tested	Gel time (sec.)	Cure Time (sec.)	Spiral Flow Length	Mid Plateau Gel Time	Plateau Width (sec.)	Molded Thickness	End of Gel time
2801 .5	6	05/11/05	05/23/05	31.8	72.0	43.0	30.8	10.5	0.132	50.4
2801 .5	7	05/11/05	05/23/05	32.7	76.2	44.5	31.5	10.8	0.131	50.7
2801 .5	8	05/11/05	05/23/05	32.4	75.0	45.0	30.8	11.1	0.127	50.4
AVERAGE				**32.3**	**74.4**	**44.2**	**31.0**	**10.8**	**0.130**	**50.5**
2801	9	05/11/05	05/23/05	24.3	60.6	42.0	23.9	5.1	0.135	39.6
2801	10	05/11/05	05/23/05	24.9	61.5	42.8	25.5	5.4	0.133	40.8
2801	11	05/11/05	05/23/05	24.3	58.5	42.5	24.5	4.5	0.133	39.3
AVERAGE				**24.5**	**60.2**	**42.4**	**24.6**	**5.0**	**0.134**	**39.9**
4501 .5	12	05/11/05	05/23/05	35.7	85.8	28.0	24.8	32.1	0.161	64.5
4501 .5	13	05/11/05	05/23/05	36.0	81.3	32.0	24.9	32.4	0.151	60.6
4501 .5	14	05/11/05	05/23/05	33.9	78.9	32.0	34.1	8.1	0.145	57.3
AVERAGE				**35.2**	**82.0**	**30.7**	**27.9**	**24.2**	**0.152**	**60.8**
4501	15	05/11/05	05/23/05	31.5	75.3	24.0	31.7	6.9	0.167	55.5
4501	16	05/11/05	05/23/05	26.1	68.7	27.0	26.3	5.7	0.163	47.4
4501	17	05/11/05	05/23/05	31.2	74.1	23.0	31.5	6.0	0.174	51.3
AVERAGE				**29.6**	**72.7**	**24.7**	**29.8**	**6.2**	**0.168**	**51.4**
3501 u	18	05/11/05	05/23/05	31.2	74.1	28.0	31.2	4.8	0.134	49.8
3501 u	19	05/11/05	05/23/05	27.6	67.5	26.0	20.4	19.8	0.133	46.2
3501 u	20	05/11/05	05/23/05	29.1	71.1	28.0	29.4	4.8	0.134	47.4
AVERAGE				**29.3**	**70.9**	**27.3**	**27.0**	**9.8**	**0.134**	**47.8**
3501	21	05/11/05	05/23/05	27.9	69.0	23.0	28.4	4.5	0.146	45.0
3501	22	05/11/05	05/23/05	25.2	65.4	26.0	18.0	18.6	0.136	40.5
3501	23	05/11/05	05/23/05	25.8	62.1	26.0	26.3	3.9	0.132	40.2
AVERAGE				**26.3**	**65.5**	**25.0**	**24.2**	**9.0**	**0.138**	**41.9**
SMC Charge Wt. 450	Molding Pressure 350		Slow Close Speed (%) 80		Cavity Temp. Setting 300		Core Temp. Setting 290		Cure Timer Setting 120	

Figure 7

A study was made with a 40 percent glass, production SMC to find correlation with Differential Scanning Calorimeter (DSC) and FACTS on completeness of cure. The cure time for the SMC, 45 seconds was established using the FACTS system. FACTS Panels were molded at the FACTS cure time, 10 seconds less than the FACTS cure time, and 20 seconds less than the FACTS cure time. See figure 8 to see the under cure progression. A panel made at each cure time and at 400 PSI was submitted to analytical for DSC analysis and no indication of residual cure was found in any of the samples. Additional panels were molded at the above cure times and quenched in ice water immediately after de-molding. These panels also showed no indication residual cure from the DSC analysis. A panel made at each cure time and 1000 PSI was submitted to analytical for DSC analysis and the amount of residual cure was found to be minimal at 45 seconds and increasing proportionally as the cure time was reduced.

45 second cure | 35 second cure | 25 second cure

Figure 8

Summary

The use of the new sensor which improves the robustness of the system, and newly developed software package to make the data more accessible to evaluate changes makes the FACTS system a useful tool for both development and quality control. The ease of analyzing the effects that changes in components and processes have on gel, cure, and flow behavior will allow the comparison of identical formulations from one run to the next, and help determine if “off-spec” material will flow enough to be used in production. This makes the FACTS system a valuable tool for both quality control and development.

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