



Processing of Tire Treads Silica, Silanes, Additives

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Outline

- History of silanes for tires
- Silica
- Formula
- Processing
 - Mixing
 - Extrusion
 - Curing
- Properties

Bifunctional Silanes

- TESPT 1970-80's
- $[\text{((CH}_3\text{CH}_2\text{O)}_3\text{Si(CH}_2\text{)}_3\text{)}_2\text{S}_4]$
- S 20%, Si 8.8%, EtO 50%
- Rauline (Michelin) 1991
 - Solution SBR, HD silica, TESPT
 - 2+1 special mix procedure
 - Low rolling resistant tread
- US patent applications (2007) 100

During the 1970-80's Degussa introduced TESPT which became the silane standard for silica compounding. The material both coupled the silica and donated sulfur to the rubber network. In the early 90's Michelin applied for patents which became the basis of a major change in the tire tread industry. This tread is based on tailored made polymers, silica, and silane coupling agents. The mixing was done with two stages before the cure system is added. This tread became known as the green tire because of the treads role in improving gas mileage. The silane is normally added at levels between 5-8% of the silica. In current US Patent applications this silane still receives the bulk of the references. These references include patents on the rubber, filler, silane, and applications beyond tire tread. The price of this silane is low because of very active competition and supply. We have this available as SCA 98 in 100% liquid, 50% on Carbon black, and 50% in pellet form. Reference books on silanes published pre90's do not discuss this class of silanes. This silane has to be considered to be an important invention for rubber compounding.

Bifunctional Silanes

- TESPDP Late 90's
- $[\text{((CH}_3\text{CH}_2\text{O)}_3\text{Si(CH}_2\text{)}_3\text{)}_2\text{S}_2]$
 - S 14%, Si 11.8%, EtO 58%
- Patent and stability
- US patent applications (2007) 40-50

The disulfide is also in wide spread use. Mostly likely initially it became part of the way around the patent of Michelin. Because it has less sulfur it can be processed under slightly more extreme conditions. It can be made under similar conditions to TESPDP so is readily available and competes on an economic basis. For both of the bifunctional silanes the sulfurs are actually have a range of oligomers which are included in the specs of the materials. For this material the nominal spec is 75% of the S₂ oligomer. We have this available as SCA 985 in the various product forms.

Blocked Mercapto

- Momentive (GE-OSi) NXT 2000's
- $(\text{EtO})_3\text{Si}(\text{CH}_2)_3\text{SC}(\text{O})\text{C}_7\text{H}_{15}$
- S 8.8%, Si 7.7%, EtO 37%
- Mixing
 - Good high temperature stability
 - Processing 1+1
- US patent applications (2007) ~ 10

The blocked mercapto class is the last commercial class to have some acceptance. It's major advantage is that processing behavior is very good. The recommended mixing procedure is one stage with high temperatures followed by adding the cure system. The lower level of sulfur and silanol groups requires some compounding adjustments, as does TESPd when compared to TESPT. The material cost has to be weighed against processing cost savings. All these silanes give off ethanol during processing. From published work the evolved ethanol is only part of that shown as theory. This VOC is part of the processing concerns of the tire industry.

Next Generation

- Lowering the Ethanol content
- Samples only
- Cost?

The lowering of the ethanol (VOC) is a direction of some of the latest product introductions.. Several suppliers have patented materials and have presented data. Whether these will become commercially viable is unknown

Silica

- High dispersible
- Surface areas 150-175m²/g
- Moisture 5-7%
 - US pat 5,403,570 (1995) Rhone-Poulenc
 - Chevallier, Rabeyrin
- Abrasion
- Wet traction
- Rolling resistance

The precipitated silicas that are used are highly dispersible. They have relatively high surface areas which many patent claims go up to 400m²/g. They have surface moisture which has to help react with the silanes but which also is driven off during the process steps. Any residue water and free ethanol can cause processing problems during the tire manufacturing steps. In combination with the coupling agents the water and the silanol groups on the silica surface react with the silane during mixing to give a silica surface which has the potential of reacting via the sulfur groups to react with the rubber double bonds during the vulcanization stage. The combination of coupling agent and filler gives viscoelastic properties that improve the tire performance. Some of the commercial products we've seen are Zeosil-Rhodia, Ultrasil-Degussa, Hi-Sil-PPG, and Zeopol-Huber.

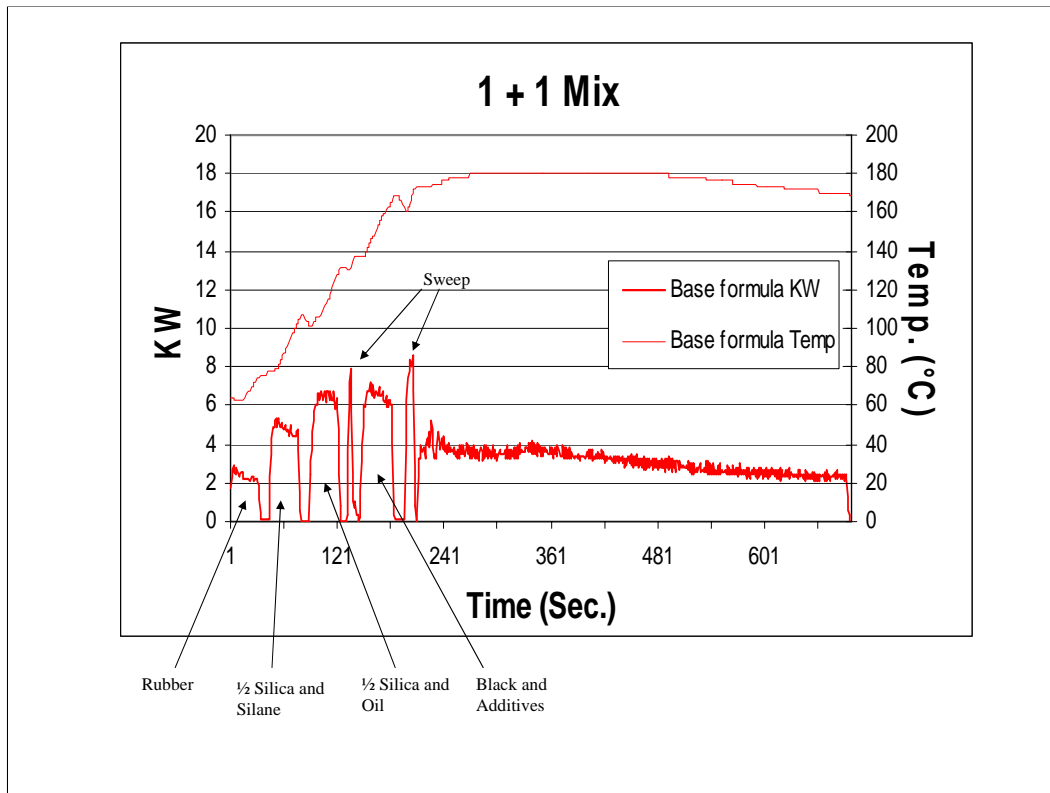
Example silica

- 13-18 hydroxyl groups/sq nm
- Particles 7-60 nm
- BET 185 m²/g
- CTAB 145 m²/g
 - Goodyear patent 2006012885
 - Huber silica

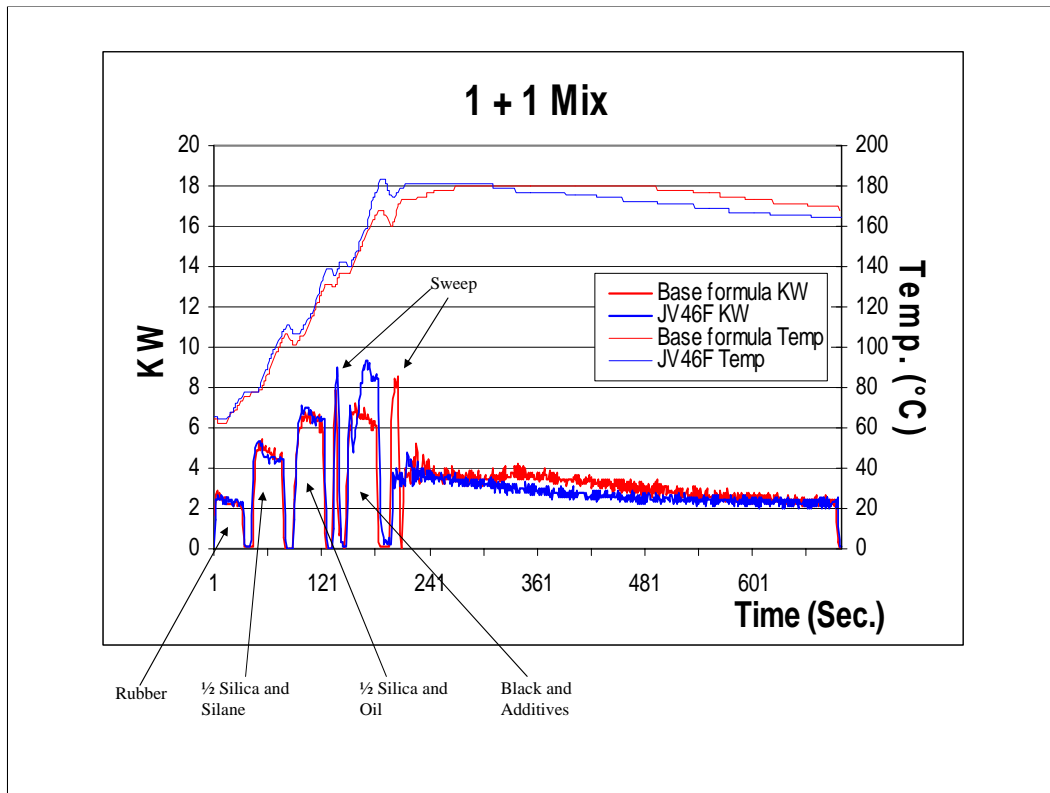
This example from a patent application for a rubber application shows how some customers (and suppliers) are now presenting surfaces of their fillers. BET is a nitrogen adsorption and CTAB is bulky surfactant which doesn't make it into all the fine porous structure.

Typical Formula

The rubber industry bases the formula's on 100 parts of rubber. This formula was taken out of the patent literature. The styrene butadiene rubber we use is a Duradene from Firestone Polymer. These are usually oil extended and are specified by viscosity, styrene content, and vinyl groups. The high cis butadiene rubber is from Lanxess. The bulk of our work is with Degussa's Ultrasil 7000 GR. The carbon black (CB) is in the tire grade series. Some of work we've done looks at varying the levels of CB to silica and then the silane is kept at the same % of the silica surface. The silane level here is 8% but lower ranges are also used. The ZnO and stearic acid react during compounding and are considered to be activators for the cure. The microcrystalline wax and the phenylene diamine protect the rubber from ozone attack. The diphenyl guanidine, cyclohexyl benzothiazole sulfenamide, and sulfur are part of the cure system and added in the last pass where the temperature and time is maintained to prevent any precuring. The process additives will be added at 2-5 parts some place early in the mix. These process additives are not in any of the early patents but are gaining acceptance as processing problems are being identified. Several additives have been developed that improve the processing of these compounds. Struktol HT254(from our European office) is a zinc free lubricant blend and Struktol JV 46F contains zinc based surfactants.



Shown is the mixing curve from our 1600ml mixer. The normal fill factor of 70% (~1300g) is based on the gravity of the ingredients. Because at the start of the mix the bulk density is high a ram is used to force the materials into the mixing chamber. The mixing chamber is warmed and cooled with fluid at about 50C. The rubber is 1st added and then the liquid silane is added with ½ the silica. The process oil is then added with the rest of the silica, residue powders are swept back into the chamber and all the secondary additives are added. After the sweep the rpm is changed to try to maintain the temperature at about 180C. Not shown is the ram position which finally reaches bottom at the inflection point at 360 secs. The stock was found to be crumbly up to this time and it became smooth coherent mass after this time. The chemical reactions of the silane for hydrolysis and coupling with silica as well as distributing and dispersing the silica for maximum rubber interaction all takes place under these extreme conditions. Not shown are the 2+1 mixing curves but the object is to keep the temperature under better control and to improve the coupling and dispersion. It also enables more choices in when the various additives can be incorporated.



When the process additive is put into the mix a significant change in mix torque and temperature is noted. The mix goes into a uniform mass almost immediately so there is faster work input. Even though the fill factor is the same the ram bottoms out during this portion of the mix. The lower viscosity causes a reduction in work input even though the shear rate has not changed. We have looked at the JV 46 addition with the silica and have better mixing and good property retentions. We have also looked at mixing times and in the lab mixer have seen the best properties at a 480sec mix time.

The mixing curve for the curatives is similar for both the 2+1 and the 1+1 and adds more work. Generally it is short and of low work input to keep curing reactions reduced.

Depending on the mixer size and type 4000-5000kg per hour per mixer can be produced in a tire factory. After each stage of mixing the mass is dropped from the mixer into a secondary process such as a dump extruder or two roll mill. This cools the stock and also prepares the stock for the next processing step. In our lab work the control mix was not easy to handle on the mill until after the inflection occurred at 6 minutes. The JV 46F stock milled easily and released from the mill even on the shortest mix.

Comparing Mixing Methods

- 2+1
 - TESPT, TESP
 - Energy-680WH
 - JV 46F 630WH
 - Time-17min
 - Temperature
 - 160-140C
- 1+1
 - TESP, NXT
 - Energy-650WH
 - JV 46F 590WH
 - 430WH
 - Time-10.5min
 - 6.0min
 - Temperature
 - 180-160C

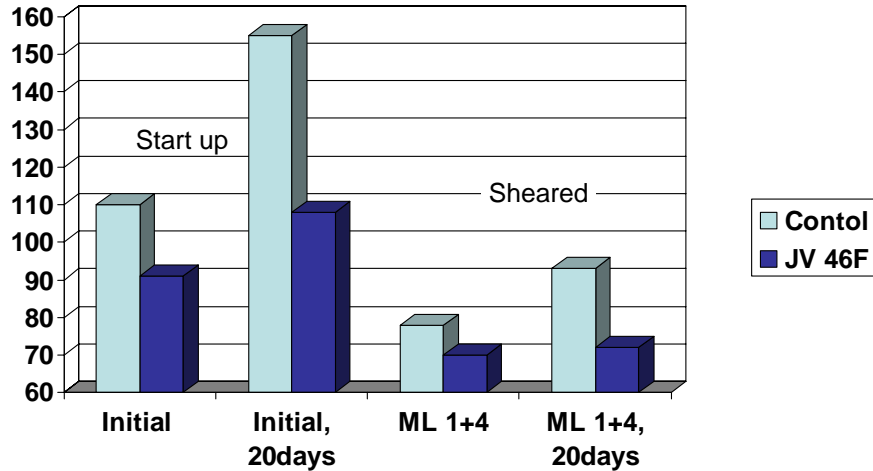
The comparisons between the two methods of mixing show why there is an interest in decreasing the handling steps. In addition to the added costs of each handling step the increased output and reduced energy to obtain an equal degree of mixing can result in significant cost savings.

The 2+1 mix is close to that of the 1990's Michelin patent, however, there have been several modifications and addition point changes made over the years and it is hard to generalize on what each manufacture is doing. The 1+1 mix is based on the recommendations of using NXT. Because of the high temperatures of this mixing crosslinking has been seen with TESPT. The work we are doing shows that TESP can also be used in this more productive procedure. References exist for 3+1 and 4+1 mixing process for extremely tough to process compounds.

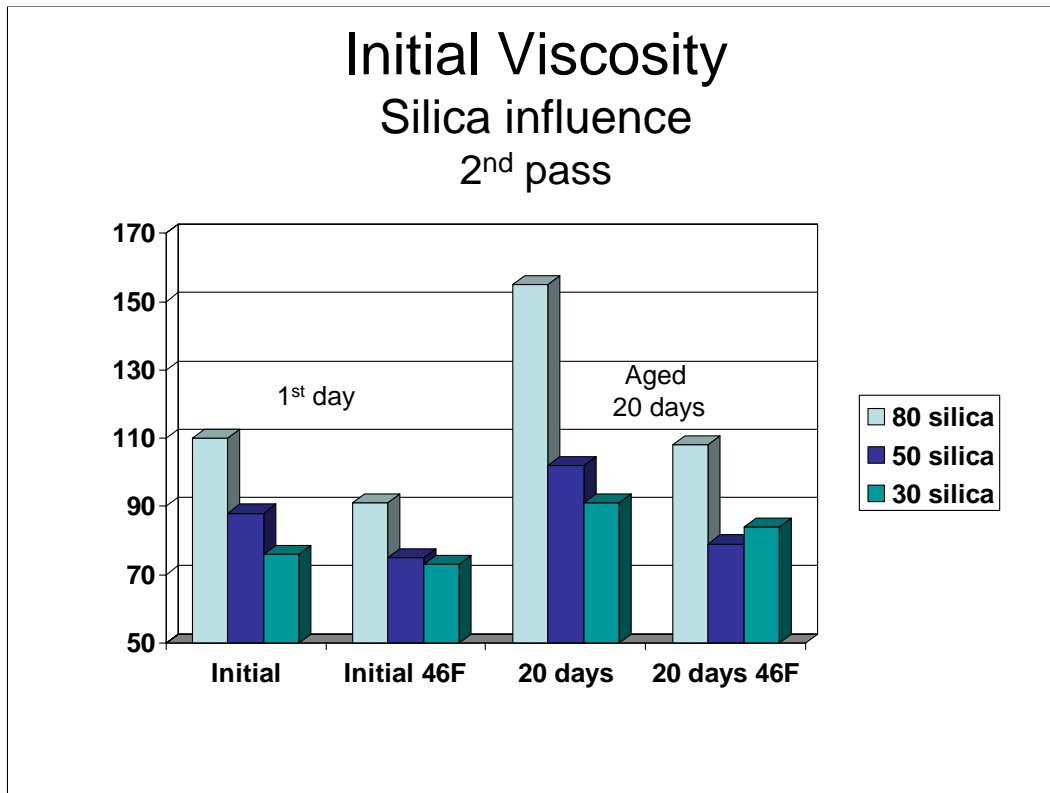
We have not seen major differences in processing properties between the mixing styles when comparing equal formula's. However, the lower temperature mix procedures have been shown to introduce some porosity during extreme extrusion stages caused probably by residue water on the silica. Some of the cured physical properties suggests better coupling reactions when the TESP is used with JV 46F in the 1+1 procedure. And maximum physicals were obtained with a 6 min mix with a 40% reduction in work compared to the standard 2+1 mix. The JV 46F data shown here is for 3 phr. At 5 phr the work input was another 50WH lower.

Mooney Viscosity

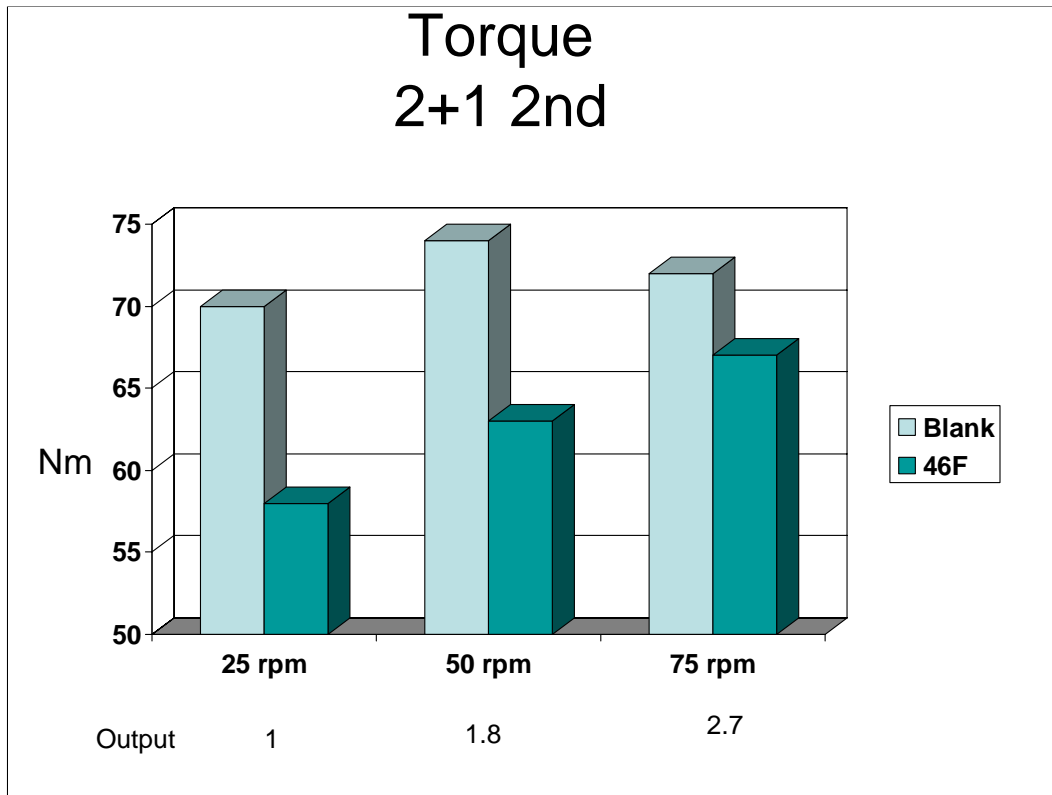
80 phr silica 2+1



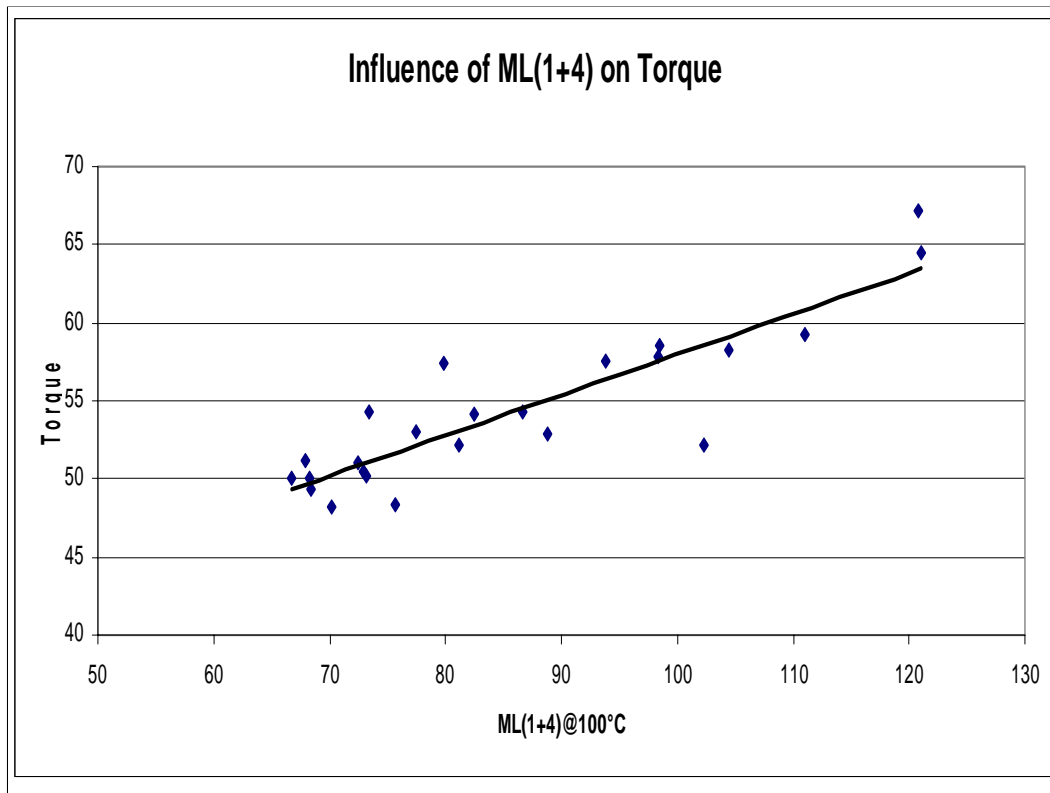
The standard low shear rate rubber viscosity test shows both high viscosity and a viscosity that changes with time. The rapid change in viscosity on storage is thought to be caused by increasing in filler-filler interactions. With some shear induced (ML 1+4) work this interactions is broken. The process additive helps decrease the viscosity changes during storage and gives a lower viscosity compound.



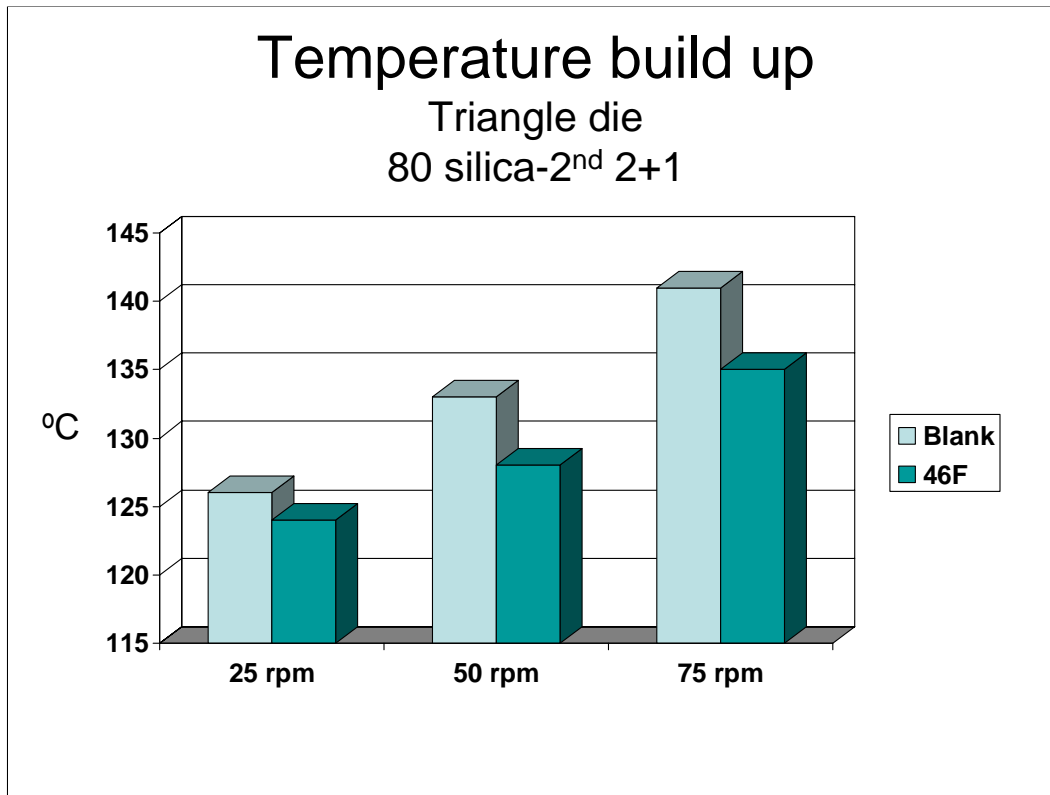
These curves are for viscosity control as a function of silica loading. Most of the viscosity increases are due to the silica content. With Struktol JV 46F the storage viscosity is as good as the initial viscosity of the unaged stocks with no additive. If the viscosity increases are due to silica reagglomeration then the surfactants are doing an excellent job of preventing that. Another issue with viscosity occurs during the molding stage where the uncured tire is forced into the mold pattern. The lower viscosity gives better flow into the mold and the process additives allows the cured rubber in the air vents and mold to release easier.



The torque on the extruder is heavily dependant on the compound viscosity. With the additive significant reduction in torque and work input occurs. There was no change in output between the stocks at a given RPM. As expected the output doubled with doubling the RPM. For a given RPM the head pressure was 20% less with the additive.



There appears to be a relationship between the torque and the Mooney viscosity. This scatter plot is for all levels of silica and also the additives in a 2+1 mix. We have not studied the influence of storage viscosity changes on processing. Based on the size of the trials some differences in time between running the viscosities and the extruder occurred which might explain some of the scatter.

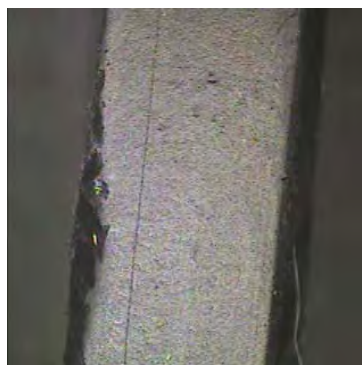


The work input by the extruder was enough to raise the stock temperature from the set point of 100C. The reductions in temperature, pressure, and torque allows for much better efficiency at the extruder. Although in our lab extruder we were able to process in excess of 150 C, concern about the onset of rubber curing (scorch) will limit the upper temperature where the materials can be processed. The change in temperature is in a similar direction to the heat rise and temperature control in the Banbury mixer during compounding.

EXTRUDATE QUALITY 80 PHR SILICA 2+1



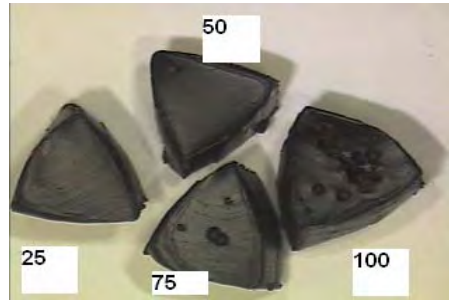
CONTROL



JV 46F

The high silica containing stocks are also extremely difficult to get a good quality extrudate. There is extensive edge tearing and knotty surfaces. There is little die swell because of the high filler levels. With the process additive excellent surfaces were seen. The combination of temperature build up, lower torque, and better quality extrudate will allow the tire builder to produce a more uniform tread at a faster output.

Extrudate Profile 50 parts Silica 2+1

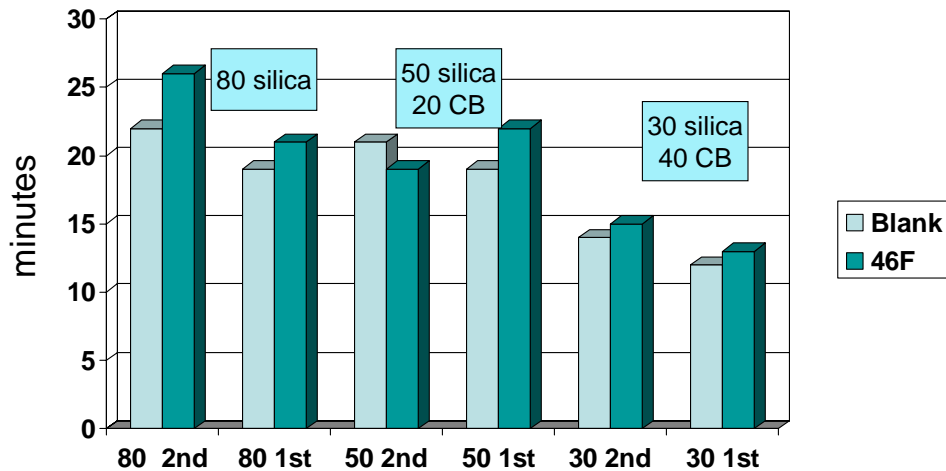


127 133/140 153 °C

Temperature

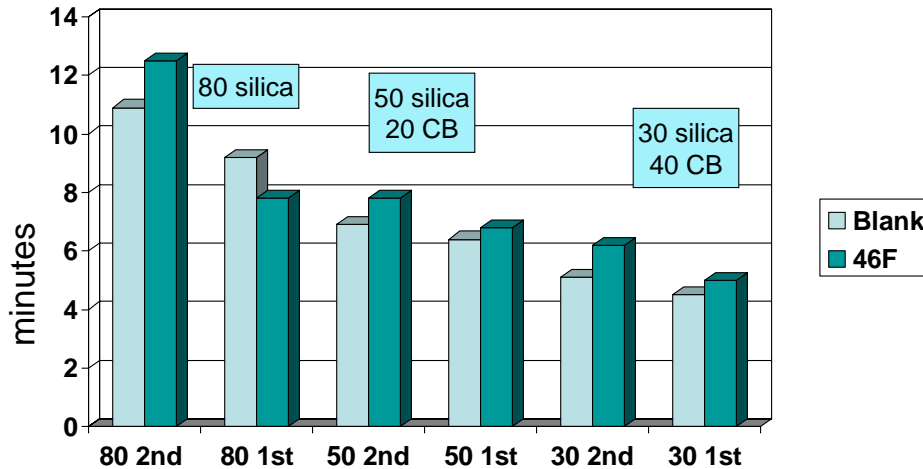
The extrudates developed voids at the higher rpms. These could be seen forming in the melt stream about 10-20 cm away from the die. The voids did not blow through the surface. Although the experiment was not designed to study this in detail, there did not appear to be a relationship to mixing procedures, additive, or silica level, except the drop temperature of the 1st pass. Whenever the melt temperature reach the mid 130's small voids were seen in a cooler 2+1 mix. Since the additives give less heat build up the voids were reduced slightly. Whether these voids could be explained by ethanol coming of from the coupling agent or from water in the stock is unknown but both are suspected. Stocks that were mixed in the 1+1 mix, where temperatures of 180 C were reached, did not show any porosity up to extruder temperatures in excess of 150C. Previous unpublished work that the author has done with water in a carbon black stock showed that porosity of this type could be expected at about 0.1% water in the compound.

Silica level-addition point Mooney T₅ 2+1



The silica/black level and the additive addition point influences the scorch time and cure times. The Mooney T₅ is industrially used to give an indication of how long the material can be processed without problems. The low silica/higher black stocks had about a 50% reduction in process safety. Additives added to the 2nd pass gave a couple of minutes of increase process safety. We have shown that in our normal lab processing studies we use up about 25% of this safety margin. This work is with TESPT.

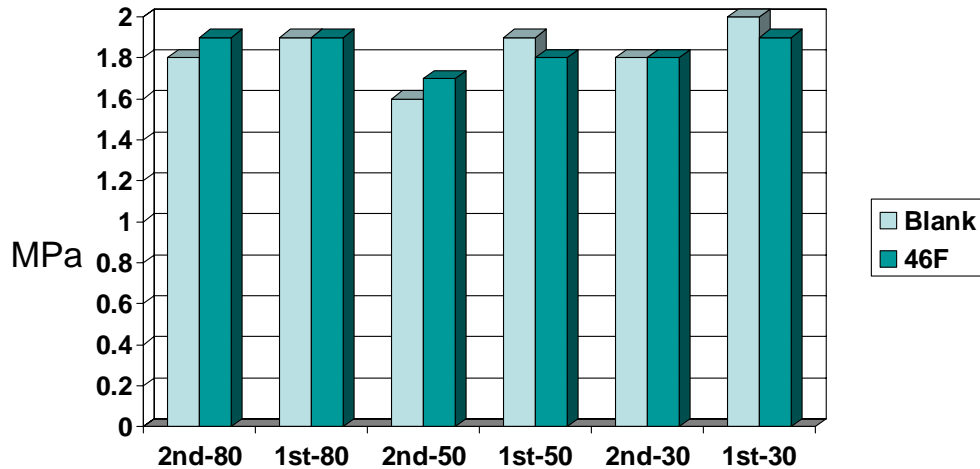
Silica and addition point Rheometer T₉₀ 2+1



The rheometer (at 160C) cure times also were influenced by the addition point with the longest cure times at the high silica level and the additives added in the 2nd pass. The cure is when the compound goes from being viscous to thermoset elastic. This work is with TESPT. Since each rubber component in the tire has it's own cure rate, the art of the industry is to get these in balance so the finished tire is cured together when it comes out of the tire press. Our work has not tried to adjust the cure packages to reach equal time of cures.

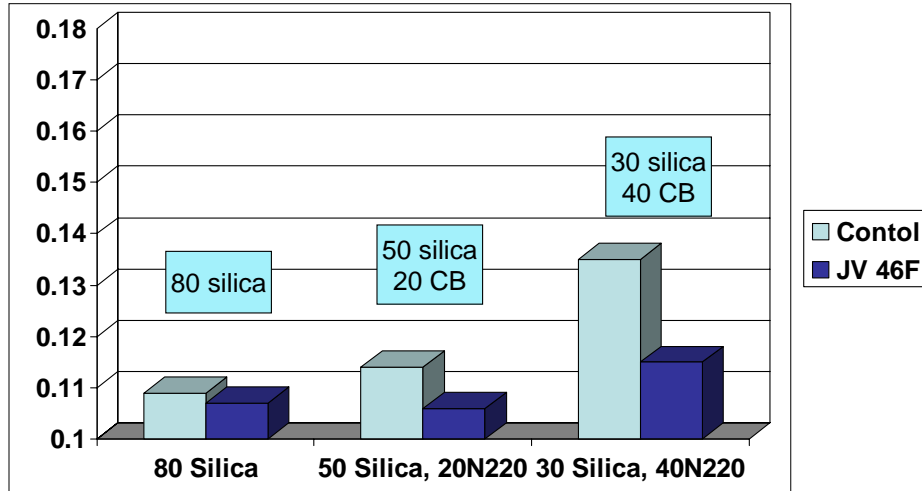
Cured Properties

100 % Modulus 2+1



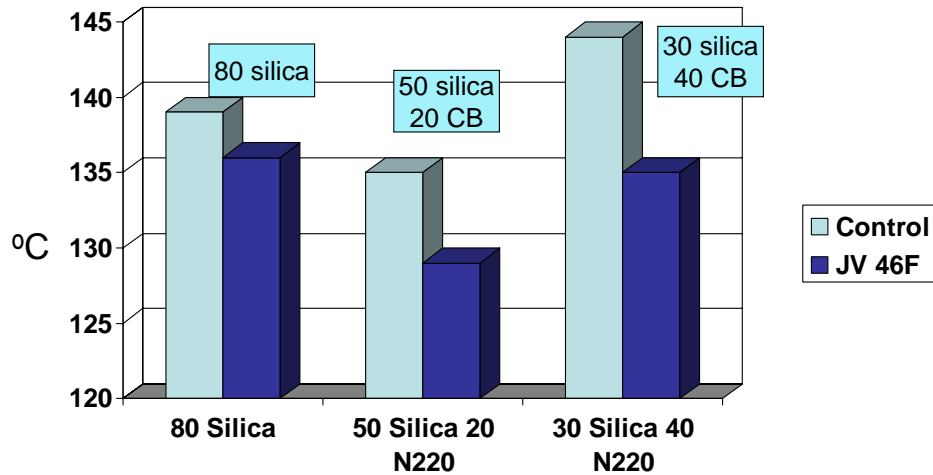
We will only show a limited amount of cured physical data. The 100% modulus trends to be slightly higher for the 1st pass addition of the process additive. When all the data is included the lubricant tends to slightly decrease the state of cure. Whether this is due to decreased coupling reactions or changes in the over all vulcanizate crosslinks has not been resolved. But based on compression set figures it suggests a more stable network.

Tan Delta 100°C



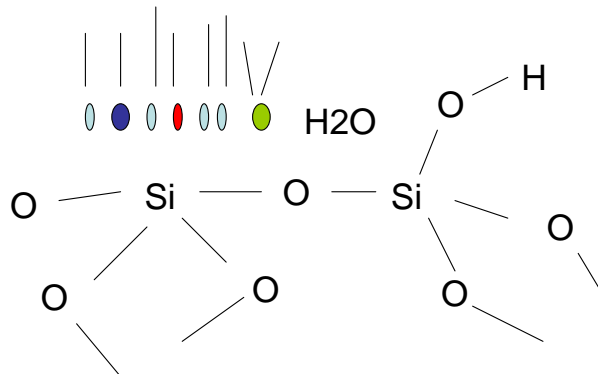
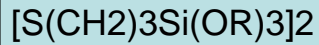
Tan delta is the relationship between the viscous to elastomeric response of the rubber to work input. At high temperatures the lower tan delta shows that improved rolling resistance is expected with the highest silica level stock. It also shows that the additive can improve these results.

Heat Build Up Firestone Flexometer



The role of hysteresis in tires causes heat build up as well. This is a lab test that generates an extreme shear induced work input on cured blocks of rubber. The trends are similar to that of the tan delta when one examines the entire components of the viscoelastic responses.

SURFACTANT/SILANE/SILICA
INTERFACE/INTERPHASE



The silica silane interactions are complicated by both dispersion of the silica, silane hydrolysis, and silanol condensation reaction of the silane with itself and with the filler and then with the sulfur entering into the rubber vulcanization chemistry. In this model we propose the selection of surfactant technology can influence the surface interface at the silica. By using different chain lengths and polar end groups the interaction with polar surfaces of silica and with the silane (or silanol formed during mixing) can be modified. In essence the process additive serves as a surface emulsifier in a non polar matrix. This thin layer, which probably is about a nano layer thick, prevents the silica particles from dewetting from the polymer during storage. It also can be chosen to influence some of the silane chemistry. The result is a good over balance of physical properties with greatly improved processing effects. This model is simplified to leave out the rubber, the pores in the silica particles, and the vulcanization chemicals and reactions that take place during the vulcanization process. The Struktol JV 46F has both the ability to change the interface chemistry but also to influence the interphase chemical interactions which leads to better vulcanization chemistry.

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