



STRUKTOL® JV 46F
Surfactant Influence
on Silica Filled Tread

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This paper introduces the use of STRUKTOL® JV 46F, a compounded surfactant, as an additive for use in a energy efficient tire tread.

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Outline

- Silica
- Additive - **STRUKTOL® JV 46F**
- Formula
- Processing
 - Mixing - reduce mixing passes
 - Extrusion
 - Curing
- Properties

The presentation will show how the additive influences both the processing and properties of a high dispersible silica in a solution SBR compound. Processing will show that it is feasible to decrease the mixing passes and improve the desirable physical properties of this type of formula.

Silica Processing

- Very polar filler, nonpolar polymer
- Strong hydrogen bonds
- Reactive silane and silanols
 - Sulfur effects TESP, TESPT
- 5-7% Water
 - Reactant and variable during process
- High filler levels
- High and changing viscosities
- Extensive mixing

The use of highly dispersible silica for passenger tread compounds was patented in the 1990's. The compound has many processing challenges. The silica surface is covered with water and this layer contributes to strong hydrogen bonds and requires energy to break and evaporate during processing. This water is also a reactant with the silane. Because of the temperature induced by shear the water is driven out of the mix along with any of the alcohol from the silane hydrolysis. The silanol that forms condenses with the silica surface to form a chemically reactive interface for the rubber vulcanization reactions.

The standard mixing procedure requires both time and temperature control. Several non productive stages are usually required to achieve successful dispersion and coupling. With the original silane (TESPT) the polysulfidic linkages contributed extensively to the crosslinking density. If the mixing temperature was too high the silane served as a sulfur donor and scorching could occur. If the temperature was too low processing and physicals properties were not acceptable. The mixing procedures require a pass where the silane and fillers are mixed into the polymer, followed by another pass where the other chemicals such as the AO and the zinc oxide can be added. The temperature is maintained by adjustment of the RPM. The addition of things like ZnO in the second stage mixing is thought to improve coupling efficiency by allowing the silanol reactions to take place before any side reactions which produce zinc silicates. A final low shear step of adding the curing ingredients finishes the mix. In this paper this mix is described as a 2+1 mix. The disulfide silane TESP has gained acceptance in this application but does not serve as a major sulfur donor.

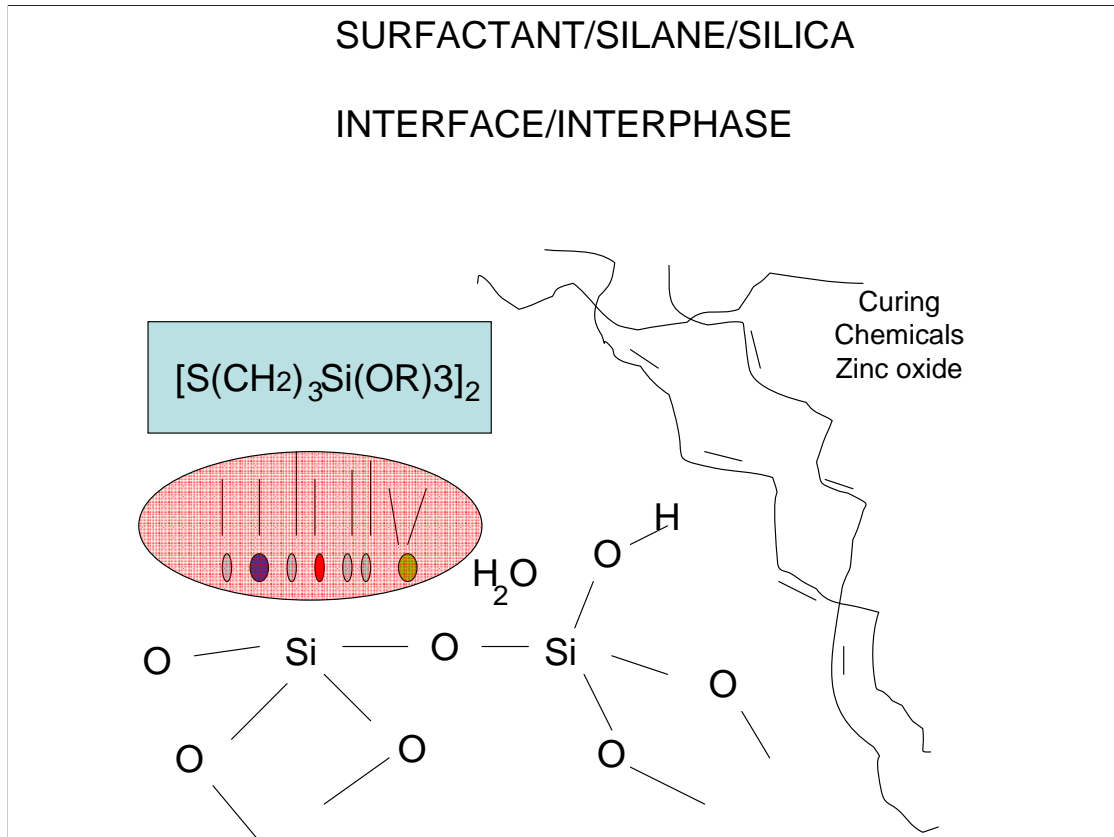
Even though the silica surface is treated with silane very high viscosities are obtained. In addition rapid viscosity increases are seen on storage of the uncured stock. The process is known as flocculation and is thought to be caused by diffusion controlled mechanisms which allow for agglomerate formation. Any flocculation which occurs during curing means higher energy losses and hence greater fuel consumption.

Process Additive **STRUKTOL® JV 46F**

- Contains 5.1% Zn as carboxylate salt
- Contains mixed surfactant
 - Amphiphilic structures
 - Amphoteric structures
- Wetting
- Surface energy
- Effective at 2-5phr

SURFACTANT/SILANE/SILICA

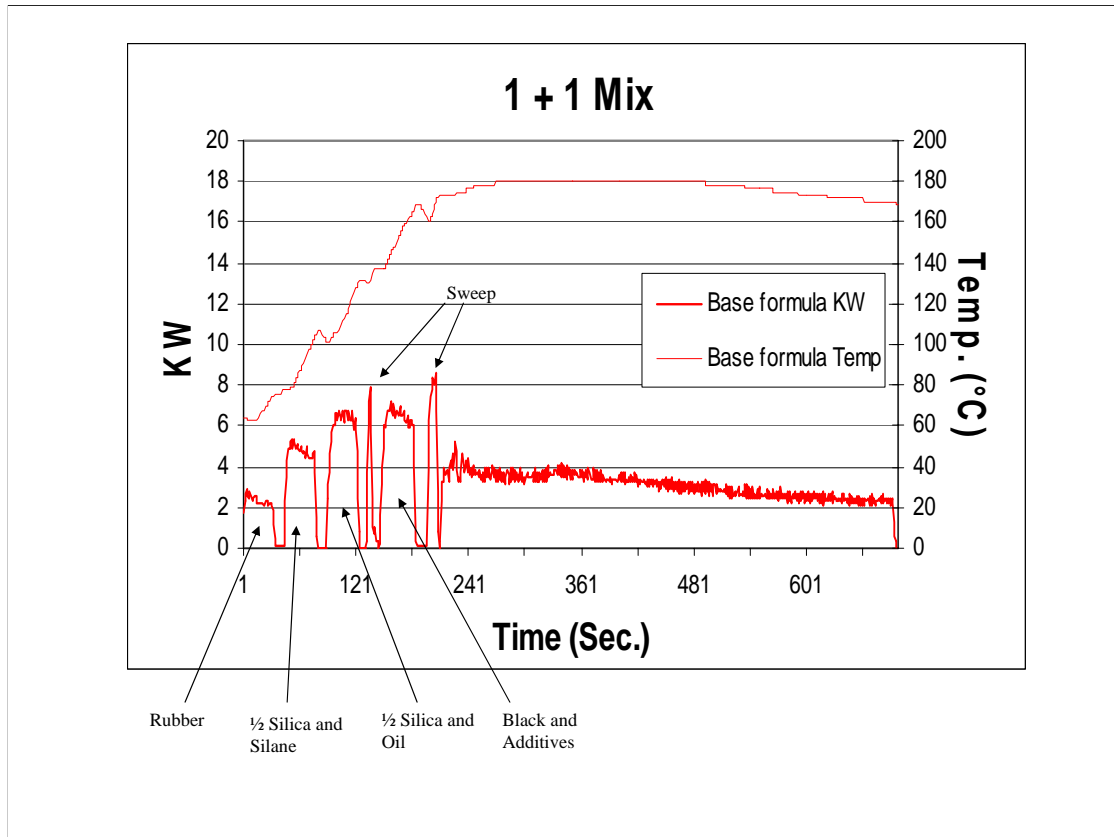
INTERFACE/INTERPHASE



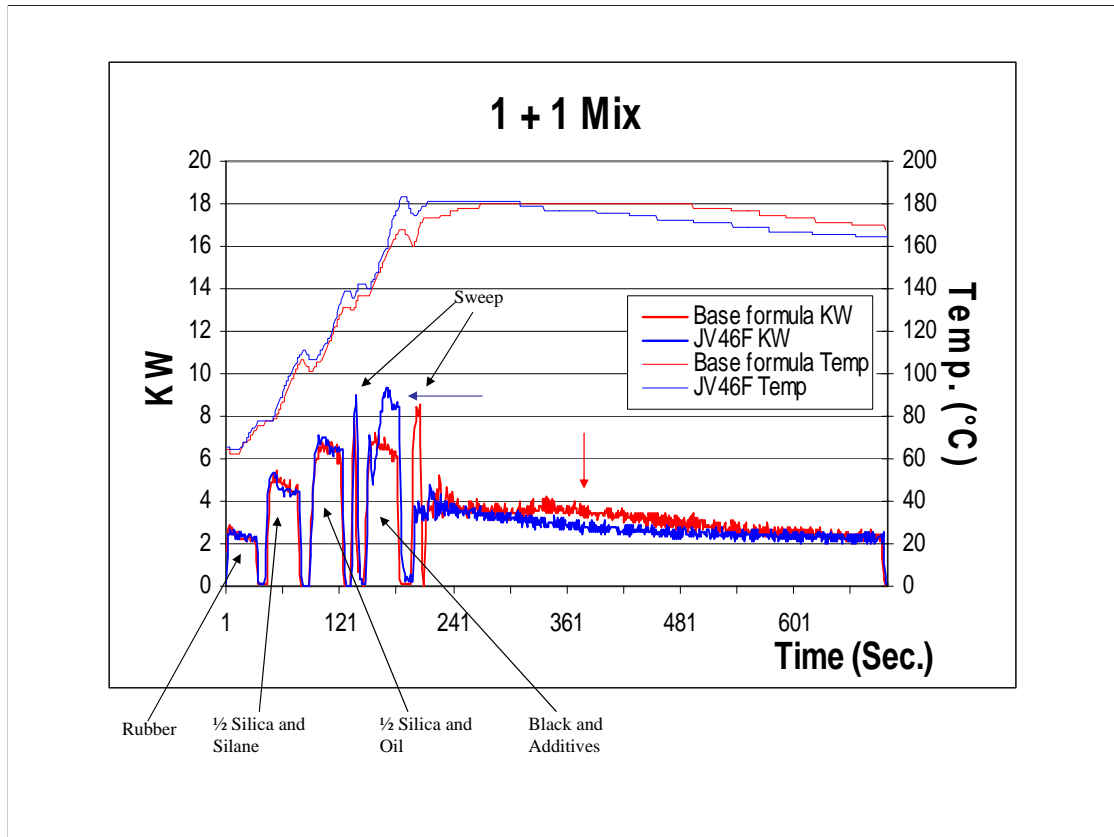
The silica silane interactions are complicated by both dispersion of the silica, silane hydrolysis, and silanol condensation reaction of the silane with itself and with the filler and then with the sulfur entering into the rubber vulcanization chemistry. In this model we propose the selection of surfactant 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 pores in the silica particles, and the 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.

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 pre-curing. 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.

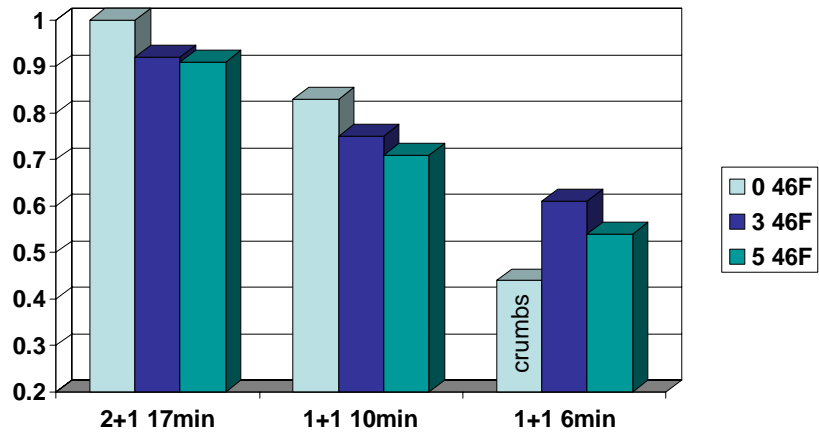


When the process additive is put into the mix a significant change in mix torque and temperature is noted. The mix goes into a uniform mass almost immediately so there is faster work input. Even though the fill factor is the same the ram bottoms out during this portion of the mix. The lower viscosity 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.

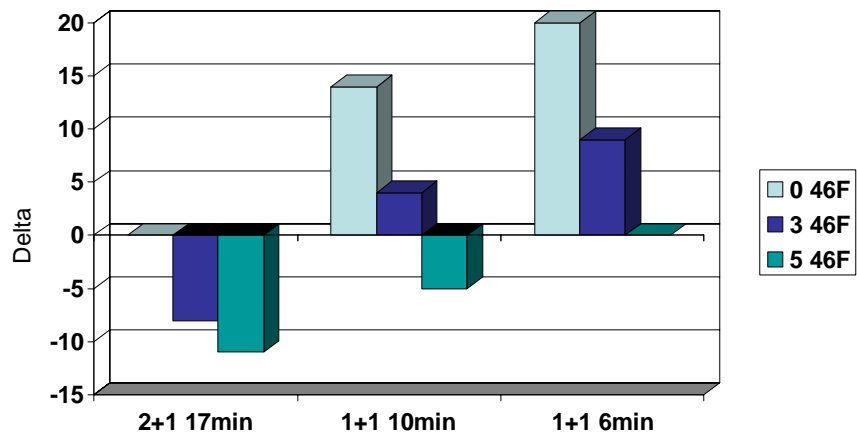
The mixing curve for the curatives is similar for both the 2+1 and the 1+1 and adds more work. Generally it is short and of low work input to keep curing reactions reduced.

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.

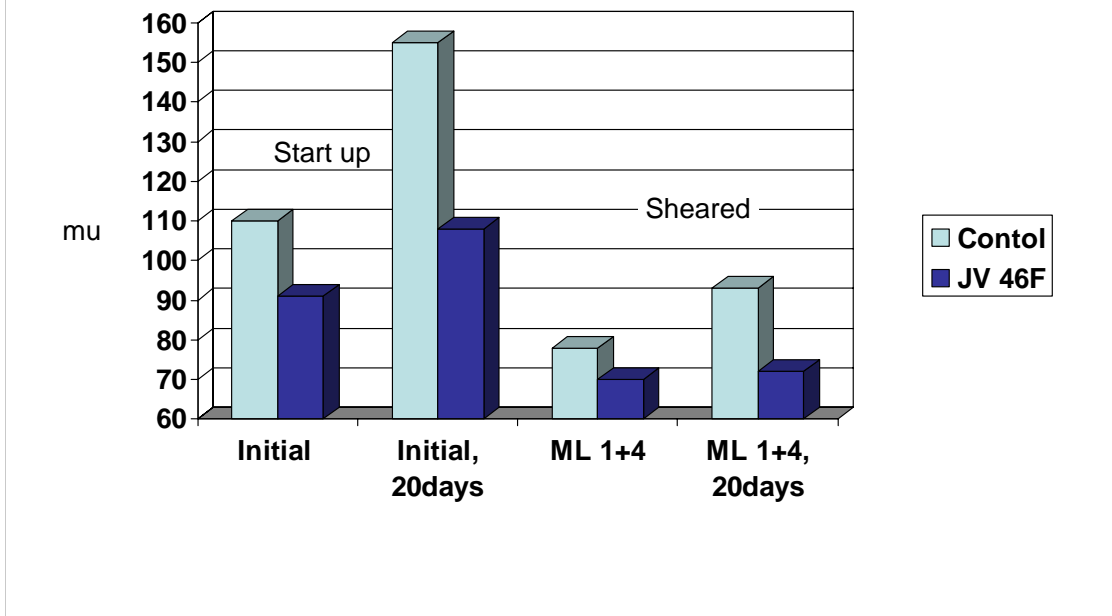
Relative mixing energy for nonproductive mixing stages



Mixing influence on ML 1+4 100 C (vs 2+1 control)



Mooney Viscosity 80 phr silica 2+1

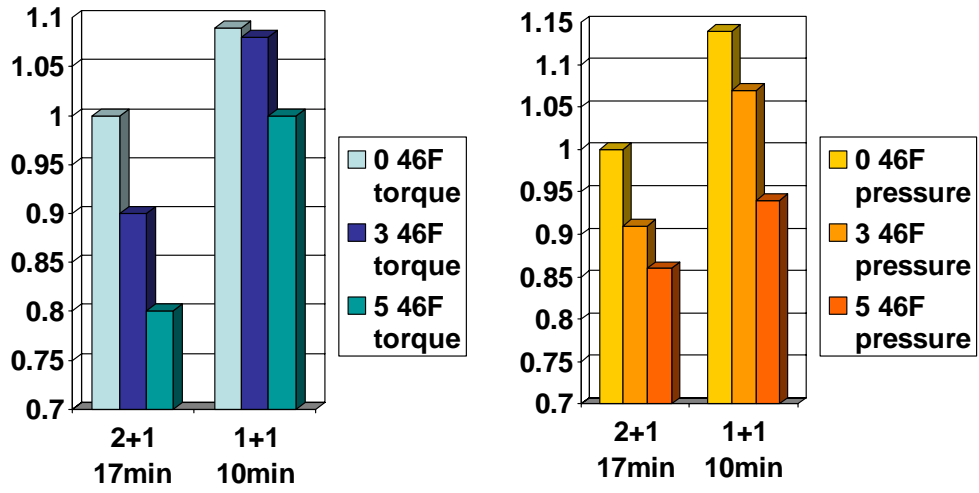


The standard low shear rate rubber viscosity test shows both high viscosity and a viscosity that changes with time. The rapid change in viscosity on storage is thought to be caused by increasing in filler-filler interactions. With some shear induced (ML 1+4) work this interactions is broken. The process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

Extruder

Torque and Head pressure

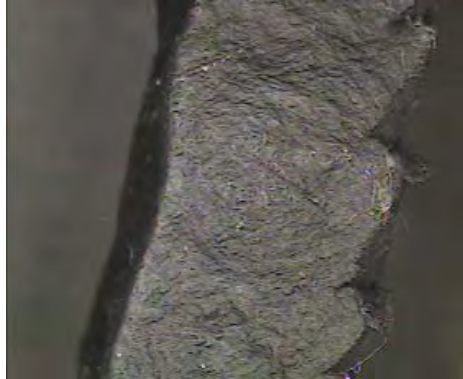
relative to 2+1 control



EXTRUDATE QUALITY

80 PHR SILICA

2+1 17min



CONTROL



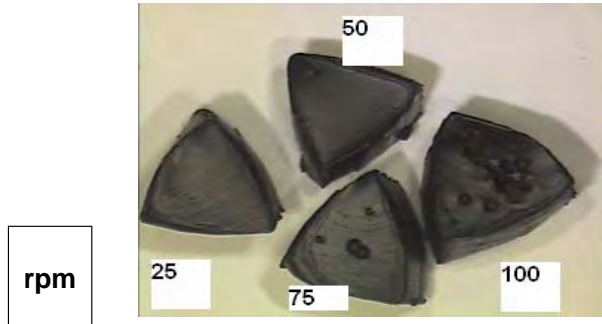
JV 46F
3 phr

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 17min

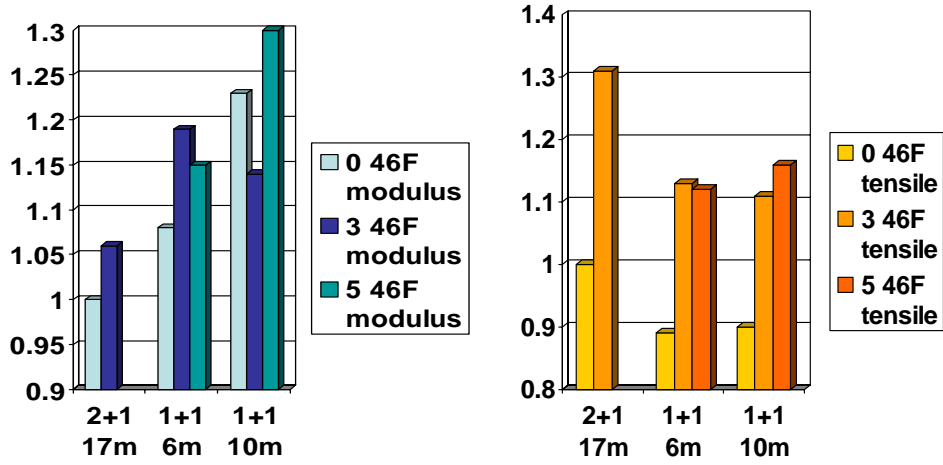


127 133/140 153 °C

Melt Temp

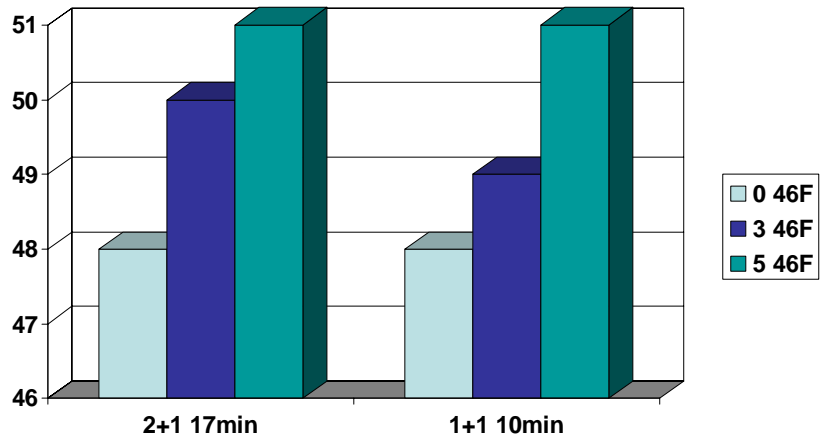
The extrudates developed voids at the higher rpms. These could be seen forming in the melt stream about 10-20 cm away from the die. The voids did not blow through the surface. Although the experiment was not designed to study this in detail, there did not appear to be a relationship to mixing procedures, 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.

Relative Tensile 300/100 modulus ratio Ultimate strength 2+1 control=1

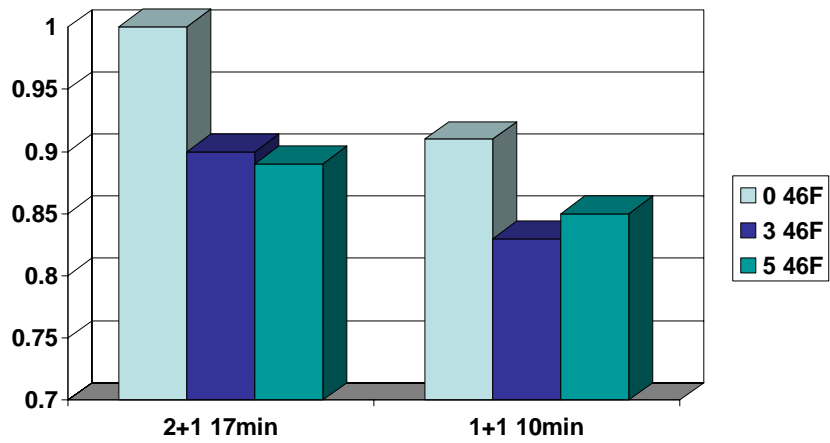


The modulus ratio and the ultimate strength is shown normalized to the standard 2 non productive mix. The

Rebound 100 C



Relative tan delta 100 C 1hz 2+1 control=1



Conclusion

- Silica brings unique processing challenges
 - Processing
 - Complex mixing
 - Steps, time, temperature
 - High and changing viscosity
 - Difficult to extrude
 - Chemistry
 - Silane-silanol-coupling
 - Sulfur vulcanization
 - Physicals
 - Demanding dynamic performance

- **STRUKTOL® JV 46F** surfactant
 - Mixing improvements
 - Possible reduced mixing stages
 - Faster cycles
 - Lower and stable viscosity
 - Better extrudate-quality & quantity
 - Chemistry
 - Enhanced coupling and vulcanization
 - Physicals
 - Outstanding dynamic performance