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Energy Savings of Treated Silicas

Abstract

More stringent performance demands are leading to an increase in the use of highly dispersible silica in tire compounds. However, conventional silica technology has a variety of production limitations, with long mixing times at high temperatures required. PPG AGILON® performance silicas are treated precipitated silicas that overcome the manufacturing limitations associated with conventional HDS/in-situ silane technology. These treated silicas do not require a silanization step and provide significant energy savings. This paper discusses how mixing conditions can be adjusted to optimize compound performance while minimizing energy consumption.

Introduction

Rising fuel costs, a wide range of environmental legislation, and increased public consideration for energy usage and the environment continue to encourage the pursuit of fuel efficient and longer lasting automobile tires. These demands require the expansion of the tire industry's "magic" triangle comprising fuel efficiency, traction, and treadwear. The use of silica as a filler in passenger tires is driven by the fuel efficiency gains that silica provides over carbon black, the traditional filler in tire rubber compounds. While silica provides reduced rolling resistance and fuel consumption savings during the lifetime of the tire, it negatively impacts energy usage during tire manufacturing.



It is widely known in the industry that silica mixing in rubber compounds requires long mixing times and high temperatures to provide adequate silica dispersion and an efficient silanization reaction.^{1,2} Thus, the manufacturing drawbacks of silica include reduced productivity due to longer mixing times, higher mixer energy consumption, higher mixer wear and volatile organic compound (VOC) emissions.

The introduction of PPG AGILON® performance silica allowed the possibility to address these manufacturing challenges.³⁻⁶ *Agilon* performance silica is pretreated with silane coupling agents, as well as other compatibilizers. These are pre-reacted onto the silica surface so that tire and industrial rubber manufacturers do not need to perform the silanization reaction during compounding. Since the silane is already covalently bound to the silica surface, *in-situ* silanization during mixing is not necessary, and, therefore, a less energy intensive mixing process is possible.

The capability to mix *Agilon* silica at lower mixing temperatures avoiding natural rubber (NR) degradation, and an already completed silanization reaction, makes *Agilon* ideal for implementing silica use in NR-based compounds. *Agilon* performance silicas use in NR-based compounds have been extensively studied.⁷⁻¹³ It has been found that *Agilon* silica provides dramatic improvements in hysteresis and fuel efficiency compared to carbon black filled NR compounds. PPG researchers, Okel and Martin studied the energy savings from using *Agilon* silica in NR compounds, using different type of rotors, when compared to untreated silica and carbon black. **Figure 1** shows the energy savings they were able to obtain by eliminating one mixing pass when using *Agilon* 454G silica.

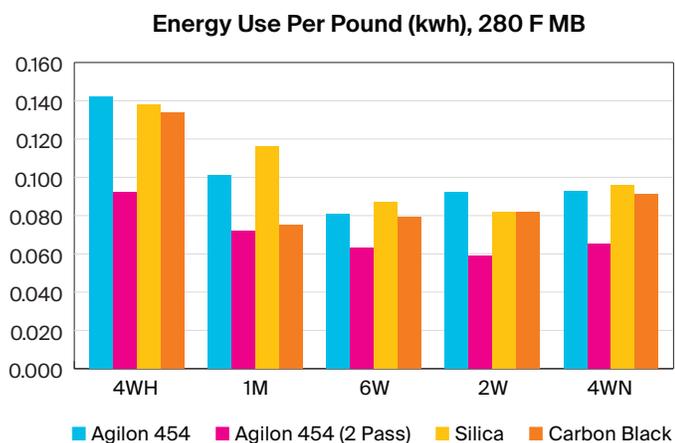


Figure 1. Energy use in NR compounds.⁷

In this paper, we evaluate the energy savings obtained when using *Agilon* 400G performance silica in place of untreated silica in synthetic rubber compounds. While the potential to mix at low temperature makes possible the use of *Agilon* silica in NR compounds, this is not a necessary characteristic for synthetic rubber compounds that can be mixed at higher temperatures. Nevertheless, since *Agilon* silica is already silanized, we can take advantage of this and reduce the mixing time and temperature. It is of interest to determine how much energy and mixing time can be saved when using *Agilon* 400G silica, while still obtaining optimal compound performance properties.

Experimental

The chemically modified amorphous precipitated silica *Agilon* 400G-D silica and the highly dispersible amorphous precipitated silica PPG HI-SIL® EZ160G silica characteristics have been described in previous publications.³⁻⁶ Compound formulations used are shown in **Table 1**. The compounds were mixed in a Farrel IM1.5E mixer fitted with intermeshing rotors. Data was analyzed with Advise ES 2.3 software.

	Untreated silica compound	Treated silica compound
SLF30H41	103.1	103.1
Budene 1207	25	25
<i>Hi-Sil</i> EZ160G silica	80	-
<i>Agilon</i> 400G silica	-	80
Si 266	6.4	-
Vivatec 500 US	10	10
ZnO	2.5	2.5
Stearic Acid	2.0	2.0
Santoflex 13	1.5	1.5
RM Sulfur	1.5	2.0
CBS	3.0	3.0
DPG	1.5	0.5
Total phr:	236.5	229.6

Table 1. Compound formulations.



For the first mixing stage, the mixer temperature was set at 85°C, the rotors speed was set at 50 rpm and the ram pressure was 35 psi. Fill factor was varied as described later. The styrene-butadiene rubber and butadiene rubber were added in the mixer and timing was started. At 30 seconds into the mix, the fillers and other ingredients were added and the rotors speed was increased to 90 rpm. At 90 seconds, a sweep was performed. Compounds were mixed for a total of six minutes. The dropped compounds were milled for 60 seconds on a two-roll mill with the rolls at room temperature.

For the second mixing stage, the starting mixer temperature was 85°C and the starting rotor speed was 70 rpm. A mixer fill factor of 71% was used. The mix was initiated by adding the master batch from the first stage mix and the additional filler if required. At two minutes into the mix a sweep was performed. The compound was dropped at four and a half minutes of mix time. The dropped compounds were milled for 60 seconds on a two-roll mill with the rolls at room temperature.

For the final pass, the mixer temperature was 65°C and the starting rotor speed was 50 rpm. A mixer fill factor of 65% was used. The masterbatch from the previous pass was added in the mixer together with the curatives. At 90 seconds a sweep was performed, and the rotor speed was increased to 80 rpm. The compound was dropped at three minutes of mix time, at which time the compound temperature was about 105°C. The dropped compound was milled for 60 seconds on a two-roll mill with the rolls at room temperature.

The Mooney viscosities were measured according to ASTM D1646. The cure profiles were determined using a Moving Die Rheometer (MDR) according to ASTM D2084. The compounds were cured for T90 + five minutes at 150°C. Test specimens were produced as indicated in the respective test procedures.

Shore A hardness was determined following ASTM D2240-02 using a Zwick Digital Durometer at room temperature and 100°C. Stress / strain properties were measured according to ASTM D412 using ASTM type die C dumbbell specimens at 23°C. Dynamic properties (i.e. $\tan \delta$ and loss modulus) were determined following ASTM D5992-96, parallel plate geometry using an ARES-G2 Rheometer. Rebound was measured according to ISO 4662 at 23°C and 100°C. Heat build-up and permanent set were measured according to ASTM D623. Tear strength was measured according to ASTM D624 Die C at 23°C.

Results and Discussion

Fill Factor Determination

There are fundamental differences on how PPG AGILON® silicas and untreated silicas disperse and behave during rubber mixing. Unlike *Agilon* silica, untreated silicas generate VOCs which must escape the mixer through the hopper. There is also higher compound weight loss during mixing due to the elimination of these volatile compounds generated. Additionally, the surface of *Agilon* silica is more hydrophobic, allowing it to disperse faster in the mixer. Because of these characteristics, it was necessary to first determine which are the optimum mixer fill factors for the compounds.

Figures 2 and 3 show the ram position during mixing for the first mixing stage when using different fill factors. According to the mixer manufacturer recommendations, the fill factor for the first mixing pass should be such that the mixer ram bottoms towards the end of the mix time.

Figure 2 shows that, for the compound with PPG HI-SIL® EZ160G silica, 79% fill factor is too high, and the ram does not sit even after 6 minutes of mixing. A 76% fill factor seems to be ideal. **Figure 3** shows that a 79% fill factor is possible when using PPG *Agilon* 400G-D silica. Also when using PPG *Agilon* silica, the ram position does not fluctuate as much. It is hypothesized that this behavior is due to the better incorporation of the silica and the absence of VOCs trying to escape from the mixer.

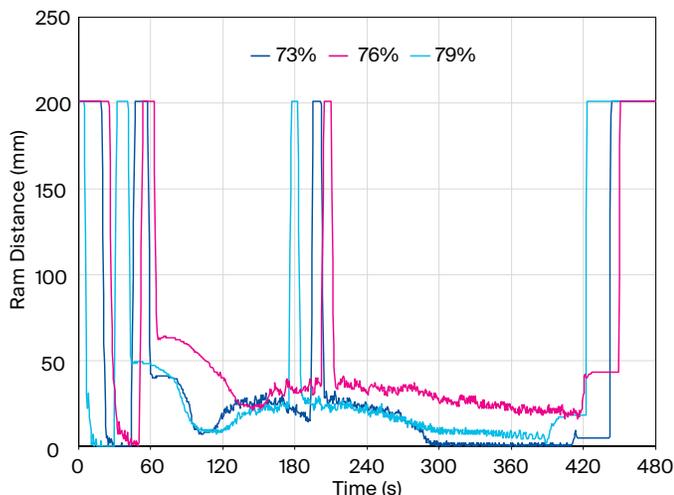


Figure 2. Ram position during mixing of *Hi-Sil* EZ160G silica compound.

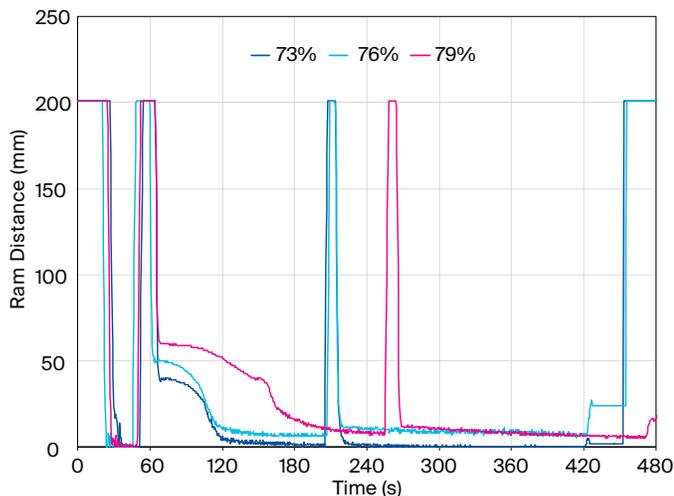


Figure 3. Ram position during mixing of *Agilon* 400G silica compound.

Table 2 shows basic compound properties. When increasing the fill factor in the PPG AGILON® compounds, the properties do not worsen, and at 79% fill factor a good balance of dynamic stiffness (G') and hysteresis is obtained while maximizing productivity per batch. When increasing the fill factor from 76% to 79% in the compounds with PPG HI-SIL® EZ160G silica, a 27% increase in hysteresis is observed. This, together with the ram position observation, indicates that this fill factor is too large for the untreated silica compound.

Filler	<i>Hi-Sil</i> EZ160G silica			<i>Agilon</i> 400G silica		
	73	76	79	73	76	79
Fill factor, %	73	76	79	73	76	79
ML(1+4)	56	53	61	59	80	71
Dispersion, %	71	90	92	96	95	96
Dispersion, white area	6	2	2	1	1	1
Hardness @ 23 °C	54	55	55	54	57	57
Rebound @ 23 °C, %	44	41	41	38	35	36
G' @ 6%, 60°C, MPa	1.27	1.35	1.38	1.21	1.75	1.50
Tan δ @ 6%, 60 °C	0.070	0.055	0.070	0.061	0.074	0.067

Table 2. Lab compound indicators obtained when using different fill factors.

Different fill factors were also evaluated for the second and final mixing stages. Data not shown indicated that both silicas behave similarly. It was concluded that once VOCs were eliminated, and the silicas were mostly dispersed, both silicas behaved similarly during mixing. While further work was performed using 76% and 79% fill factor respectively for *Hi-Sil* EZ160G silica and *Agilon* 400G silica in the first mixing stage, the same fill factor was used for the subsequent stages.

Compound Mixing

Once the optimum fill factors were determined, compounds were prepared using the mixing procedures shown in **Table 3**. First, Compounds 1 and 5 were mixed using a standard untreated silica mixing procedure. In this procedure, two non-productive mixing stages were used, and enough time and temperature was used for the silanization reaction to take place. Due to the relatively large silica loading (80phr), 60phr of silica were added in the first mixing pass and 20phr in the second mixing pass. Since eventually the goal was to eliminate the second non-productive mixing stage, it is necessary for this to add all the silica in the first mixing stage. Compounds 2 and 6 were prepared adding the 80phr of silica in the first mixing stage. Compounds 3 and 7 were mixed like Compounds 2 and 6 for the first pass, but no second pass was performed. Finally, Compounds 4 and 8 were prepared reducing the mixing temperature, since high mixing temperature is not needed when mixing *Agilon* silicas.

Filler	Hi-Sil EZ160G silica			
Hi-Sil EZ160G silica	1	2	3	4
Agilon 400G silica	5	6	7	8
Mix temperature, °C	160			130
2nd pass	No		No	
Silica in 1st pass	60	80		
Silica in 2nd pass	20	0		

Table 3. Different mixing strategies evaluated.

Figure 4 shows the temperature evolution during the first mixing stage for the compounds with PPG HI-SIL® EZ160G silica. In Compound 1, the temperature reaches 160°C and can be controlled at that temperature to perform the silanization reaction. In Compounds 2 and 3, with 80phr of silica, the mixer struggles to reach 160°C. Mixing time was extended to allow for two minutes of silanization, but this is not desirable. For Compound 4, there were no problems maintaining temperature at the lower 130°C.

Figure 5 shows a slower temperature rise for the PPG AGILON® silica compounds. It is believed that the more hydrophobic silica surface, and ease of mixing, does not generate as much heat as untreated silicas. Nevertheless, this is not a problem for Agilon silica, since no silanization temperature is required.

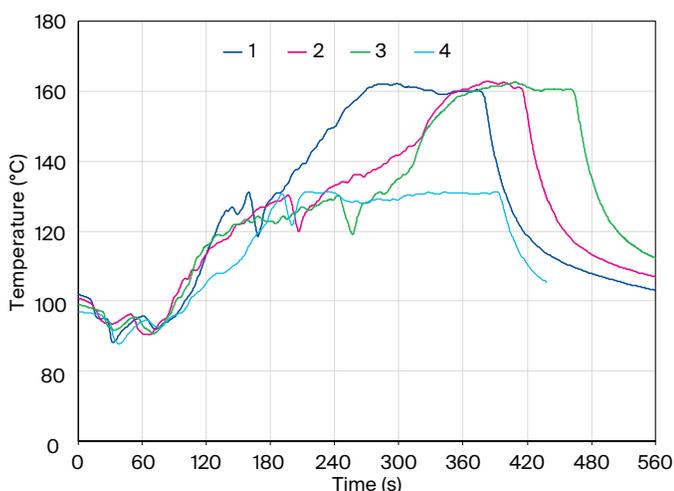


Figure 4. Temperature evolution during mixing of Hi-Sil EZ160G silica compounds.

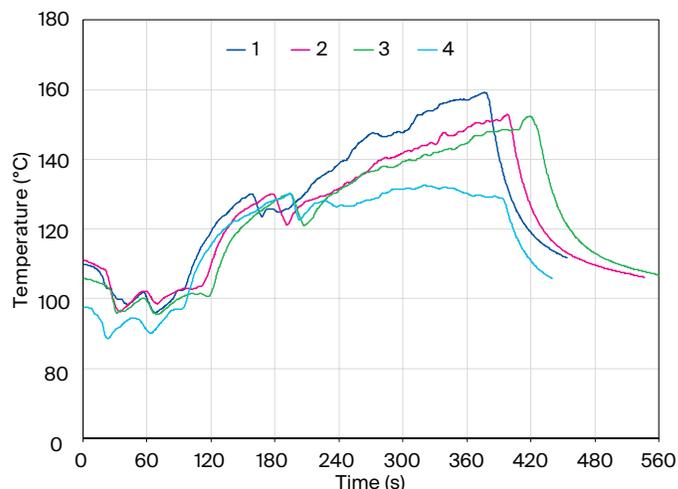


Figure 5. Temperature evolution during mixing of Agilon 400G compounds.



Compound Performance

Dynamic stiffness obtained from ARES strain sweeps, shown in Figures 6 and 7, were used to evaluate the efficiency of the mixing procedure. Figure 6 shows the G' vs. strain at 30°C for the compounds with Hi-Sil EZ160G silica. Compound 1 is considered to be the control compound using the standard *in-situ* silanization mixing procedure generally used for untreated silicas. In Compound 2, when all the silica was introduced in the first mixing stage, there is a small reduction in G'. This indicates that silica was better dispersed, which is a desirable result. This is a reasonable result considering that silica was introduced earlier in the overall mixing process, and as explained in Figure 4, the first stage was extended for about two minutes.

In Compound 3, when the second pass was eliminated, G' increases as expected. Finally, when the mixing temperature is reduced to 130°C, the silanization reaction is not efficient, and the G' at low strain significantly increases.

Figure 7 shows the G' vs. strain for the PPG AGILON® silica compounds. As with the PPG HI-SIL® EZ160G silica compounds, when all the silica is introduced in the first mixing stage (Compound 6), there is a slight reduction in G' compared to the compound with split silica additions (Compound 5). Also, when a mixing stage is eliminated (Compound 7), G' slightly increases. There is a significant difference between *Hi-Sil* EZ160G and *Agilon* 400G silicas when the compounds are mixed at 130°C. While **Figure 6** showed that there is a significant increase in filler-filler interaction (indicated by the large G' at low strain and high Payne effect (G'@0.5% - G'@20%)) for the *Hi-Sil* EZ160G compound, there is not a significant increase in the *Agilon* 400G silica compound. This demonstrates that high silanization temperature is not needed for *Agilon* silicas.

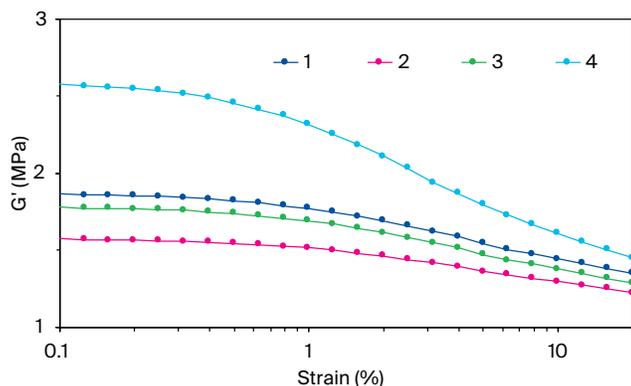


Figure 6. ARES strain sweep at 30°C for *Hi-Sil* EZ160G silica compounds.

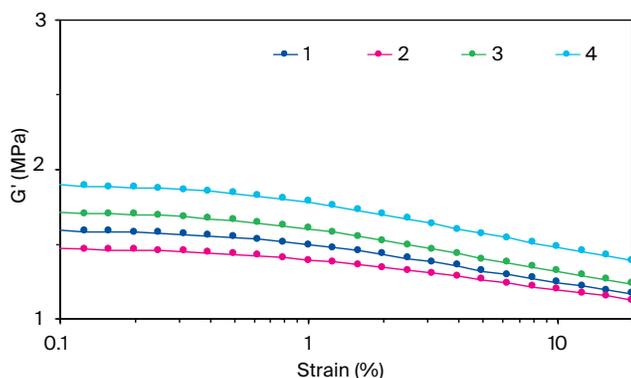


Figure 7. ARES strain sweep at 30°C for *Agilon* 400G silica compounds.

Table 4 shows lab compound performance indicators for the two extreme mixing procedures with both silicas. Compound 1 shows the performance of the *Hi-Sil* EZ160G silica compound when mixed with the standard *in-situ* silanization procedure for untreated silicas. Compound 4 shows that when the mixing temperature is reduced and the second mixing pass eliminated, the Payne effect and hysteresis significantly increase, thus this procedure is not adequate for the untreated silica. Compound 5 shows the performance when *Agilon* 400G silica is mixed with a silanization mixing procedure used for untreated silicas. When *Agilon* 400G silica is mixed with an optimized mixing procedure for treated silicas, comparable Payne effect and lower hysteresis is obtained. This indicates that not only we were able to reduce mixing time by eliminating the second mixing stage, but the performance of the *Agilon* 400G silica is comparable or better than when using the longer mixing procedure used for untreated silicas.

Compound	1	4	5	8
Filler	<i>Hi-Sil</i> EZ160G silica		<i>Agilon</i> 400G silica	
Mixing temperature (°C)	160	130	160	130
Number of passes	2	1	2	1
ML(1+4)	67	70	65	89
Dispersion, %	77	87	93	89
Tensile, MPa	16.4	16.3	12.4	14.5
Elongation, %	287	321	320	262
Modulus @ 100 %, MPa	4.2	3.9	2.5	3.9
Modulus @ 300 %, MPa	-	14.8	11.4	-
300/100 % Modulus ratio	-	3.8	4.6	-
Hardness @ 23 °C	58	59	52	58
Rebound @ 23 °C, %	48	46	55	58
G' @ 1%, 30 °C, MPa	1.77	2.32	1.49	1.78
G'@0.5% - G'@20%, MPa	0.47	1.01	0.38	0.44
Tan δ peak, 30 °C	0.132	0.161	0.145	0.133
DIN Abrasion index	100	118	98	108
Die Tear	29.9	35.2	26.0	24.9

Table 4. Final lab compound performance indicators.

Energy Savings

The energy consumption during mixing was monitored with the Advise ES 2.3 software. Cumulative energy consumption when using the optimized mixing procedures for untreated silica and PPG AGILON® silica (Compounds 1 and 8), are shown in **Figure 8**. During the first pass, the *Agilon* 400G silica compound consumed less energy than the PPG HI-SIL® EZ160G silica compound. This is likely due to the hydrophobicity of *Agilon* silica. The presence of a second pass in Compound 1 further increases energy consumption for this compound. As demonstrated by the final performance of Compound 8 in **Table 4**, no second pass is necessary for the *Agilon* 400G compound. Energy consumption for the final productive stage is comparable for both compounds. When adding the energy consumption of the different stages, Compound 1 required 4,603 kJ/kg, while Compound 8 required 2,377kJ/kg. The total mixing time for Compound 1 was 845 seconds and the total time for Compound 8 was 582 seconds. These results indicate that the *Agilon* 400G silica compound was prepared in 31% shorter time, with a 48% lower energy consumption. At the same time, this was performed without a drop in performance, as indicated in **Table 4**. While a *Hi-Sil* EZ160G silica compound (Compound 4) could be prepared with comparable energy consumption and mixing time than the *Agilon* 400G silica compound, the performance of this compound would not be acceptable.

Conclusions

The effect of using different mixing strategies for synthetic rubber compounds filled with *Hi-Sil* EZ160G and *Agilon* 400G silicas was evaluated. First, the optimum mixer fill factor was determined for each type of silica. It was concluded that *Agilon* 400G silica should be mixed with a slightly higher fill factor than *Hi-Sil* EZ160G silica. It is hypothesized that this is due to the absence of VOCs generated during mixing and the higher hydrophobicity of *Agilon* silica. Using the optimized mixer fill factors, compounds were mixed using standard mixing procedures generally used for untreated silica-silane mixing, and a more sustainable mixing procedure. It was concluded that *Agilon* 400G can be mixed for significantly shorter times, while reducing mixer energy consumption by 48%. As a result of this, higher plant productivity and less mixer wear can also be obtained. These manufacturing benefits can be achieved without any loss of compound performance.

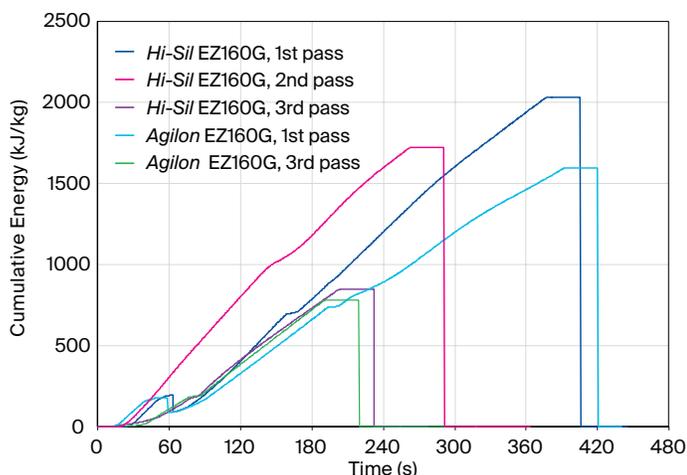


Figure 8. Cumulative energy consumption curves.

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