A FORMULATION STUDY OF LONG FIBER THERMOPLASTIC POLYPROPYLENE (PART 1): THE EFFECTS OF COUPLING AGENT, GLASS CONTENT & RESIN PROPERTIES ON THE MECHANICAL PROPERTIES

Creig Bowland

PPG Industries, Shelby, North Carolina

Abstract

The relationship between the resin and fiber properties in Polypropylene Long Fiber Thermoplastics is presented. The effects of glass content, Maleic anhydride grafted polypropylene additives (coupling agent) and melt flow of the resin are presented. Various samples of Polypropylene Long Fiber Thermoplastics pellets (PP GLFT) were compounded with various coupling agent loadings and using different melt flow homopolymer polypropylene resins. The glass content of the pellets was varied from 30% to 50%. The pellets were then molded and tested for normal mechanical properties. The results of the study are presented.

Introduction

Long Fiber Thermoplastics have enjoyed a long run of double digit growth and have found general acceptance as structural materials. PP LFT materials offer strength and stiffness and are recyclable having a long shelf life. Consequently, their introduction has lead to an increased penetration of the automotive market for structural thermoplastic composites. These applications typically are metal replacement and facilitate both part weight reduction and part consolidation. Polypropylene based Long Fiber Thermoplastics (PP LFT) are the largest segment of this market and are also experiencing the largest growth. Within the PP LFT segment there are three distinct methods of making and using these materials. The classic method is the pultrusion impregnation and/or cross head extrusion method of generating LFT pellets that are subsequently injection molded. For the purpose of this paper this type of material is labeled Granulate Long Fiber Thermoplastics (GLFT). The second main method of producing LFT is In Line Compounding(IC). Within the IC segment there are two distinct methods of producing parts. In one method, the IC material is compression molded into parts in a process similar to that used for the manufacture of Glass Mat Thermoplastics and thermoset parts. In the second method the IC material is fed directly into an injection molding machine for either standard Injection molding or Injection compression molding. For the purpose of this paper both are labeled as Direct Long Fiber Thermoplastics (DLFT) and are differentiated as compression and injection DLFT.

PP LFT materials exhibit their best performance when the polypropylene resin has Maleic anhydride grafted polypropylene added to the matrix. The amount and characteristics of this additive are well documented in short glass polypropylene compounds [4-7] but are not well reported for PP LFT materials. There are a number of factors that affect the performance of the coupling agent in PP LFT parts.

- Coupling Agent concentration
- Fiber glass content and sizing
- Polypropylene properties such as melt flow, molecular weight and crystallinity.
- Mold Design and temperature
- Method of making PP LFT: GLFT vs. IC DLFT. The DLFT and GLFT processes are distinct and can lead to different part performance based upon the heat history, ultimate fiber length retention, fiber

orientation in the part and time at temperature to allow effective coupling.

Experimental

PPG TufRov® 4599 225 yield 17 micron fiber glass rovings and PPG TufRov® 4576 225 yield 17 micron fiber glass rovings were processed through a cross head pultrusion GLFT line and pelletized into 12 mm (1/2 inch) long pellets. TufRov® 4599 and TufRov® 4576 are both designed for compatibility with Polypropylene resin and react with and promote the adhesion of the matrix resin to the fiber. TufRov® 4576 has a higher specific reactivity to the Maleic Anhydride coupling agent and has significantly higher mechanical properties performance. TufRov® 4576 is also designed for excellent hot water and color performance. Homopolymer polypropylene from Total Petrochemicals grade 3860X 100 MFI resin was used. Other ingredients used include:

- Polyram BondyRam® 1001 100 MFI Maleic Anhydride grafted PP with 1% Maleic Anhydride (w/w)
- A heat stabilizer package
- Carbon Black.

The heat stabilizer package used will allow the molded parts to survive stringent 1000 hour heat stability tests at 140 ºC as per current automotive standards. Glass content of the pellets was controlled and varied to produce GLFT materials of 30% to 50% glass loading (w/w). The coupling agent loading was varied from 0.5% to 3% (w/w) with samples being collected at each glass content and coupling agent loading.

A second set of trials was done varying the polypropylene resin to determine the effects of different melt flow homopolymer grades upon the mechanical properties of the molded GLFT parts. For this study the glass content was held constant at 50% and the coupling agent loading was held constant at 2% (w/w). Total homopolymer polypropylene 3860X (100 MFI), 3925WZ (60 MFI), 3825WZ (30 MFI) and Huntsman P4G3Z-039 (5 MFI) homopolymer polypropylene were used in the formulations. Table I shows the test matrix of all samples produced, molded and tested

Samples were subsequently dried at 120 ºC for four hours and the moisture was measured for each sample prior to molding with maximum allowed moisture of 0.6% (w/w). A Van Dorn 55 injection molding machine was used for molding test specimens. A free flow check valve was installed on the screw tip prior to the initiation of this work. The mold used was standard ISO tensile test specimen mold with large diameter sprues and runners and large radius curves. The gate is a fan gate to the tensile specimens. The mold is a balanced design producing two tensile specimens per shot. Impact and flex specimens were cut from the tensile bars by removing the tab section of the specimen. All test specimens conformed to ISO requirements. The exact profile used for the molding is recorded in Table II.

Unless otherwise stated, all mechanical property testing was performed at 23ºC and at a relative humidity of 50%. All testing was done in the A2LA accredited laboratory at the PPG Fiber Glass Science and Technology Center in Shelby, North Carolina. Tensile properties were tested according to ISO 527-2 using 10 specimens and a crosshead rate of 5 mm/min (0.2 in/min) with an extensometer gauge length of 50 mm (2 in). Flex properties were tested according to ISO 14125 using 10 specimens and a crosshead rate of 2.0 mm/min (0.8 in/min) and a span of 64 mm (2.56 in). Charpy notched impact properties were tested according to ISO 179-1 with 10 specimens and a Type A notch. Charpy UnNotched impact properties were tested according to ISO 179-1. Heat Distortion Temperature (HDT) properties were tested according to ISO 75.

Table I: GLFT Sample Test Matrix

Sample #	PP MFI	Fiber glass	% Glass
292-02	100	4573	30
292-04	100	4573	30
292-03	100	4573	30
292-04	100	4573	30
291-02	100	4573	40
291-04	100	4573	40
291-06	100	4573	40
291-08	100	4573	40
290-02	100	4573	50
290-04	100	4573	50
290-06	100	4573	50
290-08	100	4573	50
311-01	100	4576	30
311-02	100	4576	30
311-03	100	4576	30
311-04	100	4576	30
312-01	100	4576	40
312-02	100	4576	40
312-03	100	4576	40
312-04	100	4576	40
313-01	100	4576	50
313-02	100	4576	50
313-03	100	4576	50
313-04	100	4576	50
342-01	5	4573	50
293-01	100	4573	50
293-02	60	4573	50
293-03	30	4573	50

Table II: Van Dorn 55 Injection Molding Profile for GLFT specimens

Molding Profile	
Rear Zone	225ºC
Center Zone	240ºC
Front Zone	250ºC
Nozzle	250ºC
Mold	50ºC
Shot Size, inch	2.25
Boost Pressure , psi	1000
Injection Speed in/s	1.5
Hold Pressure, psi	925
Screw Speed	90
Back Pressure, psi	50

Results

The results of the study for both fiber glass grades used in the PP GLFT materials mimic each other. The trends and relative changes in performance are similar. The differences in the fiber glass grades evaluated are related to the sizing on the fiber and the interfacial adhesion promotion with the resin that each offers. TufRov® 4599 is a polypropylene compatible fiber that has been on the market for several years and TufRov® 4576 is a new composition with improved properties. Figure 1 shows the performance of both fibers in Flexural Strength. The three dimensional curves overlay each other and are offset by the improvement shown in performance with 4576. Because of this similarity in performance and trends, the remainder of the results and discussion will focus on the results generated with TufRov® 4576.

Figure 1 also shows that the amount of coupling agent plays an extremely important role in the performance of PP GLFT composite. The 0.5% coupling agent was chosen to try and find the lower limit of coupling agent for PP GLFT. Reasonable properties are achievable with either one of these fiber glass samples at a loading of 1.5% to 2% in the 30% and 40% glass samples. With higher glass content there is a trend to higher properties with greater loadings of Maleic Anhydride coupling agent and this is attributable to the larger surface area of fiber. The coupling agent is attracted to the amino silane functional group on the fiber glass and bridges the interfacial area between the resin and fiber. Figure 2 and Figure 3 show that there is very little benefit to the use of higher loading of the coupling agent for either 30% or 40% PP GLFT. Indeed, there may be very good reasons for not adding too much coupling agent to the formulation. Some studies have indicated that the addition of excess coupling agent reduces the crystallinity of the PP and can be detrimental to the mechanical performance of the composite [6]. However; there is a continued improvement in 50% PP GLFT with higher doses of coupling agent. More data needs to be generated, but it is possible that the 50% data would better fit as a curve with a drop off in properties below 2% coupling agent. Further work needs to be done to determine the % glass content vs. % Maleic anhydride grafted polypropylene for peak performance in PP GLFT. Evaluation of other coupling agents with various levels of Maleic Anhydride and different melt flows will be addressed in subsequent papers.

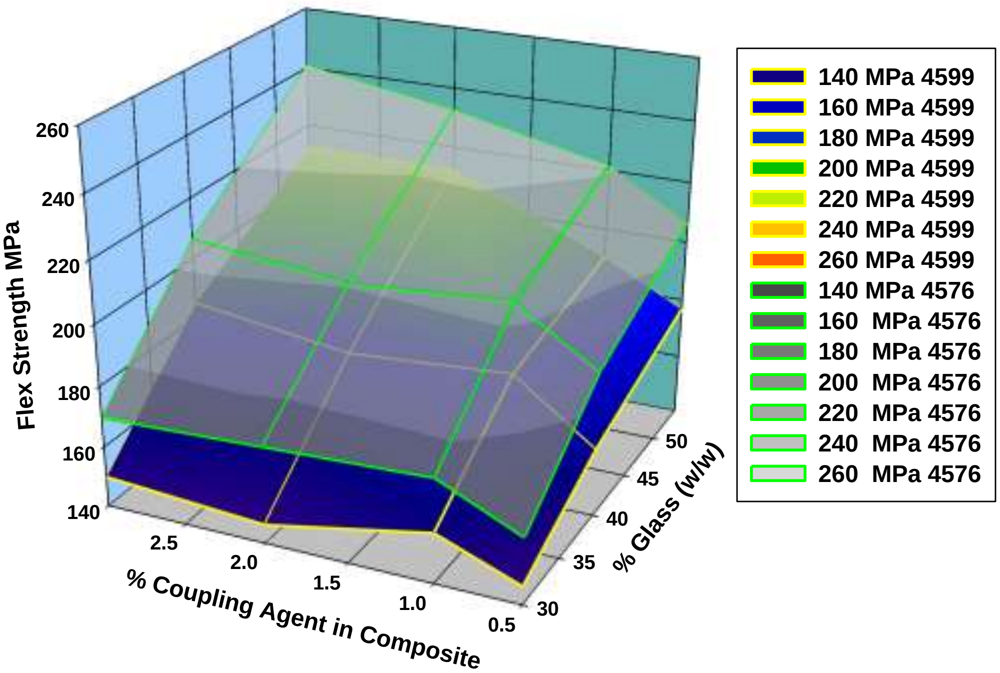

Figure 1: 4599 verses 4576 Flex Strength vs % Coupling Agent and % Fiber Glass in PP GLFT Composites

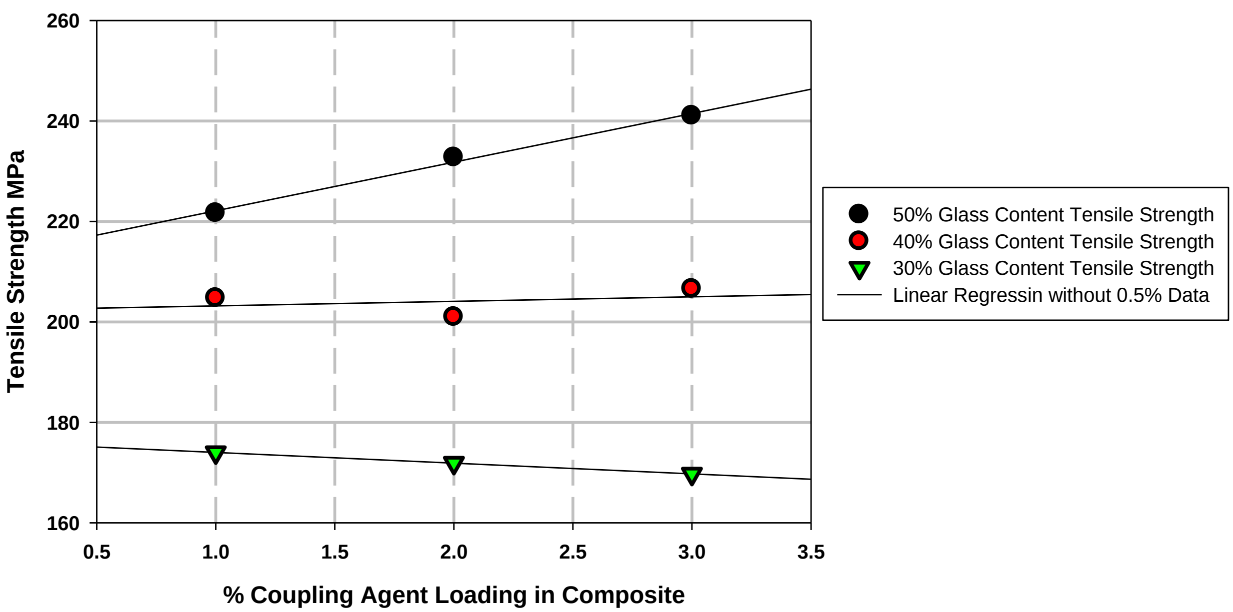

Figure 2: Tensile Strength versus Coupling Agent Loading 4576 225 yield Fiber Glass

Figure 4 and Figure 5 show the relationship between coupling agent loading and performance in Charpy Impact. Notched and UnNotched Charpy both show similar trends in performance with changing levels of coupling agent. As with both Tensile and Flex strength, the 30% and 40% glass content PP GLFT show little or no improvement with the addition of more coupling agent once you have reached a level that supplies enough Maleic Anhydride to the surface of the fiber glass. The 50% glass products show a significant drop in performance until at least 2% coupling agent is present. The scatter in the data for the Notched Charpy data does not allow this differentiation and it is only visible in the more reliable Un-Notched test data.

Figure 6 shows the effect of coupling agent loading and glass content on Flexural Modulus. As is expected, the glass content is the controlling variable for modulus and the coupling agent loading has little effect.

Figure 7 shows the relationship between Tensile and Flexural properties and the polypropylene MFI used in the PP GLFT formulation at a constant loading of 50% by weight TufRov® 4573 fiberglass. The data indicates that the Flexural and Tensile Strengths are higher with the high melt flow polymer while there is no change in impact properties with the change in base polypropylene. The HDT data also indicated better performance with the higher melt flow polymer. Furthermore, the rate of production dropped in the cross head pultrusion process with the higher viscosity resin and the wet out and quality of the pellets produced decreased with lower MFI. The data from this study indicate that optimal properties for PP GLFT are achieved with a homopolymer MFI between 60 to 100 MFI.

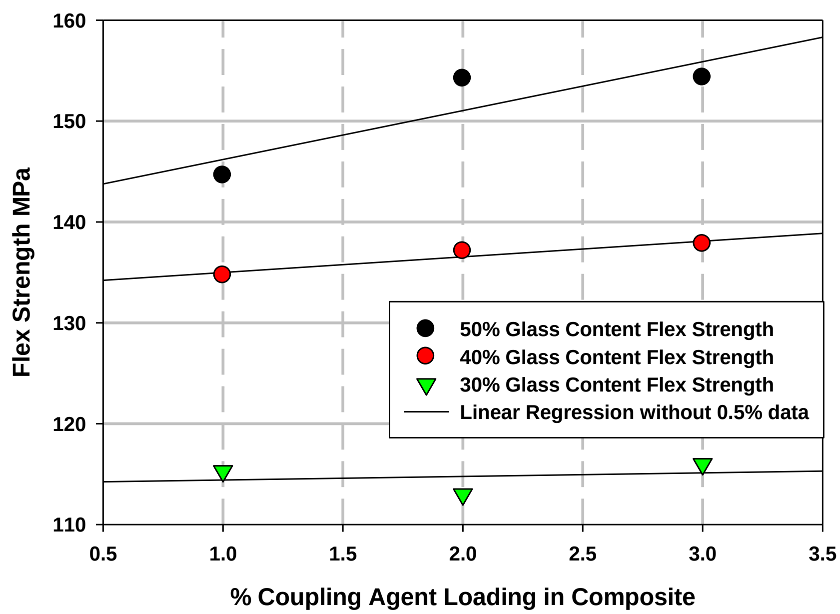

Figure 3: Flex Strength versus Coupling Agent Loading 4576 225 yield Fiber Glass

Summary and Next Steps

In PP GLFT composites the best performance is obtained with the addition of a Maleic Anhydride coupling agent. A nominal level is necessary for optimal performance at any given glass loading. With PPG TufRov® 4576 and TufRov® 4599 a 1.2% to 2% coupling agent loading delivers acceptable properties at 30% and 40% glass loading. The coupling agent levels must be increased as the glass content increases and a 2% minimum coupling agent loading is necessary for 50% glass content. For 50% glass loading the 2% coupling agent level is minimal and the data indicates that higher levels could deliver better properties.

The concentration and performance of the coupling agent are dependent upon the grade of Maleic Anhydride grafted polypropylene used. Higher Maleic Content in the coupling agent may allow lower coupling agent levels in the composite. Typically, the higher Maleic Anhydride content coupling agents are also higher melt flow. This may have a beneficial affect as well, allowing better migration of the coupling agent to the fiber surface. Since the coupling agent is one of the most expensive components of the PP GLFT matrix; controlling the amount and formulation of coupling agent used can have a significant financial effect. One thing is certain, the level of coupling agent is important to control for cost purposes. The use of excess coupling agent has no beneficial effects.

The modulus of the composite is controlled by the amount of fiber glass in the formulation and is not affected in any significant way by the presence of coupling agent. This follows the classic rule of mixtures that is commonly used to predict the modulus of a fiber glass composite.

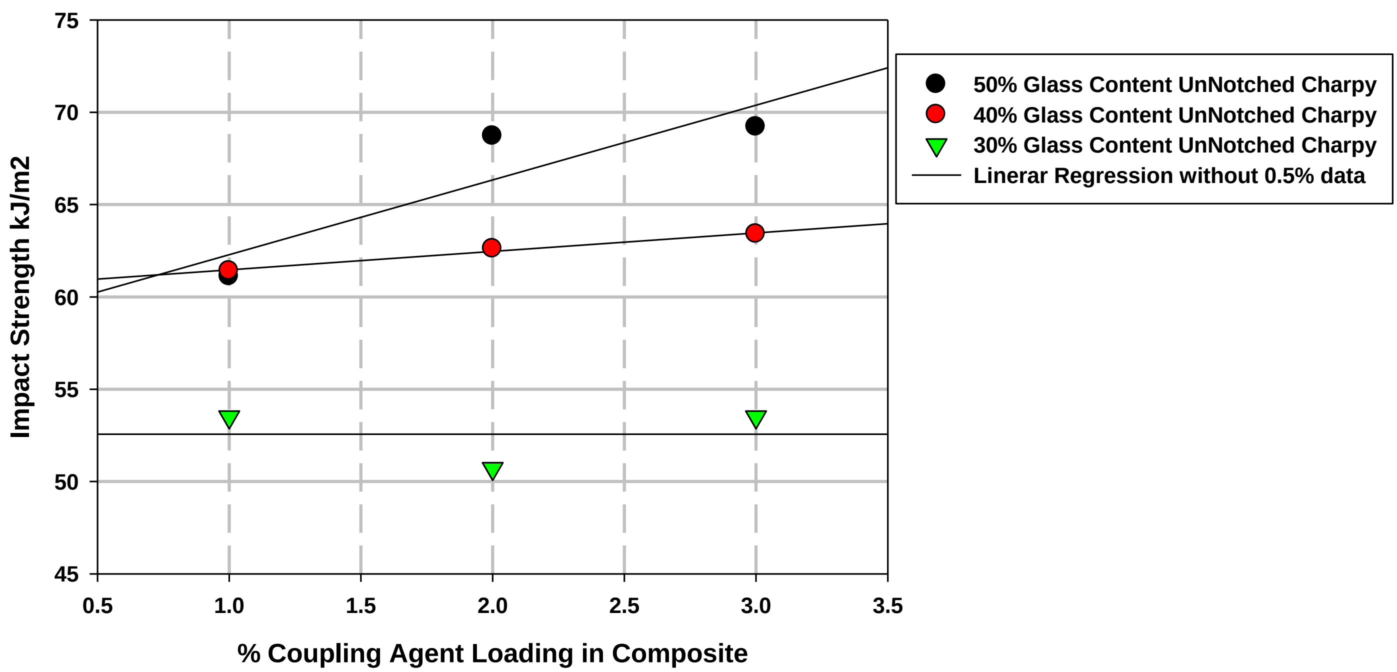

Figure 4: UnNotched Charpy Impact versus Coupling Agent Loading

The melt flow of the homopolymer polypropylene used in PP GLFT production has an interesting effect upon the performance and properties of the composite and is counter intuitive at first glance. One would expect that the impact and HDT would be influenced positively as the MFI of the resin decreases and the molecular weight of the polypropylene increases. However there are a number of clues to explain these results. The leading theory is that the impregnation and wet out of the fiber glass is better with the higher melt flow resin. This leads to better load transfer between the resin and fiber glass and controls the relationship between MFI and properties [8-12]. The lower impregnation efficiency also leads to higher loss of fiber length during the molding process. This is the second major contributor to the lower mechanical properties. Published reports indicate that the faster the PP GLFT process runs, the lower the properties and this can be attributed to the decrease in wet out and load transfer with the higher through put for a given resin and fiber glass formulation [8-11]. Confirmation of this is found in the HDT data where the HDT increases with lower MFI PP resin. All four of the resins used in this trial have the same reported melt temperature.

Incremental increase of the glass content in PP GLFT produces incremental increases in all the mechanical properties as measured in this study. Future work needs to be done to show the upper limit of PP GLFT glass content since at some point the resin matrix will not be able to support further reinforcement. Published reports indicate this drop off in performance may happen around the 60% glass loading, but the ultimate load bearing characteristics of the polypropylene based composite may be dependent upon the fiber glass sizing composition and resin properties. Subsequent work is underway to define the load bearing limit of PP GLFT composites. However; within the limits of this study, the properties increased with every increase in the fiber glass content in the composite.

The fiber glass sizing plays a major role in the performance of PP GLFT composites. Figure 1 shows that with an identical formulation the TufRov® 4576 gave a 14% to 20% improvement in mechanical properties when compared to TufRov® 4599. This indicates that 4576 is superior to 4599 in PP LFT applications and this advantage can be used by the formulator to reduce costs. The coupling agent loading can be reduced in the formulation when using 4576 and still achieve the same or superior performance. Thus, by switching fiber glass and reducing the coupling agent the overall cost of the composites can be lowered.

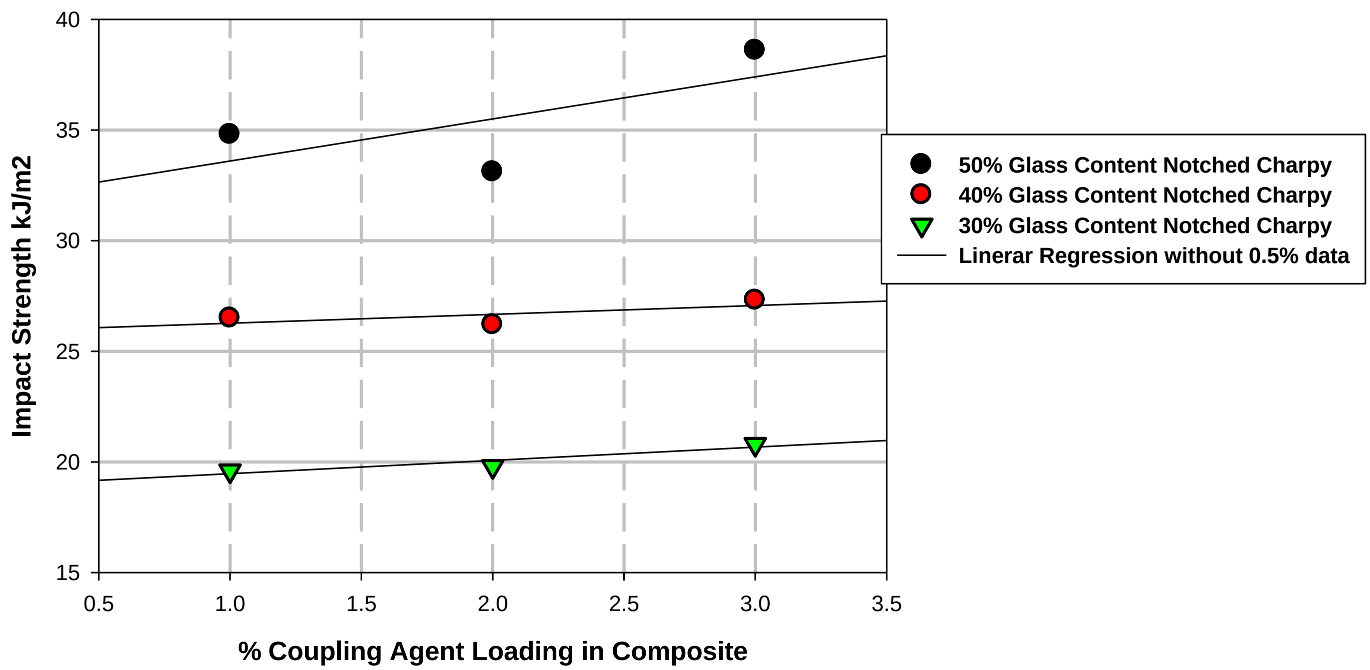

Figure 5: Notched Charpy Impact versus Coupling Agent Loading

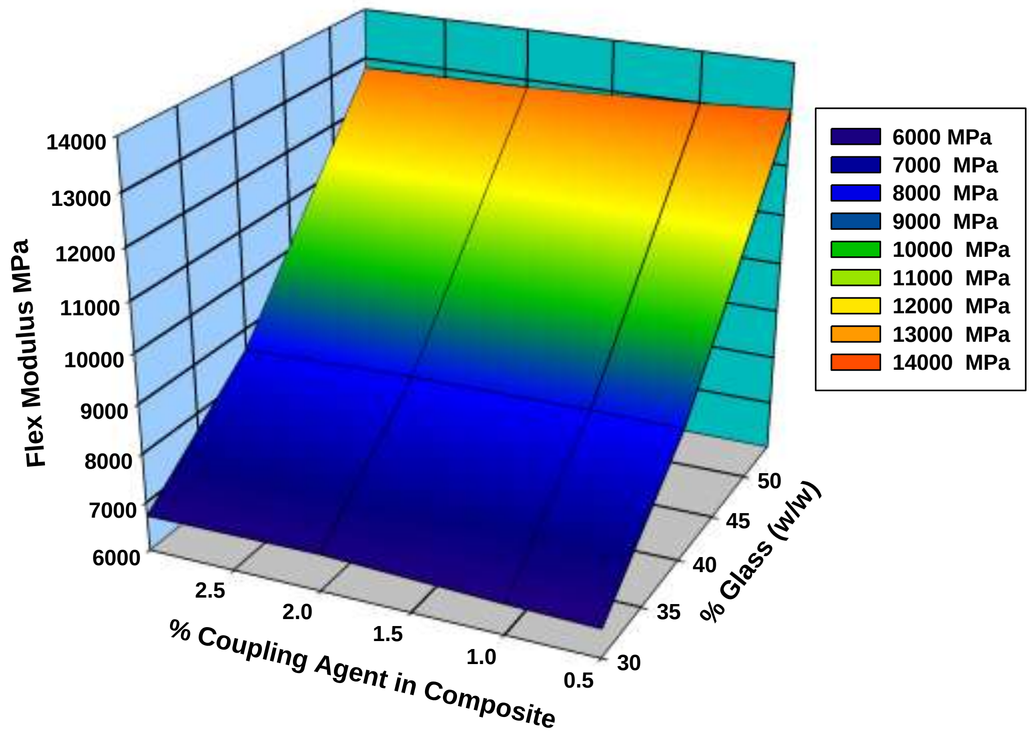

Figure 6: 4576 Flex Modulus verses % Coupling Agent and % Glass in PP GLFT Composites

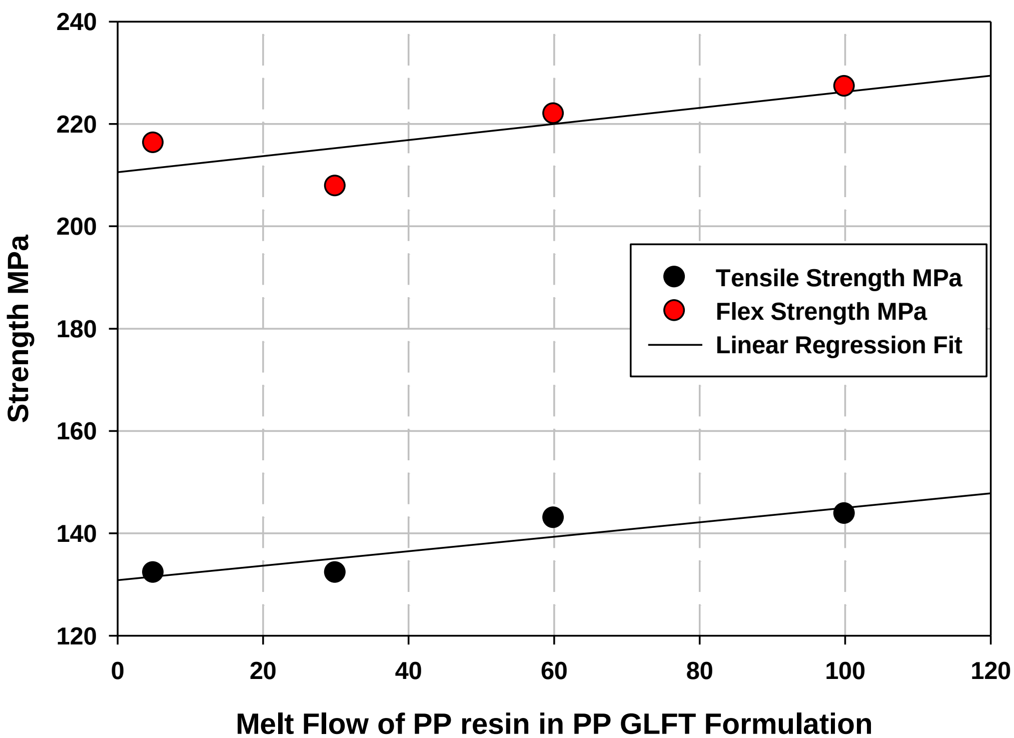

Figure 7: PP Melt Flow in 50% Fiberglass Loaded GLFT verses Tensile and Flex Strength

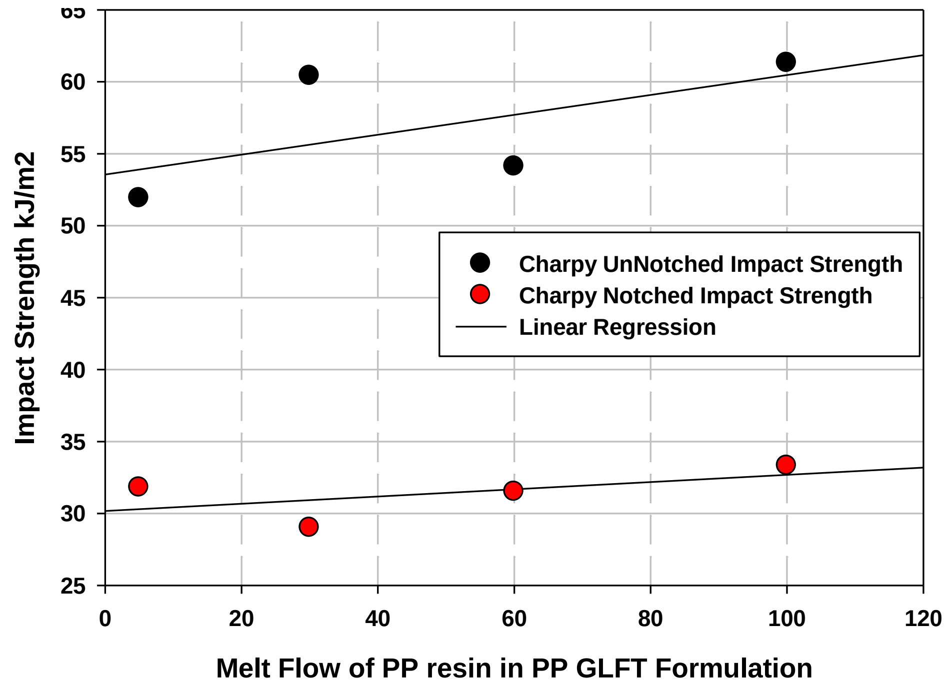

Figure 8: PP Melt Flow in 50% Fiberglass Loaded GLFT verses Charpy Notched and Charpy UnNotched

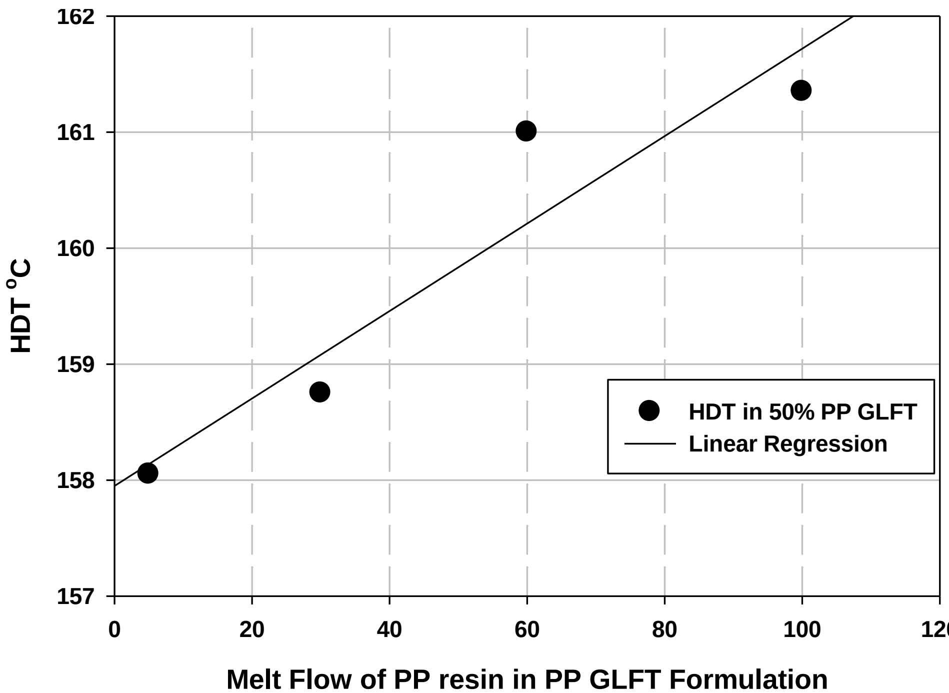

Figure VIII: PP Melt Flow in 50% Fiberglass Loaded GLFT verses Heat Distortion Temperature

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